DISCLAIMER

The U.S. Environmental Protection Agency's Office of Solid Waste (EPA or the Agency) has compiled this methods manual in order to provide comprehensive guidance to analysts, data users, and other interested parties regarding test methods that may be employed for the evaluation of solid waste and other testing specified in regulations issued under the Resource Conservation and Recovery Act (RCRA). Except where explicitly specified in a regulation, the use of SW-846 methods is not mandatory in response to Federal testing requirements.

The Agency does not intend to restrict the use of new analytical techniques. Advances in technologies applicable to the sampling and analysis of environmental media and hazardous wastes outpace the ability of the Agency to promulgate revisions to this manual. In addition, given the large number of manufacturers and vendors of scientific equipment, glassware, reagents, and supplies, it is not feasible to cite all possible sources for these materials. Thus, the mention of trade names or commercial products in this manual is for illustrative purposes only, and does not constitute an endorsement or exclusive recommendation for use by EPA. The products and instrument settings cited in SW-846 methods represent those products and settings used during method development or subsequently evaluated by the Agency. Glassware, reagents, supplies, equipment, and settings other than those listed in this manual may be employed provided that method performance appropriate for the intended RCRA application has been documented as described in Chapter Two (see Sec. 2.1).

EPA generally does not intend these methods to be overly prescriptive. The words "shall," "must," or "require" are used to indicate aspects of the method that are considered essential to its performance, based on sound analytical practices (e.g., an instrument must be calibrated before use). In contrast, the words "should," "may," or "recommend" are used to provide guidance on aspects of the method that are useful but not essential. This flexibility does not apply to those method-defined parameters where the analytical result is wholly dependant on the process used to make the measurement.

EPA emphasizes that the ultimate responsibility for producing reliable analytical results lies with the entity subject to the Federal, State, or local regulation. Thus, members of the regulated community are advised to refer to the information in Chapter Two and to consult with knowledgeable laboratory personnel when choosing the most appropriate suite of analytical methods. The regulated community is further advised that the methods here or from other sources need only be used for those specific analytes of concern that are subject to regulation or other monitoring requirements.

Many of the methods include performance data that are intended as guidance on the performance that may be achieved in typical matrices and may be used by the analyst to select the appropriate method for the intended application. These performance data are not intended to be used as absolute QC acceptance criteria. Rather, each laboratory should develop performance criteria as described in Chapter Two and elsewhere in the manual.

In summary, the methods included here provide guidance to the analyst and the regulated community in making judgements necessary to generate data that meet the data quality objectives for the intended use of the results.

ACKNOWLEDGEMENTS

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NOTE: A suffix of "A" in the method number indicates revision one (the method has been revised once). A suffix of "B" in the method number indicates revision two (the method has been revised twice). A suffix of "C" in the method number indicates revision three (the method has been revised three times). **In order to properly document the method used for analysis, the entire method number including the suffix letter designation (e.g., A, B, or C) must be identified by the analyst.** A method reference found within the text of SW-846 methods and chapters refers to the latest revision of the method, even though the method number does not include the appropriate letter suffix.

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NOTE: A suffix of "A" in the method number indicates revision one (the method has been revised once). A suffix of "B" in the method number indicates revision two (the method has been revised twice). A suffix of "C" in the method number indicates revision three (the method has been revised three times). **In order to properly document the method used for analysis, the entire method number including the suffix letter designation (e.g., A, B, or C) must be identified by the analyst.** A method reference found within the text of SW-846 methods and chapters refers to the latest revision of the method, even though the method number does not include the appropriate letter suffix.

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Referral to the EPA Office of Solid Waste guidance document entitled "RCRA Ground-water Monitoring: Draft Technical Guidance," published in 1992.

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NOTE: A suffix of "A" in the method number indicates revision one (the method has been revised once). A suffix of "B" in the method number indicates revision two (the method has been revised twice). A suffix of "C" in the method number indicates revision three (the method has been revised three times). **In order to properly document the method used for analysis, the entire method number including the suffix letter designation (e.g., A, B, or C) must be identified by the analyst.** A method reference found within the text of SW-846 methods and chapters refers to the latest revision of the method, even though the method number does not include the appropriate letter suffix.

Method Number, Third Edition	Chapter Number, Third Edition	Method Number, Second Edition	Current Revision Number
0010	Ten	0010	0
0020	Ten	0020	0
0030	Ten	0030	0
1010	Eight (8.1)	1010	0
1020	Eight (8.1)	1020	0
1110	Eight (8.2)	1110	0
1310	Eight (8.4)	1310	0
1320	Six	1320	0
1330	Six	1330	0
3005	Three	3005	0
3010	Three	3010	0
3020	Three	3020	0
3040	Three	3040	0
3050	Three	3050	0
3500	Four (4.2.1)	None (new method)	0
3510	Four (4.2.1)	3510	0
3520	Four (4.2.1)	3520	0
3540	Four (4.2.1)	3540	0
3550	Four (4.2.1)	3550	0
3580	Four (4.2.1)	None (new method)	0
3600	Four (4.2.2)	None (new method)	0
3610	Four (4.2.2)	None (new method)	0
3611	Four (4.2.2)	3570	0
3620	Four (4.2.2)	None (new method)	0
3630	Four (4.2.2)	None (new method)	0
3640	Four (4.2.2)	None (new method)	0
3650	Four (4.2.2)	None (new method)	0
3660	Four (4.2.2)	None (new method)	0
3810	Four (4.4)	5020	0
3820	Four (4.4)	None (new method)	0
5030	Four (4.2.1)	5030	0
5040	Four (4.2.1)	3720	0
6010	Three	6010	0
7000	Three	7000	0
7020	Three	7020	0

Method Number, Third Edition	Chapter Number, Third Edition	Method Number, Second Edition	Current Revision Number
7040	Three	7040	0
7041	Three	7041	0
7060	Three	7060	0
7061	Three	7061	0
7080	Three	7080	0
7090	Three	7090	0
7091	Three	7091	0
7130	Three	7130	0
7131	Three	7131	0
7140	Three	7140	0
7190	Three	7190	0
7191	Three	7191	0
7195	Three	7195	0
7196	Three	7196	0
7197	Three	7197	0
7198	Three	7198	0
7200	Three	7200	0
7201	Three	7201	0
7210	Three	7210	0
7380	Three	7380	0
7420	Three	7420	0
7421	Three	7421	0
7450	Three	7450	0
7460	Three	7460	0
7470	Three	7470	0
7471	Three	7471	0
7480	Three	7480	0
7481	Three	7481	0
7520	Three	7520	0
7550	Three	7550	0
7610	Three	7610	0
7740	Three	7740	0
7741	Three	7741	0
7760	Three	7760	0
7770	Three	7770	0

Method Number, Third Edition	Chapter Number, Third Edition	Method Number, Second Edition	Current Revision Number
7840	Three	7840	0
7841	Three	7841	0
7870	Three	7870	0
7910	Three	7910	0
7911	Three	7911	0
7950	Three	7950	0
8000	Four (4.3.1)	None (new method)	0
8010	Four (4.3.1)	8010	0
8015	Four (4.3.1)	8015	0
8020	Four (4.3.1)	8020	0
8030	Four (4.3.1)	8030	0
8040	Four (4.3.1)	8040	0
8060	Four (4.3.1)	8060	0
8080	Four (4.3.1)	8080	0
8090	Four (4.3.1)	8090	0
8100	Four (4.3.1)	8100	0
8120	Four (4.3.1)	8120	0
8140	Four (4.3.1)	8140	0
8150	Four (4.3.1)	8150	0
8240	Four (4.3.2)	8240	0
8250	Four (4.3.2)	8250	0
8270	Four (4.3.2)	8270	0
8280	Four (4.3.2)	None (new method)	0
8310	Four (4.3.3)	8310	0
9010	Five	9010	0
9020	Five	9020	0
9022	Five	9022	0
9030	Five	9030	0
9035	Five	9035	0
9036	Five	9036	0
9038	Five	9038	0
9040	Six	9040	0
9041	Six	9041	0
9045	Six	9045	0
9050	Six	9050	0

METHOD INDEX AND CONVERSION TABLE
(Continued)

Method Number, Third Edition	Chapter Number, Third Edition	Method Number, Second Edition	Current Revision Number
9060	Five	9060	0
9065	Five	9065	0
9066	Five	9066	0
9067	Five	9067	0
9070	Five	9070	0
9071	Five	9071	0
9080	Six	9080	0
9081	Six	9081	0
9090	Six	9090	0
9095	Six	9095	0
9100	Six	9100	0
9131	Five	9131	0
9132	Five	9132	0
9200	Five	9200	0
9250	Five	9250	0
9251	Five	9251	0
9252	Five	9252	0
9310	Six	9310	0
9315	Six	9315	0
9320	Five	9320	0
HCN Test Method	Seven	HCN Test Method	0
H_2S Test Method	Seven	H_2S Test Method	0

STATUS TABLES FOR
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REVISED MARCH 2009

HOW TO USE THIS DOCUMENT

This document provides historical information regarding EPA-published SW-846 methods and chapters. It contains two status tables, namely; the "SW-846 Method Status Table," which is a listing of SW-846 methods; and the "Status Table for SW-846 Chapter Text and Other Documents," which lists all other documents in SW-846 (e.g., chapters).

Use the "SW-846 Method Status Table" as a reference guide to identify the historical and latest versions of SW-846 methods. Methods in this status table are listed sequentially by method number. The column showing "Other Methods" includes those new and revised methods that appear as new SW-846 methods at EPA's Office of Resource Conservation and Recovery Methods Team internet site, http://www.epa.gov/SW-846/. An integrated version of the manual through Final Update IV is also available at the Methods Team internet site.

Methods that have "deleted" as the latest status are those methods that have been removed from SW-846 for various reasons, and you will not find that method at the Methods Team web site. See the associated update rulemakings or notices for an explanation regarding why a method was deleted from SW-846.

Letter suffixes (e.g, A, B, C) to a method number identify the revision status of the method. New methods, i.e., Revision 0 methods, do not have a letter suffix. A suffix of “A” in a method number indicates Revision 1 (the method has been revised once and distributed as final), a suffix of “B” indicates Revision 2, and so on. The date in the footer of an SW-846 method (e.g., February 2007 in the bottom right corner of Final Update IV methods) is the approximate date for when the method was last revised.

Use the "Status Table for SW-846 Chapter Text and Other Documents" as a reference guide to identify the historical and latest versions of chapters and other SW-846 documents (e.g., the Disclaimer).

With the publication of the final Methods Innovation Rule, SW-846 and its methods are no longer required in general by any RCRA regulation. See 40 CFR 260.11(a)(11) for a listing of those SW-846 methods that may be still required by the RCRA regulations for the analysis of method-defined parameters.

Do **not** use a status table as a guide for putting together a paper version of SW-846. Refer to the "Table of Contents" of the update for the order in which chapters and methods should appear in SW-846.

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0010	--	--	--	--	--	Modified Method 5 Sampling Train
--	--	--	0011 (Up. III)	--	--	Sampling for Selected Aldehyde and Ketone Emissions from Stationary Sources
0020	--	--	--	--	--	Source Assessment Sampling System (SASS)
--	--	--	0023A (Up. III)	--	--	Sampling Method for Polychlorinated Dibenzo-*p*-Dioxins and Polychlorinated Dibenzofuran Emissions from Stationary Sources (Note: This method is a revision of Method 23, 40 CFR Part 60.)
--	--	--	--	25D Referral	--	Determination of the Volatile Organic Concentration of Waste Samples
--	--	--	--	25E Referral	--	Determination of Vapor Phase Organic Concentration in Waste Samples
0030	--	--	--	--	--	Volatile Organic Sampling Train
--	--	--	0031 (Up. III)	--	--	Sampling Method for Volatile Organic Compounds (SMVOC)
--	--	--	0040 (Up. III)	--	--	Sampling of Principal Organic Hazardous Constituents from Combustion Sources Using Tedlar® Bags
--	--	--	0050 (Up. III)	--	--	Isokinetic HCl/Cl_2 Emission Sampling Train
--	--	--	0051 (Up. III)	--	--	Midget Impinger HCl/Cl_2 Emission Sampling Train
--	--	--	0060 (Up. III)	--	--	Determination of Metals in Stack Emissions

METHOD NUMBER (Date in parenthesis is found at bottom right-hand corner of method)						METHOD TITLE
THIRD EDITION (9/86)	FINAL UPDATE I (7/92)	FINAL UPDATE II (9/94) IIA (8/93) IIB (1/95)	FINAL UPDATE III (12/96) IIIA (4/98) IIIB (11/04)	FINAL UPDATE IV (2/07)	OTHER METHODS (www.epa.gov/ SW-846)	
--	--	--	0061 (Up. III)	--	--	Determination of Hexavalent Chromium Emissions from Stationary Sources
--	--	--	0100 (Up. III)	--	--	Sampling for Formaldehyde and Other Carbonyl Compounds in Indoor Air
--	--	--	--	207 Referral	--	A Method for Measuring Isocyanates in Stationary Source Emissions
1010	--	--	1010A (Up. IIIB)	--	--	Test Methods for Flash Point by Pensky-Martens Closed Cup Tester (Method text is a referral to ASTM Standard D 93-79 or Standard D 93-80)
1020	1020A	--	1020B (Up. IIIB)	--	--	Standard Test Methods for Flash Point by Setaflash (Small Scale) Closed-cup Apparatus (Method text is a referral to ASTM Standard D 3278-78)
--	--	--	1030 (Up. III)	--	--	Ignitability of Solids
--	--	--	--	1040	--	Test Method for Oxidizing Solids
--	--	--	--	1050	--	Test Methods to Determine Substances Likely to Spontaneously Combust
1110	--	--	1110A (Up. IIIB)	--	--	Corrosivity Toward Steel
--	--	--	1120 (Up. III)	--	--	Dermal Corrosion
1310	1310A	--	1310B (Up. IIIB)	--	--	Extraction Procedure (EP) Toxicity Test Method and Structural Integrity Test
--	1311	--	--	--	--	Toxicity Characteristic Leaching Procedure
--	--	1312	--	--	--	Synthetic Precipitation Leaching Procedure

METHOD NUMBER (Date in parenthesis is found at bottom right-hand corner of method)						METHOD TITLE
THIRD EDITION (9/86)	FINAL UPDATE I (7/92)	FINAL UPDATE II (9/94) IIA (8/93) IIB (1/95)	FINAL UPDATE III (12/96) IIIA (4/98) IIIB (11/04)	FINAL UPDATE IV (2/07)	OTHER METHODS (www.epa.gov/ SW-846)	
		(Up. II)				
1320	--	--	--	--	--	Multiple Extraction Procedure
1330	1330A	--	--	--	--	Extraction Procedure for Oily Wastes
3005	3005A	--	--	--	--	Acid Digestion of Waters for Total Recoverable or Dissolved Metals for Analysis by FLAA or ICP Spectroscopy
3010	3010A	--	--	--	--	Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by FLAA or ICP Spectroscopy
--	--	3015 (Up. II)	--	3015A	--	Microwave Assisted Acid Digestion of Aqueous Samples and Extracts
3020	3020A	--	--	--	--	Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by GFAA Spectroscopy
--	--	--	3031 (Up. III)	--	--	Acid Digestion of Oils for Metals Analysis by Atomic Absorption or ICP Spectrometry
3040	--	--	3040A (Up. III)	--	--	Dissolution Procedure for Oils, Greases, or Waxes
3050	3050A	--	3050B (Up. III)	--	--	Acid Digestion of Sediments, Sludges, and Soils
--	--	3051 (Up. II)	--	3051A	--	Microwave Assisted Acid Digestion of Sediments, Sludges, Soils, and Oils
--	--	--	3052 (Up. III)	--	--	Microwave Assisted Acid Digestion of Siliceous and Organically Based Matrices
[3060, in the 2nd Ed.]	--	--	3060A (Up. III)	--	--	Alkaline Digestion for Hexavalent Chromium
--	--	--	--	--	3200	Mercury Species Fractionation and Quantification by Microwave

METHOD NUMBER (Date in parenthesis is found at bottom right-hand corner of method)						METHOD TITLE
THIRD EDITION (9/86)	FINAL UPDATE I (7/92)	FINAL UPDATE II (9/94) IIA (8/93) IIB (1/95)	FINAL UPDATE III (12/96) IIIA (4/98) IIIB (11/04)	FINAL UPDATE IV (2/07)	OTHER METHODS (www.epa.gov/ SW-846)	
					(7/05)	Assisted Extraction, Selective Solvent Extraction and/or Solid Phase Extraction
3500	3500A	--	3500B (Up. III)	3500C	--	Organic Extraction and Sample Preparation
3510	3510A	3510B (Up. II)	3510C (Up. III)	--	--	Separatory Funnel Liquid-Liquid Extraction
--	--	--	--		3511 (11/02)	Organic Compounds in Water by Microextraction
3520	3520A	3520B (Up. II)	3520C (Up. III)	--	--	Continuous Liquid-Liquid Extraction
--	--	--	3535 (Up. III)	3535A	--	Solid-Phase Extraction (SPE)
3540	3540A	3540B (Up. II)	3540C (Up. III)	--	--	Soxhlet Extraction
--	--	3541 (Up. II)	--	--	--	Automated Soxhlet Extraction
--	--	--	3542 (Up. III)	--	3542A (5/05)	Extraction of Semivolatile Analytes Collected Using Method 0010 (Modified Method 5 Sampling Train)
--	--	--	3545 (Up. III)	3545A	--	Pressurized Fluid Extraction (PFE)
--	--	--	--	3546	--	Microwave Extraction
3550	--	3550A (Up. II)	3550B (Up. III)	3550C	--	Ultrasonic Extraction
--	--	--	3560 (Up. III)	--	--	Supercritical Fluid Extraction of Total Recoverable Petroleum Hydrocarbons

METHOD NUMBER (Date in parenthesis is found at bottom right-hand corner of method)						METHOD TITLE
THIRD EDITION (9/86)	FINAL UPDATE I (7/92)	FINAL UPDATE II (9/94) IIA (8/93) IIB (1/95)	FINAL UPDATE III (12/96) IIIA (4/98) IIIB (11/04)	FINAL UPDATE IV (2/07)	OTHER METHODS (www.epa.gov/ SW-846)	
--	--	--	3561 (Up. III)	--	--	Supercritical Fluid Extraction of Polynuclear Aromatic Hydrocarbons
--	--	--	--	3562	--	Supercritical Fluid Extraction of Polychlorinated Biphenyls (PCBs) and Organochlorine Pesticides
--	--	--	--	--	3570 (11/02)	Microscale Solvent Extraction (MSE)
--	--	--	--	--	3571 (7/07)	Extraction of Solid and Aqueous Samples for Chemical Agents
--	--	--	--	--	3572 (7/07)	Extraction of Wipe Samples for Chemical Agents
3580	3580A	--	--	--	--	Waste Dilution
--	--	--	3585 (Up. III)	--	--	Waste Dilution for Volatile Organics
3600	3600A	3600B (Up. II)	3600C (Up. III)	--	--	Cleanup
3610	3610A	--	3610B (Up. III)	--	--	Alumina Cleanup
3611	3611A	--	3611B (Up. III)	--	--	Alumina Column Cleanup and Separation of Petroleum Wastes
3620	3620A	--	3620B (Up. III)	3620C	--	Florisil Cleanup
3630	3630A	3630B (Up. II)	3630C (Up. III)	--	--	Silica Gel Cleanup
3640	--	3640A (Up. II)	--	--	--	Gel-Permeation Cleanup

METHOD NUMBER (Date in parenthesis is found at bottom right-hand corner of method)						METHOD TITLE
THIRD EDITION (9/86)	FINAL UPDATE I (7/92)	FINAL UPDATE II (9/94) IIA (8/93) IIB (1/95)	FINAL UPDATE III (12/96) IIIA (4/98) IIIB (11/04)	FINAL UPDATE IV (2/07)	OTHER METHODS (www.epa.gov/ SW-846)	
3650	3650A	--	3650B (Up. III)	--	--	Acid-Base Partition Cleanup
3660	3660A	--	3660B (Up. III)	--	--	Sulfur Cleanup
--	--	3665 (Up. II)	3665A (Up. III)	--	--	Sulfuric Acid/Permanganate Cleanup
3810	--	--	--	Deleted	--	Headspace
--	--	--	--	3815	--	Screening Solid Samples for Volatile Organics
3820	--	--	--	--	--	Hexadecane Extraction and Screening of Purgeable Organics
--	--	--	4000 (Up. III)	--	--	Immunoassay
--	--	4010 (Up. IIA)	4010A (Up. III)	--	--	Screening for Pentachlorophenol by Immunoassay
--	--	--	4015 (Up. III)	--	--	Screening for 2,4-Dichlorophenoxyacetic Acid by Immunoassay
--	--	--	4020 (Up. III)	--	--	Screening for Polychlorinated Biphenyls by Immunoassay
--	--	--	--	--	4025 (10/02)	Screening for Polychlorinated Dibenzodioxins and Polychlorinated Dibenzofurans (PCDD/Fs) by Immunoassay
--	--	--	4030 (Up. III)	--	--	Soil Screening for Petroleum Hydrocarbons by Immunoassay
--	--	--	4035 (Up. III)	--	--	Soil Screening for Polynuclear Aromatic Hydrocarbons by Immunoassay
--	--	--	4040 (Up. III)	--	--	Soil Screening for Toxaphene by Immunoassay

METHOD NUMBER (Date in parenthesis is found at bottom right-hand corner of method)						METHOD TITLE
THIRD EDITION (9/86)	FINAL UPDATE I (7/92)	FINAL UPDATE II (9/94) IIA (8/93) IIB (1/95)	FINAL UPDATE III (12/96) IIIA (4/98) IIIB (11/04)	FINAL UPDATE IV (2/07)	OTHER METHODS (www.epa.gov/ SW-846)	
--	--	--	4041 (Up. III)	--	--	Soil Screening for Chlordane by Immunoassay
--	--	--	4042 (Up. III)	--	--	Soil Screening for DDT by Immunoassay
--	--	--	4050 (Up. III)	--	--	TNT Explosives in Soil by Immunoassay
--	--	--	4051 (Up. III)	--	--	Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) in Soil by Immunoassay
--	--	--	--	4425	--	Screening Extracts of Environmental Samples for Planar Organic Compounds (PAHs, PCBs, PCDDs/PCDFs) by a Reporter Gene on a Human Cell Line
--	--	--	--	--	4430 (12/2007)	Screening for Polychlorinated Dibenzo-*p*-dioxins and Furans (PCDD/Fs) by Aryl Hydrocarbon-receptor PCR Assay
--	--	--	--	--	4435 (2/2008)	Method for Toxic Equivalents (TEQs) Determinations for Dioxin-like Chemical Activity with the Calux® Bioassay
--	--	--	--	4670	--	Triazine Herbicides as Atrazine in Water by Quantitative Immunoassay
--	--	--	5000 (Up. III)	--	--	Sample Preparation for Volatile Organic Compounds
--	--	--	5021 (Up. III)	--	5021A (6/03)	5021: Volatile Organic Compounds in Soils and Other Solid Sample Matrices Using Equilibrium Headspace Analysis 5021A: Volatile Organic Compounds in Various Sample Matrices Using Equilibrium Headspace Analysis
5030	5030A	--	5030B (Up. III)	--	5030C (5/03)	Purge-and-Trap for Aqueous Samples

METHOD NUMBER (Date in parenthesis is found at bottom right-hand corner of method)						METHOD TITLE
THIRD EDITION (9/86)	FINAL UPDATE I (7/92)	FINAL UPDATE II (9/94) IIA (8/93) IIB (1/95)	FINAL UPDATE III (12/96) IIIA (4/98) IIIB (11/04)	FINAL UPDATE IV (2/07)	OTHER METHODS (www.epa.gov/ SW-846)	
--	--	--	5031 (Up. III)	--	--	Volatile, Nonpurgeable, Water-Soluble Compounds by Azeotropic Distillation
--	--	--	5032 (Up. III)	--	--	Volatile Organic Compounds by Vacuum Distillation
--	--	--	5035 (Up. III)	--	5035A (7/02)	Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples
5040	--	5040A (Up. II)	Deleted (Up. III)	--	--	Analysis of Sorbent Cartridges from Volatile Organic Sampling Train (VOST): Gas Chromatography/Mass Spectrometry Technique
--	--	5041 (Up. II)	5041A (Up. III)	--	--	Analysis for Desorption of Sorbent Cartridges from Volatile Organic Sampling Train (VOST)
--	--	5050 (Up. II)	--	--	--	Bomb Preparation Method for Solid Waste
6010	6010A	--	6010B (Up. III)	6010C	--	Inductively Coupled Plasma-Atomic Emission Spectrometry
--	--	6020 (Up. II)	--	6020A	--	Inductively Coupled Plasma-Mass Spectrometry
--	--	--	--	6200	--	Field Portable X-Ray Fluorescence Spectrometry for the Determination of Elemental Concentrations in Soil and Sediment
--	--	--	--	6500	--	Dissolved Inorganic Anions in Aqueous Matrices by Capillary Ion Electrophoresis
--	--	--	--	6800	--	Elemental and Speciated Isotope Dilution Mass Spectrometry
--	--	--	--	--	6850 (1/07)	Perchlorate in Water, Soils and Solid Wastes Using High Performance Liquid Chromatography/Electrospray Ionization/Mass Spectrometry (HPLC/ESI/MS/MS)
--	--	--	--	--	6860	Perchlorate in Water, Soils and Solid Wastes Using Ion

METHOD NUMBER (Date in parenthesis is found at bottom right-hand corner of method)						METHOD TITLE
THIRD EDITION (9/86)	FINAL UPDATE I (7/92)	FINAL UPDATE II (9/94) IIA (8/93) IIB (1/95)	FINAL UPDATE III (12/96) IIIA (4/98) IIIB (11/04)	FINAL UPDATE IV (2/07)	OTHER METHODS (www.epa.gov/ SW-846)	
					(1/07)	Chromatography/Electrospray Ionization/Mass Spectrometry (IC/ESI/MS or IC/ESI/MS/MS)
7000	7000A	--	--	7000B	--	Flame Atomic Absorption Spectrophotometry
--	--	--	--	7010	--	Graphite Furnace Atomic Absorption Spectrophotometry
7020	--	--	--	Deleted	--	Aluminum (Atomic Absorption, Direct Aspiration)
7040	--	--	--	Deleted	--	Antimony (Atomic Absorption, Direct Aspiration)
7041	--	--	--	Deleted	--	Antimony (Atomic Absorption, Furnace Technique)
7060	--	7060A (Up. II)	--	Deleted	--	Arsenic (Atomic Absorption, Furnace Technique)
7061	7061A	--	--	--	--	Arsenic (Atomic Absorption, Gaseous Hydride)
--	--	7062 (Up. II)	--	--	--	Antimony and Arsenic (Atomic Absorption, Borohydride Reduction)
--	--	--	7063 (Up. III)	--	--	Arsenic in Aqueous Samples and Extracts by Anodic Stripping Voltammetry (ASV)
7080	--	7080A (Up. II)	--	Deleted	--	Barium (Atomic Absorption, Direct Aspiration)
--	7081	--	--	Deleted	--	Barium (Atomic Absorption, Furnace Technique)
7090	--	--	--	Deleted	--	Beryllium (Atomic Absorption, Direct Aspiration)
7091	--	--	--	Deleted	--	Beryllium (Atomic Absorption, Furnace Technique)
7130	--	--	--	Deleted	--	Cadmium (Atomic Absorption, Direct Aspiration)
7131	--	7131A (Up. II)	--	Deleted	--	Cadmium (Atomic Absorption, Furnace Technique)
7140	--	--	--	Deleted	--	Calcium (Atomic Absorption, Direct Aspiration)

METHOD NUMBER (Date in parenthesis is found at bottom right-hand corner of method)						METHOD TITLE
THIRD EDITION (9/86)	FINAL UPDATE I (7/92)	FINAL UPDATE II (9/94) IIA (8/93) IIB (1/95)	FINAL UPDATE III (12/96) IIIA (4/98) IIIB (11/04)	FINAL UPDATE IV (2/07)	OTHER METHODS (www.epa.gov/ SW-846)	
7190	--	--	--	Deleted	--	Chromium (Atomic Absorption, Direct Aspiration)
7191	--	--	--	Deleted	--	Chromium (Atomic Absorption, Furnace Technique)
7195	--	--	--	--	--	Chromium, Hexavalent (Coprecipitation)
7196	7196A	--	--	--	--	Chromium, Hexavalent (Colorimetric)
7197	--	--	--	--	--	Chromium, Hexavalent (Chelation/Extraction)
7198	--	--	--	--	--	Chromium, Hexavalent (Differential Pulse Polarography)
--	--	--	7199 (Up. III)	--	--	Determination of Hexavalent Chromium in Drinking Water, Groundwater and Industrial Wastewater Effluents by Ion Chromatography
7200	--	--	--	Deleted	--	Cobalt (Atomic Absorption, Direct Aspiration)
7201	--	--	--	Deleted	--	Cobalt (Atomic Absorption, Furnace Technique)
7210	--	--	--	Deleted	--	Copper (Atomic Absorption, Direct Aspiration)
--	7211	--	--	Deleted	--	Copper (Atomic Absorption, Furnace Technique)
7380	--	--	--	Deleted	--	Iron (Atomic Absorption, Direct Aspiration)
--	7381	--	--	Deleted	--	Iron (Atomic Absorption, Furnace Technique)
7420	--	--	--	Deleted	--	Lead (Atomic Absorption, Direct Aspiration)
7421	--	--	--	Deleted	--	Lead (Atomic Absorption, Furnace Technique)
--	7430	--	--	Deleted	--	Lithium (Atomic Absorption, Direct Aspiration)
7450	--	--	--	Deleted	--	Magnesium (Atomic Absorption, Direct Aspiration)
7460	--	--	--	Deleted	--	Manganese (Atomic Absorption, Direct Aspiration)

METHOD NUMBER (Date in parenthesis is found at bottom right-hand corner of method)						METHOD TITLE
THIRD EDITION (9/86)	FINAL UPDATE I (7/92)	FINAL UPDATE II (9/94) IIA (8/93) IIB (1/95)	FINAL UPDATE III (12/96) IIIA (4/98) IIIB (11/04)	FINAL UPDATE IV (2/07)	OTHER METHODS (www.epa.gov/ SW-846)	
--	7461	--	--	Deleted	--	Manganese (Atomic Absorption, Furnace Technique)
7470	--	7470A (Up. II)	--	--	--	Mercury in Liquid Waste (Manual Cold-Vapor Technique)
7471	--	7471A (Up. II)	--	7471B	--	Mercury in Solid or Semisolid Waste (Manual Cold-Vapor Technique)
--	--	--	7472 (Up. III)	--	--	Mercury in Aqueous Samples and Extracts by Anodic Stripping Voltammetry (ASV)
--	--	--	--	7473	--	Mercury in Solids and Solutions by Thermal Decomposition, Amalgamation, and Atomic Absorption Spectrophotometry
--	--	--	--	7474	--	Mercury in Sediment and Tissue Samples by Atomic Fluorescence Spectrometry
7480	--	--	--	Deleted	--	Molybdenum (Atomic Absorption, Direct Aspiration)
7481	--	--	--	Deleted	--	Molybdenum (Atomic Absorption, Furnace Technique)
7520	--	--	--	Deleted	--	Nickel (Atomic Absorption, Direct Aspiration)
--	--	--	7521 (Up. III)	Deleted	--	Nickel (Atomic Absorption, Furnace Method)
7550	--	--	--	Deleted	--	Osmium (Atomic Absorption, Direct Aspiration)
--	--	--	7580 (Up. III)	--	--	White Phosphorus (P_4) by Solvent Extraction and Gas Chromatography
7610	--	--	--	Deleted	--	Potassium (Atomic Absorption, Direct Aspiration)
7740	--	--	--	Deleted	--	Selenium (Atomic Absorption, Furnace Technique)
7741	--	7741A (Up. II)	--	--	--	Selenium (Atomic Absorption, Gaseous Hydride)

METHOD NUMBER (Date in parenthesis is found at bottom right-hand corner of method)						METHOD TITLE
THIRD EDITION (9/86)	FINAL UPDATE I (7/92)	FINAL UPDATE II (9/94) IIA (8/93) IIB (1/95)	FINAL UPDATE III (12/96) IIIA (4/98) IIIB (11/04)	FINAL UPDATE IV (2/07)	OTHER METHODS (www.epa.gov/ SW-846)	
--	--	7742 (Up. II)	--	--	--	Selenium (Atomic Absorption, Borohydride Reduction)
7760	7760A	--	--	Deleted	--	Silver (Atomic Absorption, Direct Aspiration)
--	7761	--	--	Deleted	--	Silver (Atomic Absorption, Furnace Technique)
7770	--	--	--	Deleted	--	Sodium (Atomic Absorption, Direct Aspiration)
--	7780	--	--	Deleted	--	Strontium (Atomic Absorption, Direct Aspiration)
7840	--	--	--	Deleted	--	Thallium (Atomic Absorption, Direct Aspiration)
7841	--	--	--	Deleted	--	Thallium (Atomic Absorption, Furnace Technique)
7870	--	--	--	Deleted	--	Tin (Atomic Absorption, Direct Aspiration)
7910	--	--	--	Deleted	--	Vanadium (Atomic Absorption, Direct Aspiration)
7911	--	--	--	Deleted	--	Vanadium (Atomic Absorption, Furnace Technique)
7950	--	--	--	Deleted	--	Zinc (Atomic Absorption, Direct Aspiration)
--	7951	--	--	Deleted	--	Zinc (Atomic Absorption, Furnace Technique)
8000	8000A	--	8000B (Up. III)	--	8000C (3/03)	Determinative Chromatographic Separations
8010	8010A	8010B (Up. II)	Deleted (Up. III)	--	--	Halogenated Volatile Organics by Gas Chromatography
--	8011	--	--	--	--	1,2-Dibromoethane and 1,2-Dibromo-3-chloropropane by Microextraction and Gas Chromatography
8015	8015A	--	8015B	8015C	8015D (6/03)	8015C: Nonhalogenated Organics by Gas Chromatography 8015D: Nonhalogenated Organics by Gas Chromatography Using GC/FID
8020	--	8020A	Deleted	--	--	Aromatic Volatile Organics by Gas Chromatography

METHOD NUMBER (Date in parenthesis is found at bottom right-hand corner of method)						METHOD TITLE
THIRD EDITION (9/86)	FINAL UPDATE I (7/92)	FINAL UPDATE II (9/94) IIA (8/93) IIB (1/95)	FINAL UPDATE III (12/96) IIIA (4/98) IIIB (11/04)	FINAL UPDATE IV (2/07)	OTHER METHODS (www.epa.gov/ SW-846)	
		(Up. II)	(Up. III)			
--	8021	8021A (Up. II)	8021B (Up. III)	--	--	Aromatic and Halogenated Volatiles by Gas Chromatography Using Photoionization and/or Electrolytic Conductivity Detectors
8030	8030A	--	Deleted (Up. III)	--	--	Acrolein and Acrylonitrile by Gas Chromatography
--	--	8031 (Up. II)	--	--	--	Acrylonitrile by Gas Chromatography
--	--	8032 (Up. II)	8032A (Up. III)	--	--	Acrylamide by Gas Chromatography
--	--	--	8033 (Up. III)	--	--	Acetonitrile by Gas Chromatography with Nitrogen-Phosphorus Detection
8040	8040A	--	Deleted (Up. III)	--	--	Phenols by Gas Chromatography
--	--	--	8041 (Up. III)	8041A	--	Phenols by Gas Chromatography
8060	--	--	Deleted (Up. III)	--	--	Phthalate Esters
--	--	8061 (Up. II)	8061A (Up. III)	--	--	Phthalate Esters by Gas Chromatography with Electron Capture Detection (GC/ECD)
--	8070	--	8070A (Up. III)	--	--	Nitrosamines by Gas Chromatography
8080	--	8080A (Up. II)	Deleted (Up. III)	--	--	Organochlorine Pesticides and Polychlorinated Biphenyls by Gas Chromatography
--	--	8081 (Up. II)	8081A (Up. III)	8081B	--	Organochlorine Pesticides by Gas Chromatography

METHOD NUMBER (Date in parenthesis is found at bottom right-hand corner of method)						METHOD TITLE
THIRD EDITION (9/86)	FINAL UPDATE I (7/92)	FINAL UPDATE II (9/94) IIA (8/93) IIB (1/95)	FINAL UPDATE III (12/96) IIIA (4/98) IIIB (11/04)	FINAL UPDATE IV (2/07)	OTHER METHODS (www.epa.gov/ SW-846)	
--	--	--	8082 (Up. III)	8082A	--	Polychlorinated Biphenyls (PCBs) by Gas Chromatography
				8085	--	Compound-independent Elemental Quantitation of Pesticides by Gas Chromatography with Atomic Emission Detection (GC/AED)
8090	--	--	Deleted (Up. III)	--	--	Nitroaromatics and Cyclic Ketones
--	--	--	8091 (Up. III)	--	--	Nitroaromatics and Cyclic Ketones by Gas Chromatography
--	--	--	--	8095	--	Explosives by Gas Chromatography
8100	--	--	--	--	--	Polynuclear Aromatic Hydrocarbons
--	8110	--	Deleted (Up. III)	--	--	Haloethers by Gas Chromatography
--	--	--	8111 (Up. III)	--	--	Haloethers by Gas Chromatography
8120	--	8120A (Up. II)	Deleted (Up. III)	--	--	Chlorinated Hydrocarbons by Gas Chromatography
--	--	8121 (Up. II)	--	--	--	Chlorinated Hydrocarbons by Gas Chromatography: Capillary Column Technique
--	--	--	8131 (Up. III)	--	--	Aniline and Selected Derivatives by Gas Chromatography
8140	--	--	Deleted (Up. III)	--	--	Organophosphorus Pesticides
--	8141	8141A (Up. II)	--	8141B	--	Organophosphorus Compounds by Gas Chromatography

METHOD NUMBER (Date in parenthesis is found at bottom right-hand corner of method)						METHOD TITLE
THIRD EDITION (9/86)	FINAL UPDATE I (7/92)	FINAL UPDATE II (9/94) IIA (8/93) IIB (1/95)	FINAL UPDATE III (12/96) IIIA (4/98) IIIB (11/04)	FINAL UPDATE IV (2/07)	OTHER METHODS (www.epa.gov/ SW-846)	
8150	8150A	8150B (Up. II)	Deleted (Up. III)	--	--	Chlorinated Herbicides by Gas Chromatography
--	--	8151 (Up. II)	8151A (Up. III)	--	--	Chlorinated Herbicides by GC Using Methylation or Pentafluorobenzylation Derivatization
--	--	--	--	--	8170 (7/2007)	Assay of Chemical Agents in Solid and Aqueous Samples by Gas Chromatography/Flame Photometric (GC/FPD) Detection
8240	8240A	8240B (Up. II)	Deleted (Up. III)	--	--	Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)
8250	--	8250A (Up. II)	Deleted (Up. III)	--	--	Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)
--	8260	8260A (Up. II)	8260B (Up. III)	--	8260C (8/06)	Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)
--	--	--	--	8261	8261A (10/06)	Volatile Organic Compounds by Vacuum Distillation in Combination with Gas Chromatography/Mass Spectrometry (VD/GC/MS)
--	--	--	--	--	8265 (3/02)	Volatile Organic Compounds in Water, Soil, Soil Gas and Air by Direct Sampling Ion Trap Mass Spectrometry (DSITMS)
8270	8270A	8270B (Up. II)	8270C (Up. III)	8270D	--	Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)
--	--	--	--	--	8271 (7/07)	Assay of Chemical Agents in Solid and Aqueous Samples by Gas Chromatography/Mass Spectrometry/Electron Impact (GC/MS/EI)
--	--	--	--	--	8272 (12/07)	Parent and Alkyl Polycyclic Aromatics in Sediment Pore Water by Solid-phase Microextraction and Gas Chromatography/Mass Spectrometry in Selected Ion Monitoring Mode

METHOD NUMBER (Date in parenthesis is found at bottom right-hand corner of method)						METHOD TITLE
THIRD EDITION (9/86)	FINAL UPDATE I (7/92)	FINAL UPDATE II (9/94) IIA (8/93) IIB (1/95)	FINAL UPDATE III (12/96) IIIA (4/98) IIIB (11/04)	FINAL UPDATE IV (2/07)	OTHER METHODS (www.epa.gov/ SW-846)	
--	--	8275 (Up. II)	8275A (Up. III)	--	--	Semivolatile Organic Compounds (PAHs and PCBs) in Soils/Sludges and Solid Wastes Using Thermal Extraction/Gas Chromatography/Mass Spectrometry (TE/GC/MS)
8280	--	--	8280A (Up. III)	8280B	--	Polychlorinated Dibenzo-*p*-Dioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) by High-Resolution Gas Chromatography/Low Resolution Mass Spectrometry (HRGC/LRMS)
--	--	8290 (Up. II)	--	8290A	--	Polychlorinated Dibenzo-*p*-dioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) by High-Resolution Gas Chromatography/ High-Resolution Mass Spectrometry (HRGC/HRMS)
8310	--	--	--	--	--	Polynuclear Aromatic Hydrocarbons
--	--	8315 (Up. II)	8315A (Up. III)	--	--	Determination of Carbonyl Compounds by High Performance Liquid Chromatography (HPLC)
--	--	8316 (Up. II)	--	--	--	Acrylamide, Acrylonitrile and Acrolein by High Performance Liquid Chromatography (HPLC)
--	--	8318 (Up. II)	--	8318A	--	*N*-Methylcarbamates by High Performance Liquid Chromatography (HPLC)
--	--	8321 (Up. II)	8321A (Up. III)	8321B	--	Solvent-Extractable Nonvolatile Compounds by High-Performance Liquid Chromatography/Thermospray/Mass Spectrometry (HPLC/TS/MS) or Ultraviolet (UV) Detection
--	--	--	--	--	8323 (1/03)	Determination of Organotins by Micro-liquid Chromatography-electrospray Ion Trap Mass Spectrometry
--	--	--	8325 (Up. III)	--	--	Solvent Extractable Nonvolatile Compounds by High Performance Liquid Chromatography/Particle Beam/Mass Spectrometry (HPLC/PB/MS)

METHOD NUMBER (Date in parenthesis is found at bottom right-hand corner of method)						METHOD TITLE
THIRD EDITION (9/86)	FINAL UPDATE I (7/92)	FINAL UPDATE II (9/94) IIA (8/93) IIB (1/95)	FINAL UPDATE III (12/96) IIIA (4/98) IIIB (11/04)	FINAL UPDATE IV (2/07)	OTHER METHODS (www.epa.gov/ SW-846)	
--	--	8330 (Up. II)	--	8330A	8330B (10/06)	Nitroaromatics and Nitramines by High Performance Liquid Chromatography (HPLC)
--	--	8331 (Up. II)	--	--	--	Tetrazene by Reverse Phase High Performance Liquid Chromatography (HPLC)
--	--	--	8332 (Up. III)	--	--	Nitroglycerine by High Performance Liquid Chromatography
--	--	8410 (Up. II)	--	--	--	Gas Chromatography/Fourier Transform Infrared (GC/FT-IR) Spectrometry for Semivolatile Organics: Capillary Column
--	--	--	8430 (Up. III)	--	--	Analysis of Bis(2-chloroethyl) Ether and Hydrolysis Products by Direct Aqueous Injection GC/FT-IR
--	--	--	8440 (Up. III)	--	--	Total Recoverable Petroleum Hydrocarbons by Infrared Spectrophotometry
				8510	--	Colorimetric Screening Procedure for RDX and HMX in Soil
--	--	--	8515 (Up. III)	--	--	Colorimetric Screening Method for Trinitrotoluene (TNT) in Soil
--	--	--	8520 (Up. III)	--	--	Continuous Measurement of Formaldehyde in Ambient Air
--	--	--	--	8535	--	Screening Procedure for Total Volatile Organic Halides in Water
--	--	--	--	8540	--	Pentachlorophenol by UV-induced Colorimetry
--	--	--	--	9000	--	Determination of Water in Waste Materials by Karl Fischer Titration
--	--	--	--	9001	--	Determination of Water in Waste Materials by Quantitative Calcium Hydride Reaction
9010	9010A	--	9010B (Up. III)	--	--	Total and Amenable Cyanide: Distillation

METHOD NUMBER (Date in parenthesis is found at bottom right-hand corner of method)						METHOD TITLE
THIRD EDITION (9/86)	FINAL UPDATE I (7/92)	FINAL UPDATE II (9/94) IIA (8/93) IIB (1/95)	FINAL UPDATE III (12/96) IIIA (4/98) IIIB (11/04)	FINAL UPDATE IV (2/07)	OTHER METHODS (www.epa.gov/ SW-846)	
			9010C (Up. IIIB)			
9012	--	--	9012A (Up. III) 9012B (Up. IIIB)	--	--	Total and Amenable Cyanide (Automated Colorimetric, with Off-line Distillation)
--	9013	--	--	--	9013A (11/04)	Cyanide Extraction Procedure for Solids and Oils
--	--	--	9014 (Up. III)	--	--	Titrimetric and Manual Spectrophotometric Determinative Methods for Cyanide
--	--	--	--	--	9015 (11/04)	Metal Cyanide Complexes by Anion Exchange Chromatography and UV Detection
9020	9020A	9020B (Up. II)	--	--	--	Total Organic Halides (TOX)
--	9021	--	--	--	--	Purgeable Organic Halides (POX)
9022	--	--	--	--	--	Total Organic Halides (TOX) by Neutron Activation Analysis
--	--	--	9023 (Up. III)	--	--	Extractable Organic Halides (EOX) in Solids
9030	9030A	--	9030B (Up. III)	--	--	Acid-Soluble and Acid-Insoluble Sulfides: Distillation
--	9031	--	--	--	--	Extractable Sulfides
--	--	--	9034 (Up. III)	--	--	Titrimetric Procedure for Acid-Soluble and Acid-Insoluble Sulfides
9035	--	--	--	--	--	Sulfate (Colorimetric, Automated, Chloranilate)

METHOD NUMBER (Date in parenthesis is found at bottom right-hand corner of method)						METHOD TITLE
THIRD EDITION (9/86)	FINAL UPDATE I (7/92)	FINAL UPDATE II (9/94) IIA (8/93) IIB (1/95)	FINAL UPDATE III (12/96) IIIA (4/98) IIIB (11/04)	FINAL UPDATE IV (2/07)	OTHER METHODS (www.epa.gov/ SW-846)	
9036	--	--	--	--	--	Sulfate (Colorimetric, Automated, Methylthymol Blue, AA II)
9038	--	--	--	--	--	Sulfate (Turbidimetric)
9040	--	9040A (Up. II) 9040B (Up. IIB)	9040C (Up. IIIB)	--	--	pH Electrometric Measurement
9041	9041A	--	--	--	--	pH Paper Method
9045	9045A	9045B (Up. II) 9045C (Up. IIB)	9045D (Up. IIIB)	--	--	Soil and Waste pH
9050	--	--	9050A (Up. III)	--	--	Specific Conductance
--	--	9056 (Up. II)	--	9056A	--	Determination of Inorganic Anions by Ion Chromatography
--	--	--	9057 (Up. III)	--	--	Determination of Chloride from HCl/Cl_2 Emission Sampling Train (Methods 0050 and 0051) by Anion Chromatography
9060	--	--	9060A (Up. IIIB)	--	--	Total Organic Carbon
9065	--	--	--	--	--	Phenolics (Spectrophotometric, Manual 4-AAP with Distillation)
9066	--	--	--	--	--	Phenolics (Colorimetric, Automated 4-AAP with Distillation)
9067	--	--	--	--	--	Phenolics (Spectrophotometric, MBTH with Distillation)
9070	--	--	9070	--	--	n-Hexane Extractable Material (HEM) for Aqueous Samples

METHOD NUMBER (Date in parenthesis is found at bottom right-hand corner of method)						METHOD TITLE
THIRD EDITION (9/86)	FINAL UPDATE I (7/92)	FINAL UPDATE II (9/94) IIA (8/93) IIB (1/95)	FINAL UPDATE III (12/96) IIIA (4/98) IIIB (11/04)	FINAL UPDATE IV (2/07)	OTHER METHODS (www.epa.gov/ SW-846)	
			(Up. IIIA) 9070A (Up. IIIB)			(Note: Method text is a referral to Method 1664: n-Hexane Extractable Material (HEM; Oil and Grease) and Silica Gel Treated n-Hexane Extractable Material (SGT-HEM; Non-polar Material) by Extraction and Gravimetry)
9071	--	9071A (Up. II)	9071B (Up. IIIA)	--	--	n-Hexane Extractable Material (HEM) for Sludge, Sediment, and Solid Samples
--	--	--	--	9074	--	Turbidimetric Screening Method for Total Recoverable Petroleum Hydrocarbons in Soil
--	--	9075 (Up. II)	--	--	--	Test Method for Total Chlorine in New and Used Petroleum Products by X-Ray Fluorescence Spectrometry (XRF)
--	--	9076 (Up. II)	--	--	--	Test Method for Total Chlorine in New and Used Petroleum Products by Oxidative Combustion and Microcoulometry
--	--	9077 (Up. II)	--	--	--	Test Methods for Total Chlorine in New and Used Petroleum Products (Field Test Kit Methods)
--	--	--	9078 (Up. III)	--	--	Screening Test Method for Polychlorinated Biphenyls in Soil
--	--	--	9079 (Up. III)	--	--	Screening Test Method for Polychlorinated Biphenyls in Transformer Oil
9080	--	--	--	--	--	Cation-Exchange Capacity of Soils (Ammonium Acetate)
9081	--	--	--	--	--	Cation-Exchange Capacity of Soils (Sodium Acetate)
9090	9090A	--	--	--	--	Compatibility Test for Wastes and Membrane Liners
9095	--	--	9095A (Up. III) 9095B	--	--	Paint Filter Liquids Test

METHOD NUMBER (Date in parenthesis is found at bottom right-hand corner of method)						METHOD TITLE
THIRD EDITION (9/86)	FINAL UPDATE I (7/92)	FINAL UPDATE II (9/94) IIA (8/93) IIB (1/95)	FINAL UPDATE III (12/96) IIIA (4/98) IIIB (11/04)	FINAL UPDATE IV (2/07)	OTHER METHODS (www.epa.gov/ SW-846)	
			(Up. IIIB)			
--	--	9096 (Up. II)	--	--	--	Liquid Release Test (LRT) Procedure
9100	--	--	--	--	--	Saturated Hydraulic Conductivity, Saturated Leachate Conductivity, and Intrinsic Permeability
9131	--	--	--	--	--	Total Coliform: Multiple Tube Fermentation Technique
9132	--	--	--	--	--	Total Coliform: Membrane-Filter Technique
9200	--	--	Deleted (Up. III)	--	--	Nitrate
--	--	--	9210 (Up. III)	9210A	--	Potentiometric Determination of Nitrate in Aqueous Samples with an Ion-Selective Electrode
--	--	--	9211 (Up. III)	--	--	Potentiometric Determination of Bromide in Aqueous Samples with Ion-Selective Electrode
--	--	--	9212 (Up. III)	--	--	Potentiometric Determination of Chloride in Aqueous Samples with Ion-Selective Electrode
--	--	--	9213 (Up. III)	--	--	Potentiometric Determination of Cyanide in Aqueous Samples and Distillates with Ion-Selective Electrode
--	--	--	9214 (Up. III)	--	--	Potentiometric Determination of Fluoride in Aqueous Samples with Ion-Selective Electrode
--	--	--	9215 (Up. III)	--	--	Potentiometric Determination of Sulfide in Aqueous Samples and Distillates with Ion-Selective Electrode
--	--	--	--	9216	--	Potentiometric Determination of Nitrite in Aqueous Samples with Ion-Selective Electrode
9250	--	--	--	--	--	Chloride (Colorimetric, Automated Ferricyanide AAI)

METHOD NUMBER (Date in parenthesis is found at bottom right-hand corner of method)						METHOD TITLE
THIRD EDITION (9/86)	FINAL UPDATE I (7/92)	FINAL UPDATE II (9/94) IIA (8/93) IIB (1/95)	FINAL UPDATE III (12/96) IIIA (4/98) IIIB (11/04)	FINAL UPDATE IV (2/07)	OTHER METHODS (www.epa.gov/ SW-846)	
9251	--	--	--	--	--	Chloride (Colorimetric, Automated Ferricyanide AAII)
9252	--	9252A (Up. II)	Deleted (Up. III)	--	--	Chloride (Titrimetric, Mercuric Nitrate)
--	--	9253 (Up. II)	--	--	--	Chloride (Titrimetric, Silver Nitrate)
9310	--	--	--	--	--	Gross Alpha and Gross Beta
9315	--	--	--	--	--	Alpha-Emitting Radium Isotopes
9320	--	--	--	--	--	Radium-228
HCN and H_2S Test Methods	HCN and H_2S Test Methods	HCN and H_2S Test Methods (Up. II)	HCN and H_2S Test Methods (Up. III) Deleted (Up. IIIB)	--	--	Test Method to Determine Hydrogen Cyanide Released from Wastes and Test Method to Determine Hydrogen Sulfide Released from Wastes

Note: Draft Update IV Method 9058, "Determination of Perchlorate Using Ion Chromatography with Chemical Suppression Conductivity Detection," and Method 4500, "Mercury in Soil by Immunoassay," were not finalized as part of Final Update IV. See the Final Update IV Federal Register Notice.

STATUS TABLE FOR SW-846 CHAPTER TEXT AND OTHER DOCUMENTS

TITLE	THIRD ED. (9/86)	FINAL UP. I (7/92)	FIN. UP. II (9/94) IIA (8/93) IIB (1/95)	FINAL UP. III (12/96) IIIA (4/98) IIIB (11/04)	FINAL UP. IV (2/07)	CURRENT FINAL VERSION
Disclaimer	--	✓	--	✓ (Up. III)	--	Rev 1 (12/96)
Abstract	✓	✓	✓ (Up. II)	--	--	Rev 2 (9/94)
Table of Contents	✓	✓	✓ (Up. II & IIB)	✓ (Up. III, IIIA, and IIIB)	✓	Rev 7 (2/07)
Method Index and Conversion Table	✓	--	--	--	--	Rev 0 (9/86)
Preface and Overview	✓	--	--	✓ (Up. III)	--	Rev 1 (12/96)
Acknowledgments	✓	--	--	--	--	Rev 0 (9/86)
Chapter One -- Quality Control	✓	✓	--	--	--	Rev 1 (7/92)
Chapter Two -- Choosing the Correct Procedure	✓	✓	✓ (Up. II)	✓ (Up. III)	✓	Rev 4 (2/07)
Chapter Three -- Inorganic Analytes	✓	✓	✓ (Up. II)	✓ (Up. III)	✓	Rev 4 (2/07)
Chapter Four -- Organic Analytes	✓	--	✓ (Up. II)	✓ (Up. III)	✓	Rev 4 (2/07)
Chapter Five -- Miscellaneous Test Methods	✓	--	✓ (Up. II)	✓ (Up. III, IIIA and IIIB)	✓	Rev 5 (2/07)
Chapter Six -- Properties	✓	--	✓	✓ (Up. III and	✓	Rev 5

TITLE	THIRD ED. (9/86)	FINAL UP. I (7/92)	FIN. UP. II (9/94) IIA (8/93) IIB (1/95)	FINAL UP. III (12/96) IIIA (4/98) IIIB (11/04)	FINAL UP. IV (2/07)	CURRENT FINAL VERSION
			(Up. II & IIB)	IIIB)		(2/07)
Chapter Seven -- Characteristics Introduction and Regulatory Definitions	✓	✓	✓ (Up. II)	✓ (Up. III and IIIB)	--	Rev 4 (11/04)
Chapter Eight --Methods for Determining Characteristics	✓	--	✓ (Up. II)	✓ (Up. III and IIIB)	--	Rev 3 (11/04)
Chapter Nine -- Sampling Plan	✓	--	--	--	--	Rev 0 (9/86)
Chapter Ten -- Sampling Methods	✓	--	--	✓ (Up. III)	✓	Rev 3 (2/07)
Chapter Eleven -- Ground Water Monitoring	✓	--	--	--	✓	Rev 1 (2/07)
Chapter Twelve -- Land Treatment Monitoring	✓	--	--	--	--	Rev 0 (9/86)
Chapter Thirteen -- Incineration	✓	--	--	--	--	Rev 0 (9/86)
Appendix -- Company References	✓	--	--	--	--	Rev 0 (9/86)

ABSTRACT

Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846) provides test procedures and guidance which are recommended for use in conducting the evaluations and measurements needed to comply with the Resource Conservation and Recovery Act (RCRA), Public Law 94-580, as amended. These methods are approved by the U.S. Environmental Protection Agency for obtaining data to satisfy the requirements of 40 **CFR** Parts 122 through 270 promulgated under RCRA, as amended. This manual presents the state-of-the-art in routine analytical tested adapted for the RCRA program. It contains procedures for field and laboratory quality control, sampling, determining hazardous constituents in wastes, determining the hazardous characteristics of wastes (toxicity, ignitability, reactivity, and corrosivity), and for determining physical properties of wastes. It also contains guidance on how to select appropriate methods.

Several of the hazardous waste regulations under Subtitle C of RCRA require that specific testing methods described in SW-846 be employed for certain applications. Refer to 40 *Code of Federal Regulations* (CFR), Parts 260 through 270, for those specific requirements. Any reliable analytical method may be used to meet other requirements under Subtitle C of RCRA.

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CHAPTER ONE
QUALITY CONTROL

1.0 INTRODUCTION

It is the goal of the U.S. Environmental Protection Agency's (EPA's) quality assurance (QA) program to ensure that all data be scientifically valid, defensible, and of known precision and accuracy. The data should be of sufficient known quality to withstand scientific and legal challenge relative to the use for which the data are obtained. The QA program is management's tool for achieving this goal.

For RCRA analyses, the recommended minimum requirements for a QA program and the associated quality control (QC) procedures are provided in this chapter.

The data acquired from QC procedures are used to estimate the quality of analytical data, to determine the need for corrective action in response to identified deficiencies, and to interpret results after corrective action procedures are implemented. Method-specific QC procedures are incorporated in the individual methods since they are not applied universally.

A total program to generate data of acceptable quality should include both a QA component, which encompasses the management procedures and controls, as well as an operational day-to-day QC component. This chapter defines fundamental elements of such a data collection program. Data collection efforts involve:

1. design of a project plan to achieve the data quality objectives (DQOs);

2. implementation of the project plan; and

3. assessment of the data to determine if the DQOs are met.

The project plan may be a sampling and analysis plan or a waste analysis plan if it covers the QA/QC goals of the Chapter, or it may be a Quality Assurance Project Plan as described later in this chapter.

This chapter identifies the minimal QC components that should be used in the performance of sampling and analyses, including the QC information which should be documented. Guidance is provided to construct QA programs for field and laboratory work conducted in support of the RCRA program.

2.0 QA PROJECT PLAN

It is recommended that all projects which generate environment-related data in support of RCRA have a QA Project Plan (QAPjP) or equivalent. In some instances, a sampling and analysis plan or a waste analysis plan may be equivalent if it covers all of the QA/QC goals outlined in this chapter. In addition, a separate QAPjP need not be prepared for routine analyses or

activities where the procedures to be followed are described in a Standard Operating Procedures manual or similar document and include the elements of a QAPjP. These documents should be available and referenced in the documentation and/or records for the analysis activities. The term "QAPjP" in this chapter refers to any of these QA/QC documents.

The QAPjP should detail the QA/QC goals and protocols for a specific data collection activity. The QAPjP sets forth a plan for sampling and analysis activities that will generate data of a quality commensurate with their intended use. QAPjP elements should include a description of the project and its objectives; a statement of the DQOs of the project; identification of those involved in the data collection and their responsibilities and authorities; reference to (or inclusion of) the specific sample collection and analysis procedures that will be followed for all aspects of the project; enumeration of QC procedures to be followed; and descriptions of all project documentation. Additional elements should be included in the QAPjP if needed to address all quality related aspects of the data collection project. Elements should be omitted only when they are inappropriate for the project or when absence of those elements will not affect the quality of data obtained for the project (see reference 1).

The role and importance of DQOs and project documentation are discussed below in Sections 2.1 through 2.6. Management and organization play a critical role in determining the effectiveness of a QA/QC program and ensuring that all required procedures are followed. Section 2.7 discusses the elements of an organization's QA program that have been found to ensure an effective program. Field operations and laboratory operations (along with applicable QC procedures) are discussed in Sections 3 and 4, respectively.

2.1 DATA QUALITY OBJECTIVES

Data quality objectives (DQOs) for the data collection activity describe the overall level of uncertainty that a decision-maker is willing to accept in results derived from environmental data. This uncertainty is used to specify the quality of the measurement data required, usually in terms of objectives for precision, bias, representativeness, comparability and completeness. The DQOs should be defined prior to the initiation of the field and laboratory work. The field and laboratory organizations performing the work should be aware of the DQOs so that their personnel may make informed decisions during the course of the project to attain those DQOs. More detailed information on DQOs is available from the U.S. EPA Quality Assurance Management Staff (QAMS) (see references 2 and 4).

2.2 PROJECT OBJECTIVES

A statement of the project objectives and how the objectives are to be attained should be concisely stated and sufficiently detailed to permit clear understanding by all parties involved in the data collection effort. This

includes a statement of what problem is to be solved and the information required in the process. It also includes appropriate statements of the DQOs (i.e., the acceptable level of uncertainty in the information).

2.3 SAMPLE COLLECTION

Sampling procedures, locations, equipment, and sample preservation and handling requirements should be specified in the QAPjP. Further details on quality assurance procedures for field operations are described in Section 3 of this chapter. The OSW is developing policies and procedures for sampling in a planned revision of Chapter Nine of this manual. Specific procedures for groundwater sampling are provided in Chapter Eleven of this manual.

2.4 ANALYSIS AND TESTING

Analytes and properties of concern, analytical and testing procedures to be employed, required detection limits, and requirements for precision and bias should be specified. All applicable regulatory requirements and the project DQOs should be considered when developing the specifications. Further details on the procedures for analytical operations are described in Section 4 of this chapter.

2.5 QUALITY CONTROL

The quality assurance program should address both field and laboratory activities. Quality control procedures should be specified for estimating the precision and bias of the data. Recommended minimum requirements for QC samples have been established by EPA and should be met in order to satisfy recommended minimum criteria for acceptable data quality. Further details on procedures for field and laboratory operations are described in Sections 3 and 4, respectively, of this chapter.

2.6 PROJECT DOCUMENTATION

Documents should be prepared and maintained in conjunction with the data collection effort. Project documentation should be sufficient to allow review of all aspects of the work being performed. The QAPjP discussed in Sections 3 and 4 is one important document that should be maintained.

The length of storage time for project records should comply with regulatory requirements, organizational policy, or project requirements, whichever is more stringent. It is recommended that documentation be stored for three years from submission of the project final report.

Documentation should be secured in a facility that adequately addresses/minimizes its deterioration for the length of time that it is to be

retained. A system allowing for the expedient retrieval of information should exist.

Access to archived information should be controlled to maintain the integrity of the data. Procedures should be developed to identify those individuals with access to the data.

2.7 ORGANIZATION PERFORMING FIELD OR LABORATORY OPERATIONS

Proper design and structure of the organization facilitates effective and efficient transfer of information and helps to prevent important procedures from being overlooked.

The organizational structure, functional responsibilities, levels of authority, job descriptions, and lines of communication for all project activities should be established and documented. One person may cover more than one organizational function. Each project participant should have a clear understanding of his or her duties and responsibilities and the relationship of those responsibilities to the overall data collection effort.

The management of each organization participating in a project involving data collection activities should establish that organization's operational and QA policies. This information should be documented in the QAPjP. The management should ensure that (1) the appropriate methodologies are followed as documented in the QAPjPs; (2) personnel clearly understand their duties and responsibilities; (3) each staff member has access to appropriate project documents; (4) any deviations from the QAPjP are communicated to the project management and documented; and (5) communication occurs between the field, laboratory, and project management, as specified in the QAPjP. In addition, each organization should ensure that their activities do not increase the risk to humans or the environment at or about the project location. Certain projects may require specific policies or a Health and Safety Plan to provide this assurance.

The management of the participating field or laboratory organization should establish personnel qualifications and training requirements for the project. Each person participating in the project should have the education, training, technical knowledge, and experience, or a combination thereof, to enable that individual to perform assigned functions. Training should be provided for each staff member as necessary to perform their functions properly. Personnel qualifications should be documented in terms of education, experience, and training, and periodically reviewed to ensure adequacy to current responsibilities.

Each participating field organization or laboratory organization should have a designated QA function (i.e., a team or individual trained in QA) to monitor operations to ensure that the equipment, personnel, activities, procedures, and documentation conform with the QAPjP. To the extent possible, the QA monitoring function should be entirely separate from, and independent of,

personnel engaged in the work being monitored. The QA function should be responsible for the QA review.

2.7.1 Performance Evaluation

Performance evaluation studies are used to measure the performance of the laboratory on unknown samples. Performance evaluation samples are typically submitted to the laboratory as blind samples by an independent outside source. The results are compared to predetermined acceptance limits. Performance evaluation samples can also be submitted to the laboratory as part of the QA function during internal assessment of laboratory performance. Records of all performance evaluation studies should be maintained by the laboratory. Problems identified through participation in performance evaluation studies should be immediately investigated and corrected.

2.7.2 Internal Assessment by QA Function

Personnel performing field and laboratory activities are responsible for continually monitoring individual compliance with the QAPjP. The QA function should review procedures, results and calculations to determine compliance with the QAPjP. The results of this internal assessment should be reported to management with requirements for a plan to correct observed deficiencies.

2.7.3 External Assessment

The field and laboratory activities may be reviewed by personnel external to the organization. Such an assessment is an extremely valuable method for identifying overlooked problems. The results of the external assessment should be submitted to management with requirements for a plan to correct observed deficiencies.

2.7.4 On-Site Evaluation

On-site evaluations may be conducted as part of both internal and external assessments. The focus of an on-site evaluation is to evaluate the degree of conformance of project activities with the applicable QAPjP. On-site evaluations may include, but are not limited to, a complete review of facilities, staff, training, instrumentation, procedures, methods, sample collection, analyses, QA policies and procedures related to the generation of environmental data. Records of each evaluation should include the date of the evaluation, location, the areas reviewed, the person performing the evaluation, findings and problems, and actions recommended and taken to resolve problems. Any problems identified that are likely to affect data integrity should be brought immediately to the attention of management.

2.7.4.1 Field Activities

The review of field activities should be conducted by one or more persons knowledgeable in the activities being reviewed and include evaluating, at a minimum, the following subjects:

Completeness of Field Reports -- This review determines whether all requirements for field activities in the QAPjP have been fulfilled, that complete records exist for each field activity, and that the procedures specified in the QAPjP have been implemented. Emphasis on field documentation will help assure sample integrity and sufficient technical information to recreate each field event. The results of this completeness check should be documented, and environmental data affected by incomplete records should be identified.

Identification of Valid Samples -- This review involves interpretation and evaluation of the field records to detect problems affecting the representativeness of environmental samples. Examples of items that might indicate potentially invalid samples include improper well development, improperly screened wells, instability of pH or conductivity, and collection of volatiles near internal combustion engines. The field records should be evaluated against the QAPjP and SOPs. The reviewer should document the sample validity and identify the environmental data associated with any poor or incorrect field work.

Correlation of Field Test Data -- This review involves comparing any available results of field measurements obtained by more than one method. For example, surface geophysical methods should correlate with direct methods of site geologic characterization such as lithologic logs constructed during drilling operations.

Identification of Anomalous Field Test Data -- This review identifies any anomalous field test data. For example, a water temperature for one well that is 5 degrees higher than any other well temperature in the same aquifer should be noted. The reviewer should evaluate the impact of anomalous field measurement results on the associated environmental data.

Validation of Field Analyses -- This review validates and documents all data from field analysis that are generated *in situ* or from a mobile laboratory as specified in Section 2.7.4.2. The reviewer should document whether the QC checks meet the acceptance criteria, and whether corrective actions were taken for any analysis performed when acceptance criteria were exceeded.

2.7.4.2 Laboratory Activities

The review of laboratory data should be conducted by one or more persons knowledgeable in laboratory activities and include evaluating, at a minimum, the following subjects:

Completeness of Laboratory Records -- This review determines whether: (1) all samples and analyses required by the QAPjP have been processed, (2) complete records exist for each analysis and the associated QC samples, and that (3) the procedures specified in the QAPjP have been implemented. The results of the completeness check should be documented, and environmental data affected by incomplete records should be identified.

Evaluation of Data with Respect to Detection and Quantitation Limits -- This review compares analytical results to required quantitation limits. Reviewers should document instances where detection or quantitation limits exceed regulatory limits, action levels, or target concentrations specified in the QAPjP.

Evaluation of Data with Respect to Control Limits -- This review compares the results of QC and calibration check samples to control criteria. Corrective action should be implemented for data not within control limits. The reviewer should check that corrective action reports, and the results of reanalysis, are available. The review should determine whether samples associated with out-of-control QC data are identified in a written record of the data review, and whether an assessment of the utility of such analytical results is recorded.

Review of Holding Time Data -- This review compares sample holding times to those required by the QAPjP, and notes all deviations.

Review of Performance Evaluation (PE) Results -- PE study results can be helpful in evaluating the impact of out-of-control conditions. This review documents any recurring trends or problems evident in PE studies and evaluates their effect on environmental data.

Correlation of Laboratory Data -- This review determines whether the results of data obtained from related laboratory tests, e.g., Purgeable Organic Halides (POX) and Volatile Organics, are documented, and whether the significance of any differences is discussed in the reports.

2.7.5 QA Reports

There should be periodic reporting of pertinent QA/QC information to the project management to allow assessment of the overall effectiveness of the QA program. There are three major types of QA reports to project management:

Periodic Report on Key QA Activities -- Provides summary of key QA activities during the period, stressing measures that are being taken to improve data quality; describes significant quality problems observed and corrective actions taken; reports information regarding any changes in certification/accreditation status; describes involvement in resolution of quality issues with clients or agencies; reports any QA organizational changes; and provides notice of the distribution of revised documents controlled by the QA organization (i.e., procedures).

Report on Measurement Quality Indicators -- Includes the assessment of QC data gathered over the period, the frequency of analyses repeated due to unacceptable QC performance, and, if possible, the reason for the unacceptable performance and corrective action taken.

Reports on QA Assessments -- Includes the results of the assessments and the plan for correcting identified deficiencies; submitted immediately

following any internal or external on-site evaluation or upon receipt of the results of any performance evaluation studies.

3.0 FIELD OPERATIONS

The field operations should be conducted in such a way as to provide reliable information that meets the DQOs. To achieve this, certain minimal policies and procedures should be implemented. The OSW is considering revisions of Chapter Nine and Eleven of this manual. Supplemental information and guidance is available in the RCRA Ground-Water Monitoring Technical Enforcement Guidance Document (TEGD) (Reference 3). The project documentation should contain the information specified below.

3.1 FIELD LOGISTICS

The QAPjP should describe the type(s) of field operations to be performed and the appropriate area(s) in which to perform the work. The QAPjP should address ventilation, protection from extreme weather and temperatures, access to stable power, and provision for water and gases of required purity.

Whenever practical, the sampling site facilities should be examined prior to the start of work to ensure that all required items are available. The actual area of sampling should be examined to ensure that trucks, drilling equipment, and personnel have adequate access to the site.

The determination as to whether sample shipping is necessary should be made during planning for the project. This need is established by evaluating the analyses to be performed, sample holding times, and location of the site and the laboratory. Shipping or transporting of samples to a laboratory should be done within a timeframe such that recommended holding times are met.

Samples should be packaged, labelled, preserved (e.g., preservative added, iced, etc.), and documented in an area which is free of contamination and provides for secure storage. The level of custody and whether sample storage is needed should be addressed in the QAPjP.

Storage areas for solvents, reagents, standards, and reference materials should be adequate to preserve their identity, concentration, purity, and stability prior to use.

Decontamination of sampling equipment may be performed at the location where sampling occurs, prior to going to the sampling site, or in designated areas near the sampling site. Project documentation should specify where and how this work is accomplished. If decontamination is to be done at the site, water and solvents of appropriate purity should be available. The method of accomplishing decontamination, including the required materials, solvents, and water purity should be specified.

During the sampling process and during on-site or in situ analyses, waste materials are sometimes generated. The method for storage and disposal of these waste materials that complies with applicable local, state and Federal regulations should be specified. Adequate facilities should be provided for the collection and storage of all wastes, and these facilities should be operated so as to minimize environmental contamination. Waste storage and disposal facilities should comply with applicable federal, state, and local regulations.

The location of long-term and short-term storage for field records, and the measures to ensure the integrity of the data should be specified.

3.2 EQUIPMENT/INSTRUMENTATION

The equipment, instrumentation, and supplies at the sampling site should be specified and should be appropriate to accomplish the activities planned. The equipment and instrumentation should meet the requirements of specifications, methods, and procedures as specified in the QAPjP.

3.3 OPERATING PROCEDURES

The QAPjP should describe or make reference to all field activities that may affect data quality. For routinely performed activities, standard operating procedures (SOPs) are often prepared to ensure consistency and to save time and effort in preparing QAPjPs. Any deviation from an established procedure during a data collection activity should be documented. The procedures should be available for the indicated activities, and should include, at a minimum, the information described below.

3.3.1 Sample Management

The numbering and labeling system, chain-of-custody procedures, and how the samples are to be tracked from collection to shipment or receipt by the laboratory should be specified. Sample management procedures should also specify the holding times, volumes of sample required by the laboratory, required preservatives, and shipping requirements.

3.3.2 Reagent/Standard Preparation

The procedures describing how to prepare standards and reagents should be specified. Information concerning specific grades of materials used in reagent and standard preparation, appropriate glassware and containers for preparation and storage, and labeling and record keeping for stocks and dilutions should be included.

3.3.3 Decontamination

The procedures describing decontamination of field equipment before and during the sample collection process should be specified. These procedures

should include cleaning materials used, the order of washing and rinsing with the cleaning materials, requirements for protecting or covering cleaned equipment, and procedures for disposing of cleaning materials.

3.3.4 Sample Collection

The procedures describing how the sampling operations are actually performed in the field should be specified. A simple reference to standard methods is not sufficient, unless a procedure is performed exactly as described in the published method. Methods from source documents published by the EPA, American Society for Testing and Materials, U.S. Department of the Interior, National Water Well Association, American Petroleum Institute, or other recognized organizations with appropriate expertise should be used, if possible. The procedures for sample collection should include at least the following:

- Applicability of the procedure,
- Equipment required,
- Detailed description of procedures to be followed in collecting the samples,
- Common problems encountered and corrective actions to be followed, and
- Precautions to be taken.

3.3.5 Field Measurements

The procedures describing all methods used in the field to determine a chemical or physical parameter should be described in detail. The procedures should address criteria from Section 4, as appropriate.

3.3.6 Equipment Calibration And Maintenance

The procedures describing how to ensure that field equipment and instrumentation are in working order should be specified. These describe calibration procedures and schedules, maintenance procedures and schedules, maintenance logs, and service arrangements for equipment. Calibration and maintenance of field equipment and instrumentation should be in accordance with manufacturers' specifications or applicable test specifications and should be documented.

3.3.7 Corrective Action

The procedures describing how to identify and correct deficiencies in the sample collection process should be specified. These should include specific steps to take in correcting deficiencies such as performing additional decontamination of equipment, resampling, or additional training of field personnel. The procedures should specify that each corrective action should be documented with a description of the deficiency and the corrective action taken,

and should include the person(s) responsible for implementing the corrective action.

3.3.8 Data Reduction and Validation

The procedures describing how to compute results from field measurements and to review and validate these data should be specified. They should include all formulas used to calculate results and procedures used to independently verify that field measurement results are correct.

3.3.9 Reporting

The procedures describing the process for reporting the results of field activities should be specified.

3.3.10 Records Management

The procedures describing the means for generating, controlling, and archiving project-specific records and field operations records should be specified. These procedures should detail record generation and control and the requirements for record retention, including type, time, security, and retrieval and disposal authorities.

Project-specific records relate to field work performed for a project. These records may include correspondence, chain-of-custody records, field notes, all reports issued as a result of the work, and procedures used.

Field operations records document overall field operations and may include equipment performance and maintenance logs, personnel files, general field procedures, and corrective action reports.

3.3.11 Waste Disposal

The procedures describing the methods for disposal of waste materials resulting from field operations should be specified.

3.4 FIELD QA AND QC REQUIREMENTS

The QAPjP should describe how the following elements of the field QC program will be implemented.

3.4.1 Control Samples

Control samples are QC samples that are introduced into a process to monitor the performance of the system. Control samples, which may include blanks (e.g., trip, equipment, and laboratory), duplicates, spikes, analytical standards, and reference materials, can be used in different phases of the data collection process beginning with sampling and continuing through transportation, storage, and analysis.

Each day of sampling, at least one field duplicate and one equipment rinsate should be collected for each matrix sampled. If this frequency is not appropriate for the sampling equipment and method, then the appropriate changes should be clearly identified in the QAPjP. When samples are collected for volatile organic analysis, a trip blank is also recommended for each day that samples are collected. In addition, for each sampling batch (20 samples of one matrix type), enough volume should be collected for at least one sample so as to allow the laboratory to prepare one matrix spike and either one matrix duplicate or one matrix spike duplicate for each analytical method employed. This means that the following control samples are recommended:

- Field duplicate (one per day per matrix type)
- Equipment rinsate (one per day per matrix type)
- Trip blank (one per day, volatile organics only)
- Matrix spike (one per batch [20 samples of each matrix type])
- Matrix duplicate or matrix spike duplicate (one per batch)

Additional control samples may be necessary in order to assure data quality to meet the project-specific DQOs.

3.4.2 Acceptance Criteria

Procedures should be in place for establishing acceptance criteria for field activities described in the QAPjP. Acceptance criteria may be qualitative or quantitative. Field events or data that fall outside of established acceptance criteria may indicate a problem with the sampling process that should be investigated.

3.4.3 Deviations

All deviations from plan should be documented as to the extent of, and reason for, the deviation. Any activity not performed in accordance with procedures or QAPjPs is considered a deviation from plan. Deviations from plan may or may not affect data quality.

3.4.4 Corrective Action

Errors, deficiencies, deviations, certain field events, or data that fall outside established acceptance criteria should be investigated. In some instances, corrective action may be needed to resolve the problem and restore proper functioning to the system. The investigation of the problem and any subsequent corrective action taken should be documented.

3.4.5 Data Handling

All field measurement data should be reduced according to protocols described or referenced in the QAPjP. Computer programs used for data reduction should be validated before use and verified on a regular basis. All information used in the calculations should be recorded to enable reconstruction of the final result at a later date.

Data should be reported in accordance with the requirements of the end-user as described in the QAPjP.

3.5 QUALITY ASSURANCE REVIEW

The QA Review consists of internal and external assessments to ensure that QA/QC procedures are in use and to ensure that field staff conform to these procedures. QA review should be conducted as deemed appropriate and necessary.

3.6 FIELD RECORDS

Records provide the direct evidence and support for the necessary technical interpretations, judgments, and discussions concerning project activities. These records, particularly those that are anticipated to be used as evidentiary data, should directly support current or ongoing technical studies and activities and should provide the historical evidence needed for later reviews and analyses. Records should be legible, identifiable, and retrievable and protected against damage, deterioration, or loss. The discussion in this section (3.6) outlines recommended procedures for record keeping. Organizations which conduct field sampling should develop appropriate record keeping procedures which satisfy relevant technical and legal requirements.

Field records generally consist of bound field notebooks with prenumbered pages, sample collection forms, personnel qualification and training forms, sample location maps, equipment maintenance and calibration forms, chain-of-custody forms, sample analysis request forms, and field change request forms. All records should be written in indelible ink.

Procedures for reviewing, approving, and revising field records should be clearly defined, with the lines of authority included. It is recommended that all documentation errors should be corrected by drawing a single line through the error so it remains legible and should be initialed by the responsible individual, along with the date of change. The correction should be written adjacent to the error.

Records should include (but are not limited to) the following:

Calibration Records & Traceability of Standards/Reagents -- Calibration is a reproducible reference point to which all sample measurements can be correlated. A sound calibration program should include provisions for documentation of frequency, conditions, standards, and records reflecting the calibration history of a measurement system. The accuracy of the calibration standards is important because all data will be in reference to the standards used. A program for verifying and documenting the accuracy of all working standards against primary grade standards should be routinely followed.

Sample Collection -- To ensure maximum utility of the sampling effort and resulting data, documentation of the sampling protocol, as performed in the field, is essential. It is recommended that sample collection records contain, at a minimum, the names of persons conducting the activity, sample number, sample location, equipment used, climatic conditions, documentation of adherence to protocol, and unusual observations. The actual sample collection record is usually one of the following: a bound field notebook with prenumbered pages, a pre-printed form, or digitized information on a computer tape or disc.

Chain-of-Custody Records -- The chain-of-custody involving the possession of samples from the time they are obtained until they are disposed or shipped off-site should be documented as specified in the QAPjP and should include the following information: (1) the project name; (2) signatures of samplers; (3) the sample number, date and time of collection, and grab or composite sample designation; (4) signatures of individuals involved in sample transfer; and (5) if applicable, the air bill or other shipping number.

Maps and Drawings -- Project planning documents and reports often contain maps. The maps are used to document the location of sample collection points and monitoring wells and as a means of presenting environmental data. Information used to prepare maps and drawings is normally obtained through field surveys, property surveys, surveys of monitoring wells, aerial photography or photogrammetric mapping. The final, approved maps and/or drawings should have a revision number and date and should be subject to the same controls as other project records.

QC Samples -- Documentation for generation of QC samples, such as trip and equipment rinsate blanks, duplicate samples, and any field spikes should be maintained.

Deviations -- All deviations from procedural documents and the QAPjP should be recorded in the site logbook.

Reports -- A copy of any report issued and any supporting documentation should be retained.

4.0 LABORATORY OPERATIONS

The laboratory should conduct its operations in such a way as to provide reliable information. To achieve this, certain minimal policies and procedures should be implemented.

4.1 FACILITIES

The QAPjP should address all facility-related issues that may impact project data quality. Each laboratory should be of suitable size and

construction to facilitate the proper conduct of the analyses. Adequate bench space or working area per analyst should be provided. The space requirement per analyst depends on the equipment or apparatus that is being utilized, the number of samples that the analyst is expected to handle at any one time, and the number of operations that are to be performed concurrently by a single analyst. Other issues to be considered include, but are not limited to, ventilation, lighting, control of dust and drafts, protection from extreme temperatures, and access to a source of stable power.

Laboratories should be designed so that there is adequate separation of functions to ensure that no laboratory activity has an adverse effect on the analyses. The laboratory may require specialized facilities such as a perchloric acid hood or glovebox.

Separate space for laboratory operations and appropriate ancillary support should be provided, as needed, for the performance of routine and specialized procedures.

As necessary to ensure secure storage and prevent contamination or misidentification, there should be adequate facilities for receipt and storage of samples. The level of custody required and any special requirements for storage such as refrigeration should be described in planning documents.

Storage areas for reagents, solvents, standards, and reference materials should be adequate to preserve their identity, concentration, purity, and stability.

Adequate facilities should be provided for the collection and storage of all wastes, and these facilities should be operated so as to minimize environmental contamination. Waste storage and disposal facilities should comply with applicable federal, state, and local regulations.

The location of long-term and short-term storage of laboratory records and the measures to ensure the integrity of the data should be specified.

4.2 EQUIPMENT/INSTRUMENTATION

Equipment and instrumentation should meet the requirements and specifications of the specific test methods and other procedures as specified in the QAPjP. The laboratory should maintain an equipment/instrument description list that includes the manufacturer, model number, year of purchase, accessories, and any modifications, updates, or upgrades that have been made.

4.3 OPERATING PROCEDURES

The QAPjP should describe or make reference to all laboratory activities that may affect data quality. For routinely performed activities, SOPs are often prepared to ensure consistency and to save time and effort in preparing QAPjPs.

Any deviation from an established procedure during a data collection activity should be documented. It is recommended that procedures be available for the indicated activities, and include, at a minimum, the information described below.

4.3.1 Sample Management

The procedures describing the receipt, handling, scheduling, and storage of samples should be specified.

Sample Receipt and Handling -- These procedures describe the precautions to be used in opening sample shipment containers and how to verify that chain-of-custody has been maintained, examine samples for damage, check for proper preservatives and temperature, and log samples into the laboratory sample streams.

Sample Scheduling -- These procedures describe the sample scheduling in the laboratory and includes procedures used to ensure that holding time requirements are met.

Sample Storage -- These procedures describe the storage conditions for all samples, verification and documentation of daily storage temperature, and how to ensure that custody of the samples is maintained while in the laboratory.

4.3.2 Reagent/Standard Preparation

The procedures describing how to prepare standards and reagents should be specified. Information concerning specific grades of materials used in reagent and standard preparation, appropriate glassware and containers for preparation and storage, and labeling and recordkeeping for stocks and dilutions should be included.

4.3.3 General Laboratory Techniques

The procedures describing all essentials of laboratory operations that are not addressed elsewhere should be specified. These techniques should include, but are not limited to, glassware cleaning procedures, operation of analytical balances, pipetting techniques, and use of volumetric glassware.

4.3.4 Test Methods

Procedures for test methods describing how the analyses are actually performed in the laboratory should be specified. A simple reference to standard methods is not sufficient, unless the analysis is performed exactly as described in the published method. Whenever methods from SW-846 are not appropriate, recognized methods from source documents published by the EPA, American Public Health Association (APHA), American Society for Testing and Materials (ASTM), the National Institute for Occupational Safety and Health (NIOSH), or other recognized organizations with appropriate expertise should be used, if possible.

The documentation of the actual laboratory procedures for analytical methods should include the following:

Sample Preparation and Analysis Procedures -- These include applicable holding time, extraction, digestion, or preparation steps as appropriate to the method; procedures for determining the appropriate dilution to analyze; and any other information required to perform the analysis accurately and consistently.

Instrument Standardization -- This includes concentration(s) and frequency of analysis of calibration standards, linear range of the method, and calibration acceptance criteria.

Sample Data -- This includes recording requirements and documentation including sample identification number, analyst, data verification, date of analysis and verification, and computational method(s).

Precision and Bias -- This includes all analytes for which the method is applicable and the conditions for use of this information.

Detection and Reporting Limits -- This includes all analytes in the method.

Test-Specific QC -- This describes QC activities applicable to the specific test and references any applicable QC procedures.

4.3.5 Equipment Calibration and Maintenance

The procedures describing how to ensure that laboratory equipment and instrumentation are in working order should be specified. These procedures include calibration procedures and schedules, maintenance procedures and schedules, maintenance logs, service arrangements for all equipment, and spare parts available in-house. Calibration and maintenance of laboratory equipment and instrumentation should be in accordance with manufacturers' specifications or applicable test specifications and should be documented.

4.3.6 QC

The type, purpose, and frequency of QC samples to be analyzed in the laboratory and the acceptance criteria should be specified. Information should include the applicability of the QC sample to the analytical process, the statistical treatment of the data, and the responsibility of laboratory staff and management in generating and using the data. Further details on development of project-specific QC protocols are described in Section 4.4.

4.3.7 Corrective Action

The procedures describing how to identify and correct deficiencies in the analytical process should be specified. These should include specific steps to take in correcting the deficiencies such as preparation of new standards and

reagents, recalibration and restandardization of equipment, reanalysis of samples, or additional training of laboratory personnel in methods and procedures. The procedures should specify that each corrective action should be documented with a description of the deficiency and the corrective action taken, and should include the person(s) responsible for implementing the corrective action.

4.3.8 Data Reduction and Validation

The procedures describing how to review and validate the data should be specified. They should include procedures for computing and interpreting the results from QC samples, and independent procedures to verify that the analytical results are reported correctly. In addition, routine procedures used to monitor precision and bias, including evaluations of reagent, equipment rinsate, and trip blanks, calibration standards, control samples, duplicate and matrix spike samples, and surrogate recovery, should be detailed in the procedures. More detailed validation procedures should be performed when required in the contract or QAPjP.

4.3.9 Reporting

The procedures describing the process for reporting the analytical results should be specified.

4.3.10 Records Management

The procedures describing the means for generating, controlling, and archiving laboratory records should be specified. The procedures should detail record generation and control, and the requirements for record retention, including type, time, security, and retrieval and disposal authorities.

Project-specific records may include correspondence, chain-of-custody records, request for analysis, calibration data records, raw and finished analytical and QC data, data reports, and procedures used.

Laboratory operations records may include laboratory notebooks, instrument performance logs and maintenance logs in bound notebooks with prenumbered pages; laboratory benchsheets; software documentation; control charts; reference material certification; personnel files; laboratory procedures; and corrective action reports.

4.3.11 Waste Disposal

The procedures describing the methods for disposal of chemicals including standard and reagent solutions, process waste, and samples should be specified.

4.4 LABORATORY QA AND QC PROCEDURES

The QAPjP should describe how the following required elements of the laboratory QC program are to be implemented.

4.4.1 Method Proficiency

Procedures should be in place for demonstrating proficiency with each analytical method routinely used in the laboratory. These should include procedures for demonstrating the precision and bias of the method as performed by the laboratory and procedures for determining the method detection limit (MDL). All terminology, procedures and frequency of determinations associated with the laboratory's establishment of the MDL and the reporting limit should be well-defined and well-documented. Documented precision, bias, and MDL information should be maintained for all methods performed in the laboratory.

4.4.2 Control Limits

Procedures should be in place for establishing and updating control limits for analysis. Control limits should be established to evaluate laboratory precision and bias based on the analysis of control samples. Typically, control limits for bias are based on the historical mean recovery plus or minus three standard deviation units, and control limits for precision range from zero (no difference between duplicate control samples) to the historical mean relative percent difference plus three standard deviation units. Procedures should be in place for monitoring historical performance and should include graphical (control charts) and/or tabular presentations of the data.

4.4.3 Laboratory Control Procedures

Procedures should be in place for demonstrating that the laboratory is in control during each data collection activity. Analytical data generated with laboratory control samples that fall within prescribed limits are judged to be generated while the laboratory was in control. Data generated with laboratory control samples that fall outside the established control limits are judged to be generated during an "out-of-control" situation. These data are considered suspect and should be repeated or reported with qualifiers.

Laboratory Control Samples -- Laboratory control samples should be analyzed for each analytical method when appropriate for the method. A laboratory control sample consists of either a control matrix spiked with analytes representative of the target analytes or a certified reference material.

Laboratory control sample(s) should be analyzed with each batch of samples processed to verify that the precision and bias of the analytical process are within control limits. The results of the laboratory control sample(s) are compared to control limits established for both precision and bias to determine usability of the data.

Method Blank -- When appropriate for the method, a method blank should be analyzed with each batch of samples processed to assess contamination

levels in the laboratory. Guidelines should be in place for accepting or rejecting data based on the level of contamination in the blank.

Procedures should be in place for documenting the effect of the matrix on method performance. When appropriate for the method, there should be at least one matrix spike and either one matrix duplicate or one matrix spike duplicate per analytical batch. Additional control samples may be necessary to assure data quality to meet the project-specific DQOs.

Matrix-Specific Bias -- Procedures should be in place for determining the bias of the method due to the matrix. These procedures should include preparation and analysis of matrix spikes, selection and use of surrogates for organic methods, and the method of standard additions for metal and inorganic methods. When the concentration of the analyte in the sample is greater than 0.1%, no spike is necessary.

Matrix-Specific Precision -- Procedures should be in place for determining the precision of the method for a specific matrix. These procedures should include analysis of matrix duplicates and/or matrix spike duplicates. The frequency of use of these techniques should be based on the DQO for the data collection activity.

Matrix-Specific Detection Limit -- Procedures should be in place for determining the MDL for a specific matrix type (e.g., wastewater treatment sludge, contaminated soil, etc).

4.4.4 Deviations

Any activity not performed in accordance with laboratory procedures or QAPjPs is considered a deviation from plan. All deviations from plan should be documented as to the extent of, and reason for, the deviation.

4.4.5 Corrective Action

Errors, deficiencies, deviations, or laboratory events or data that fall outside of established acceptance criteria should be investigated. In some instances, corrective action may be needed to resolve the problem and restore proper functioning to the analytical system. The investigation of the problem and any subsequent corrective action taken should be documented.

4.4.6 Data Handling

Data resulting from the analyses of samples should be reduced according to protocols described in the laboratory procedures. Computer programs used for data reduction should be validated before use and verified on a regular basis. All information used in the calculations (e.g., raw data, calibration files, tuning records, results of standard additions, interference check results, and blank- or background-correction protocols) should be recorded in order to enable reconstruction of the final result at a later date. Information on the preparation of the sample (e.g., weight or volume of sample used, percent dry

weight for solids, extract volume, dilution factor used) should also be maintained in order to enable reconstruction of the final result at a later date.

All data should be reviewed by a second analyst or supervisor according to laboratory procedures to ensure that calculations are correct and to detect transcription errors. Spot checks should be performed on computer calculations to verify program validity. Errors detected in the review process should be referred to the analyst(s) for corrective action. Data should be reported in accordance with the requirements of the end-user. It is recommended that the supporting documentation include at a minimum:

- Laboratory name and address.
- Sample information (including unique sample identification, sample collection date and time, date of sample receipt, and date(s) of sample preparation and analysis).
- Analytical results reported with an appropriate number of significant figures.
- Detection limits that reflect dilutions, interferences, or correction for equivalent dry weight.
- Method reference.
- Appropriate QC results (correlation with sample batch should be traceable and documented).
- Data qualifiers with appropriate references and narrative on the quality of the results.

4.5 QUALITY ASSURANCE REVIEW

The QA review consists of internal and external assessments to ensure that QA/QC procedures are in use and to ensure that laboratory staff conform to these procedures. QA review should be conducted as deemed appropriate and necessary.

4.6 LABORATORY RECORDS

Records provide the direct evidence and support for the necessary technical interpretations, judgements, and discussions concerning project activities. These records, particularly those that are anticipated to be used as evidentiary data, should directly support technical studies and activities, and provide the historical evidence needed for later reviews and analyses. Records should be legible, identifiable, and retrievable, and protected against damage, deterioration, or loss. The discussion in this section (4.6) outlines recommended procedures for record keeping. Organizations which conduct field

sampling should develop appropriate record keeping procedures which satisfy relevant technical and legal requirements.

Laboratory records generally consist of bound notebooks with prenumbered pages, personnel qualification and training forms, equipment maintenance and calibration forms, chain-of-custody forms, sample analysis request forms, and analytical change request forms. All records should be written in indelible ink.

Procedures for reviewing, approving, and revising laboratory records should be clearly defined, with the lines of authority included. Any documentation errors should be corrected by drawing a single line through the error so that it remains legible and should be initialed by the responsible individual, along with the date of change. The correction is written adjacent to the error.

Strip-chart recorder printouts should be signed by the person who performed the instrumental analysis. If corrections need to be made in computerized data, a system parallel to the corrections for handwritten data should be in place.

Records of sample management should be available to permit the re-creation of an analytical event for review in the case of an audit or investigation of a dubious result.

Laboratory records should include, at least, the following:

Operating Procedures -- Procedures should be available to those performing the task outlined. Any revisions to laboratory procedures should be written, dated, and distributed to all affected individuals to ensure implementation of changes. Areas covered by operating procedures are given in Sections 3.3 and 4.3.

Quality Assurance Plans -- The QAPjP should be on file.

Equipment Maintenance Documentation -- A history of the maintenance record of each system serves as an indication of the adequacy of maintenance schedules and parts inventory. As appropriate, the maintenance guidelines of the equipment manufacturer should be followed. When maintenance is necessary, it should be documented in either standard forms or in logbooks. Maintenance procedures should be clearly defined and written for each measurement system and required support equipment.

Proficiency -- Proficiency information on all compounds reported should be maintained and should include (1) precision; (2) bias; (3) method detection limits; (4) spike recovery, where applicable; (5) surrogate recovery, where applicable; (6) checks on reagent purity, where applicable; and (7) checks on glassware cleanliness, where applicable.

Calibration Records & Traceability of Standards/Reagents -- Calibration is a reproducible reference point to which all sample measurements can be correlated. A sound calibration program should include provisions for documenting frequency, conditions, standards, and records reflecting the

calibration history of a measurement system. The accuracy of the calibration standards is important because all data will be in reference to the standards used. A program for verifying and documenting the accuracy and traceability of all working standards against appropriate primary grade standards or the highest quality standards available should be routinely followed.

Sample Management -- All required records pertaining to sample management should be maintained and updated regularly. These include chain-of-custody forms, sample receipt forms, and sample disposition records.

Original Data -- The raw data and calculated results for all samples should be maintained in laboratory notebooks, logs, benchsheets, files or other sample tracking or data entry forms. Instrumental output should be stored in a computer file or a hardcopy report.

QC Data -- The raw data and calculated results for all QC and field samples and standards should be maintained in the manner described in the preceding paragraph. Documentation should allow correlation of sample results with associated QC data. Documentation should also include the source and lot numbers of standards for traceability. QC samples include, but are not limited to, control samples, method blanks, matrix spikes, and matrix spike duplicates.

Correspondence -- Project correspondence can provide evidence supporting technical interpretations. Correspondence pertinent to the project should be kept and placed in the project files.

Deviations -- All deviations from procedural and planning documents should be recorded in laboratory notebooks. Deviations from QAPjPs should be reviewed and approved by the authorized personnel who performed the original technical review or by their designees.

Final Report -- A copy of any report issued and any supporting documentation should be retained.

5.0 DEFINITIONS

The following terms are defined for use in this document:

ACCURACY — The closeness of agreement between an observed value and an accepted reference value. When applied to a set of observed values, accuracy will be a combination of a random component and of a common systematic error (or bias) component.

BATCH: — A group of samples which behave similarly with respect to the sampling or the testing procedures being employed and which are processed as a unit (see Section 3.4.1 for field

samples and Section 4.4.3 for laboratory samples). For QC purposes, if the number of samples in a group is greater than 20, then each group of 20 samples or less will all be handled as a separate batch.

BIAS: The deviation due to matrix effects of the measured value (x_s - x_u) from a known spiked amount. Bias can be assessed by comparing a measured value to an accepted reference value in a sample of known concentration or by determining the recovery of a known amount of contaminant spiked into a sample (matrix spike). Thus, the bias (B) due to matrix effects based on a matrix spike is calculated as:

$$B = (x_s - x_u) - K$$

where:

x_s = measured value for spiked sample,
x_u = measured value for unspiked sample, and
K = known value of the spike in the sample.

Using the following equation yields the percent recovery (%R).

$$\%R = 100\ (x_s - x_u)/\ K$$

BLANK: see Equipment Rinsate, Method Blank, Trip Blank.

CONTROL SAMPLE: A QC sample introduced into a process to monitor the performance of the system.

DATA QUALITY OBJECTIVES (DQOs): A statement of the overall level of uncertainty that a decision-maker is willing to accept in results derived from environmental data (see reference 2, EPA/QAMS, July 16, 1986). This is qualitatively distinct from quality measurements such as precision, bias, and detection limit.

DATA VALIDATION: The process of evaluating the available data against the project DQOs to make sure that the objectives are met. Data validation may be very rigorous, or cursory, depending on project DQOs. The available data reviewed will include analytical results, field QC data and lab QC data, and may also include field records.

DUPLICATE: see Matrix Duplicate, Field Duplicate, Matrix Spike Duplicate.

EQUIPMENT BLANK: see Equipment Rinsate.

EQUIPMENT RINSATE: A sample of analyte-free media which has been used to

	rinse the sampling equipment. It is collected after completion of decontamination and prior to sampling. This blank is useful in documenting adequate decontamination of sampling equipment.
ESTIMATED QUANTITATION LIMIT (EQL):	The lowest concentration that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions. The EQL is generally 5 to 10 times the MDL. However, it may be nominally chosen within these guidelines to simplify data reporting. For many analytes the EQL analyte concentration is selected as the lowest non-zero standard in the calibration curve. Sample EQLs are highly matrix-dependent. The EQLs in SW-846 are provided for guidance and may not always be achievable.
FIELD DUPLICATES:	Independent samples which are collected as close as possible to the same point in space and time. They are two separate samples taken from the same source, stored in separate containers, and analyzed independently. These duplicates are useful in documenting the precision of the sampling process.
LABORATORY CONTROL SAMPLE:	A known matrix spiked with compound(s) representative of the target analytes. This is used to document laboratory performance.
MATRIX:	The component or substrate (e.g., surface water, drinking water) which contains the analyte of interest.
MATRIX DUPLICATE:	An intralaboratory split sample which is used to document the precision of a method in a given sample matrix.
MATRIX SPIKE:	An aliquot of sample spiked with a known concentration of target analyte(s). The spiking occurs prior to sample preparation and analysis. A matrix spike is used to document the bias of a method in a given sample matrix.
MATRIX SPIKE DUPLICATES:	Intralaboratory split samples spiked with identical concentrations of target analyte(s). The spiking occurs prior to sample preparation and analysis. They are used to document the precision and bias of a method in a given sample matrix.
METHOD BLANK:	An analyte-free matrix to which all reagents are added in the same volumes or proportions as used in sample processing. The method blank should be carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the analytical process.

For a method blank to be acceptable for use with the accompanying samples, the concentration in the blank of any analyte of concern should not be higher than the highest of either:

(1)The method detection limit, or

(2)Five percent of the regulatory limit for that analyte, or

(3)Five percent of the measured concentration in the sample.

METHOD DETECTION LIMIT (MDL): The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix type containing the analyte.

For operational purposes, when it is necessary to determine the MDL in the matrix, the MDL should be determined by multiplying the appropriate one-sided 99% t-statistic by the standard deviation obtained from a minimum of three analyses of a matrix spike containing the analyte of interest at a concentration three to five times the estimated MDL, where the t-statistic is obtained from standard references or the table below.

No. of samples:	t-statistic
3	6.96
4	4.54
5	3.75
6	3.36
7	3.14
8	3.00
9	2.90
10	2.82

Estimate the MDL as follows:
Obtain the concentration value that corresponds to:

a) an instrument signal/noise ratio within the range of 2.5 to 5.0, or

b) the region of the standard curve where there is a significant change in sensitivity (i.e., a break in the slope of the standard curve).

Determine the variance (S^2) for each analyte as follows:

$$s^2 = \frac{1}{n-1}\left[\sum_{i=1}^{n}(x_i - \bar{x})^2\right]$$

where x_i = the ith measurement of the variable x and $\bar{x}$ = the average value of x;

$$\bar{x} = \frac{1}{n}\sum_{i=1}^{n} x_i$$

Determine the standard deviation (s) for each analyte as follows:

$$s = (S^2)^{1/2}$$

Determine the MDL for each analyte as follows:

$$MDL = t_{(n-1,\ \alpha = .99)}(s)$$

where $t_{(n-1,\ \alpha = .99)}$ is the one-sided t-statistic appropriate for the number of samples used to determine (s), at the 99 percent level.

ORGANIC-FREE REAGENT WATER:

For volatiles, all references to water in the methods refer to water in which an interferant is not observed at the method detection limit of the compounds of interest. Organic-free reagent water can be generated by passing tap water through a carbon filter bed containing about 1 pound of activated carbon. A water purification system may be used to generate organic-free deionized water. Organic-free reagent water may also be prepared by boiling water for 15 minutes and, subsequently, while maintaining the temperature at 90°C, bubbling a contaminant-free inert gas through the water for 1 hour.

For semivolatiles and nonvolatiles, all references to water in the methods refer to water in which an interferant is not observed at the method detection limit of the compounds of interest. Organic-free reagent water can be generated by passing tap water through a carbon filter bed containing about 1 pound of activated carbon. A water purification system may be used to generate organic-free deionized water.

PRECISION:

The agreement among a set of replicate measurements

without assumption of knowledge of the true value. Precision is estimated by means of duplicate/replicate analyses. These samples should contain concentrations of analyte above the MDL, and may involve the use of matrix spikes. The most commonly used estimates of precision are the relative standard deviation (RSD) or the coefficient of variation (CV),

$$RSD = CV = 100\ S/\bar{x},$$

where:
x = the arithmetic mean of the x_i measurements, and S = variance; and the relative percent difference (RPD) when only two samples are available.

$$RPD = 100\ [(x_1 - x_2)/\{(x_1 + x_2)/2\}].$$

PROJECT: Single or multiple data collection activities that are related through the same planning sequence.

QUALITY ASSURANCE PROJECT PLAN (QAPjP): An orderly assemblage of detailed procedures designed to produce data of sufficient quality to meet the data quality objectives for a specific data collection activity.

RCRA: The Resource Conservation and Recovery Act.

REAGENT BLANK: See Method Blank.

REAGENT GRADE: Analytical reagent (AR) grade, ACS reagent grade, and reagent grade are synonymous terms for reagents which conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society.

REAGENT WATER: Water that has been generated by any method which would achieve the performance specifications for ASTM Type II water. For organic analyses, see the definition of organic-free reagent water.

REFERENCE MATERIAL: A material containing known quantities of target analytes in solution or in a homogeneous matrix. It is used to document the bias of the analytical process.

SPLIT SAMPLES: Aliquots of sample taken from the same container and analyzed independently. In cases where aliquots of samples are impossible to obtain, field duplicate samples should be taken for the matrix duplicate analysis. These are usually taken after mixing or compositing and are used to document intra- or interlaboratory precision.

STANDARD ADDITION: The practice of adding a known amount of an analyte to a sample immediately prior to analysis. It is typically used to evaluate interferences.

STANDARD CURVE: A plot of concentrations of known analyte standards versus the instrument response to the analyte. Calibration standards are prepared by successively diluting a standard solution to produce working standards which cover the working range of the instrument. Standards should be prepared at the frequency specified in the appropriate section. The calibration standards should be prepared using the same type of acid or solvent and at the same concentration as will result in the samples following sample preparation. This is applicable to organic and inorganic chemical analyses.

SURROGATE: An organic compound which is similar to the target analyte(s) in chemical composition and behavior in the analytical process, but which is not normally found in environmental samples.

TRIP BLANK: A sample of analyte-free media taken from the laboratory to the sampling site and returned to the laboratory unopened. A trip blank is used to document contamination attributable to shipping and field handling procedures. This type of blank is useful in documenting contamination of volatile organics samples.

6.0 REFERENCES

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2. Development of Data Quality Objectives, Description of Stages I and II, July 16, 1986, Quality Assurance Management Staff, ORD, U.S. EPA, Washington, DC 20460.

3. RCRA Ground-Water Monitoring Technical Enforcement Guidance Document, September, 1986, Office of Waste Programs Enforcement. OSWER, U.S. EPA, Washington, DC, 20460.

4. DQO Training Software, Version 6.5, December, 1988, Quality Assurance Management Staff, ORD, U.S. EPA, Washington, DC 20460.

5. Preparing Perfect Project Plans, EPA/600/9-89/087, October 1989, Risk Reduction Engineering Laboratory (Guy Simes), Cincinnati OH.

6. ASTM Method D 1129-77, Specification for Reagent Water. 1991 Annual Book of ASTM Standards. Volume 11.01 Water and Environmental Technology.

7. Generation of Environmental Data Related to Waste Management Activities (Draft). February 1989. ASTM.

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* Definition of term.

CHAPTER TEN

SAMPLING METHODS

Prior to employing the methods in this chapter, analysts are advised to consult the disclaimer statement at the front of this manual and the information in Chapter Two for guidance on the allowed flexibility in the choice of apparatus, reagents, and supplies. In addition, unless specified in a regulation, the use of SW-846 methods is not mandatory in response to Federal testing requirements. The information contained in each procedure is provided by EPA as guidance to be used by the analyst and the regulated community in making judgements necessary to meet the data quality objectives or needs for the intended use of the data.

The following methods are found in Chapter Ten:

Method 0010:	Modified Method 5 Sampling Train **Appendix A:** Preparation of XAD-2 Sorbent Resin **Appendix B:** Total Chromatographable Organic Material Analysis
Method 0011:	Sampling for Selected Aldehyde and Ketone Emissions from Stationary Sources
Method 0020:	Source Assessment Sampling System (SASS)
Method 0023A:	Sampling Method for Polychlorinated Dibenzo-*p*-Dioxins and Polychlorinated Dibenzofuran Emissions from Stationary Sources
Method 0030:	Volatile Organic Sampling Train
Method 0031:	Sampling Method for Volatile Organic Compounds (SMVOC)
Method 0040:	Sampling of Principal Organic Hazardous Constituents from Combustion Sources Using Tedlar® Bags
Method 0050:	Isokinetic HCl/Cl_2 Emission Sampling Train
Method 0051:	Midget Impinger HCl/Cl_2 Emission Sampling Train
Method 0060:	Determination of Metals in Stack Emissions
Method 0061:	Determination of Hexavalent Chromium Emissions from Stationary Sources
Method 0100:	Sampling for Formaldehyde and Other Carbonyl Compounds in Indoor Air
Method 25D:	Determination of the Volatile Organic Concentration of Waste Samples
Method 25E:	Determination of Vapor Phase Organic Concentration in Waste Samples
Method 207:	A Method for Measuring Isocyanates in Stationary Source Emissions

PREFACE AND OVERVIEW

PURPOSE OF THE MANUAL

Test Methods for Evaluating Solid Waste (SW-846) provides a unified, up-to-date source of information on sampling and analysis related to compliance with RCRA regulations. It brings together into one reference all sampling and testing methodologies approved by the Office of Solid Waste for use in implementing the RCRA regulatory program. The manual provides methodologies for collecting and testing representative samples of waste and other materials to be monitored. Aspects of sampling and testing in SW-846 include quality control, sampling plan development and implementation, analysis of inorganic and organic constituents, the estimation of intrinsic physical properties, and the appraisal of waste characteristics.

The procedures described in this manual are meant to be comprehensive and detailed, coupled with the realization that the problems encountered in sampling and analytical situations require a certain amount of flexibility. The solutions to these problems will depend, in part, on the skill, training, and experience of the analyst. For some situations, it is possible to use this manual in rote fashion. In other situations, it will require a combination of technical abilities, using the manual as guidance rather than in a step-by-step, word-by-word fashion. Although this puts an extra burden on the user, it is unavoidable because of the variety of sampling and analytical conditions found with hazardous wastes.

ORGANIZATION AND FORMAT

This manual is divided into two volumes and thirteen chapters. Volume I focuses on laboratory activities and is divided into three sections: IA, IB, and IC. Volume IA deals with quality control procedures, selection of appropriate test methods, and analytical methods for inorganic species. Volume IB consists of methods for organic analytes. Volume IC includes a variety of test methods for miscellaneous analytes and properties, including for use in evaluating whether a waste exhibits certain hazardous waste characteristics. Volume II deals with sample acquisition and includes quality control, sampling plan design and implementation, and field sampling methods. Discussions regarding ground water monitoring, land treatment monitoring, and incineration are also included in Volume II.

Volume I begins with an overview of the quality control procedures that should be adhered to during application of the sampling and analysis methods. The quality control chapter (Chapter One) and the method chapters are interdependent. The analytical procedures cannot be used without a thorough understanding of the quality control requirements and the means to implement them. This understanding can be achieved only by reviewing Chapter One and the analytical methods together. It is expected that individual laboratories, using SW-846 as the reference source, will select appropriate methods and develop a standard operating procedure (SOP) to be followed by the laboratory. The SOP should incorporate the pertinent information from this manual adopted to the specific needs and circumstances of the individual laboratory as well as to the materials to be evaluated.

The method selection chapter (Chapter Two) presents a comprehensive discussion of the application of these methods to various matrices in the determination of groups of analytes or specific analytes. It aids the chemist in constructing the correct analytical method from the array of procedures which may cover the matrix/analyte/concentration combination of interests. The section discusses the objective of the testing program and its relationship to the choice of an analytical method. Flow charts and tables provide guidance in the selection of the correct analytical procedures to form the appropriate method.

The analytical methods are separated into distinct procedures describing specific, independent analytical operations. These include extraction, digestion, cleanup, and determination. This format allows linking of the various steps in the analysis according to the type of sample (e.g., water, soil, sludge, still

bottom); analytes(s) of interest, needed sensitivity, and available analytical instrumentation. However, Chapters Five (Miscellaneous) and Six (Properties) give complete methods which are not amenable to such segmentation to form discrete procedures. The introductory material at the beginning of Chapters Three (Inorganic Analytes) and Four (Organic Analytes) contains information on sample handling and preservation, safety, and sample preparation.

Part II, Characteristics, of Volume I describes the hazardous waste characteristics (Chapter Seven) and methods used to determine if the waste is hazardous because it exhibits a particular characteristic (Chapters Seven and Eight).

Volume II gives background information on statistical and nonstatistical aspects of sampling. It also presents practical sampling techniques appropriate for situations presenting a variety of physical conditions.

Information regarding the regulatory aspects of several monitoring categories is also found in Volume II. These categories include ground water monitoring (Chapter Eleven), land treatment (Chapter Twelve), and incineration (Chapter Thirteen). The purpose of this guidance is to orient the user to the analytical objective, and to assist in the development of data quality objectives, sampling plans, and SOPs.

Significant interferences, or other problems, may be encountered with certain samples. In these situations, the analyst is advised to contact the Methods Team (5307W), USEPA/OSW/EMRAD[1], 401 M St. SW, Washington, DC 20460 (703-308-8855) for assistance. The manual is intended to serve all those with a need to evaluate solid waste. Your comments, corrections, suggestions, and questions concerning any material contained in, or omitted from, this manual will be gratefully appreciated. Please direct your comments to the above address.

SW-846 METHOD NUMBERS

When published as a new method to SW-846, a method's number does not include a letter suffix. However, each time the method is revised and promulgated as part of an SW-846 update, it receives a new letter suffix, i.e, a suffix of "A" indicates revision one of that method, a suffix of "B" indicates revision two, etc. In order to properly document the SW-846 method used during analysis, the entire method number including the suffix letter designation must be identified by the analyst. In addition, a method reference found within the RCRA regulations and the text of SW-846 methods and chapters always refers to the latest promulgated revision of the method, even if the method number at those locations does not include the appropriate letter suffix.

[1] United States Environmental Protection Agency; Office of Solid Waste; Economic, Methods, and Risk Analysis Division

CHAPTER ELEVEN

GROUND WATER MONITORING

For guidance regarding RCRA-related ground-water monitoring, see the EPA Office of Solid Waste guidance document entitled "RCRA Ground-water Monitoring: Draft Technical Guidance," published in 1992. This document was distributed to update technical information regarding ground-water monitoring contained in other sources of USEPA guidance, including Chapter Eleven of this manual.

A PDF of the guidance document can be viewed and obtained via the following EPA web site link: http://www.epa.gov/epaoswer/hazwaste/test/info.htm

A PDF of the guidance document may also be viewed and obtained via the following EPA web site link, select "Site Characterization/Monitoring: http://www.epa.gov/epaoswer/hazwaste/ca/guidance.htm

CHAPTER TWELVE

LAND TREATMENT MONITORING

12.1 BACKGROUND

A monitoring program is an essential component at any land treatment unit and should be planned to provide assurance of appropriate facility design, to act as a feedback loop to furnish guidance on improving unit management, and to indicate the rate at which the treatment capacity is being approached. Because many assumptions must be made in the design of a land treatment unit, monitoring can be used to verify whether the initial data and assumptions were correct or if design or operational changes are needed. Monitoring cannot be substituted for careful design based on the fullest reasonable understanding of the effects of applying hazardous waste to the soil; however, for existing Hazardous Waste Land Treatment (HWLT) units (which must retrofit to comply with regulations), monitoring can provide much of the data base needed for demonstrating treatment.

Figure 12-1 shows the topics to be considered when developing a monitoring program. The program must be developed to provide the following assurances:

1. that the waste being applied does not deviate significantly from the waste for which the unit was designed;

2. that waste constituents are not leaching from the land treatment area in unacceptable concentrations;

3. that ground water is not being adversely affected by the migration of hazardous constituents of the waste(s); and

4. that waste constituents will not create a food-chain hazard if crops are harvested.

12.2 TREATMENT ZONE

As is depicted in Figure 12-2, the entire land treatment operation and monitoring program revolve about a central component, the treatment zone. Concentrating on the treatment zone is a useful approach to describing and monitoring a land treatment system. The treatment zone is the soil to which wastes are applied or incorporated; HWLT units are designed so that degradation, transformation, and immobilization of hazardous constituents and their metabolites occur within this zone.

In practice, setting a boundary to the treatment zone is difficult. In choosing the boundaries of the treatment zone, soil-forming processes and the associated decrease in biological activity with depth should be considered.

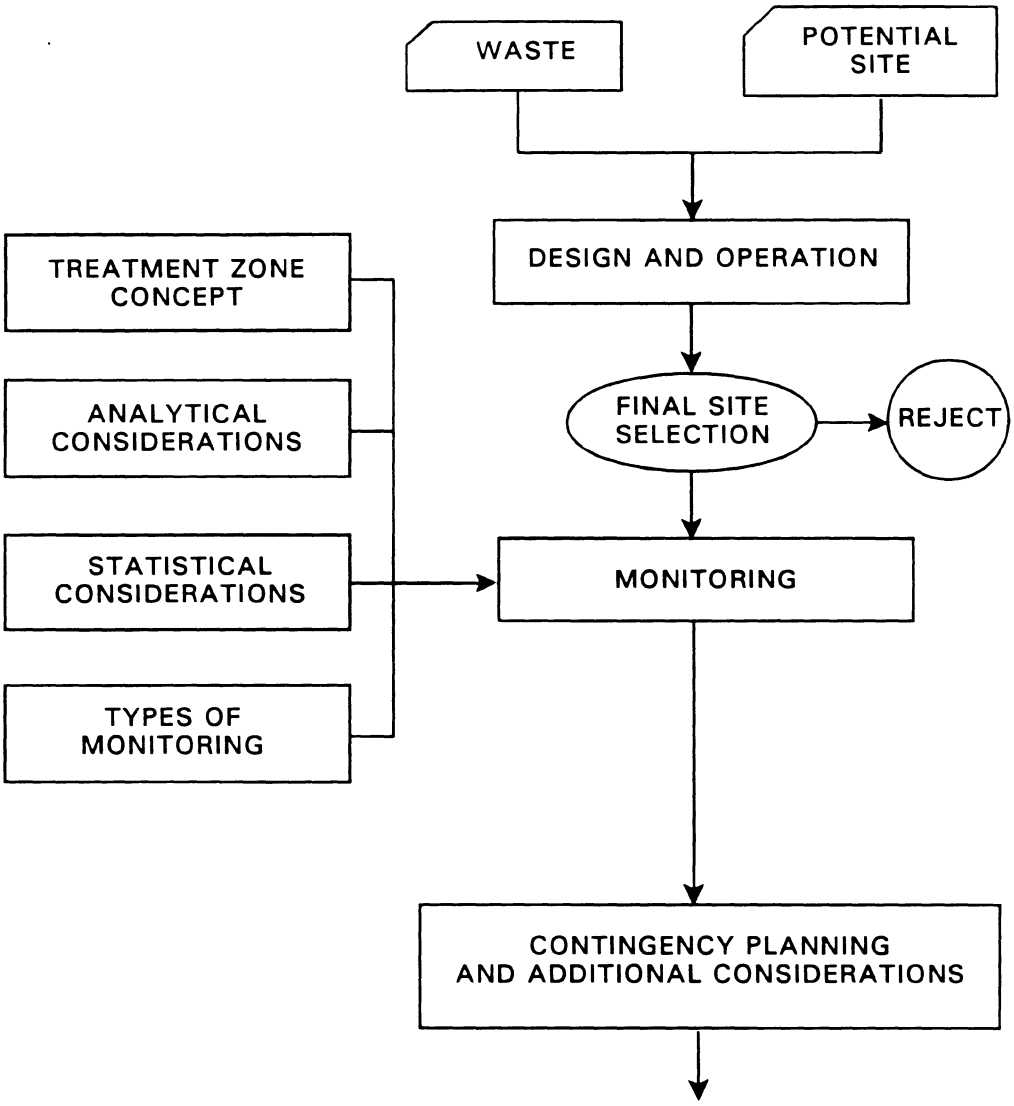

Figure 12-1. Topics to be considered in developing a monitoring program for an HWLT unit.

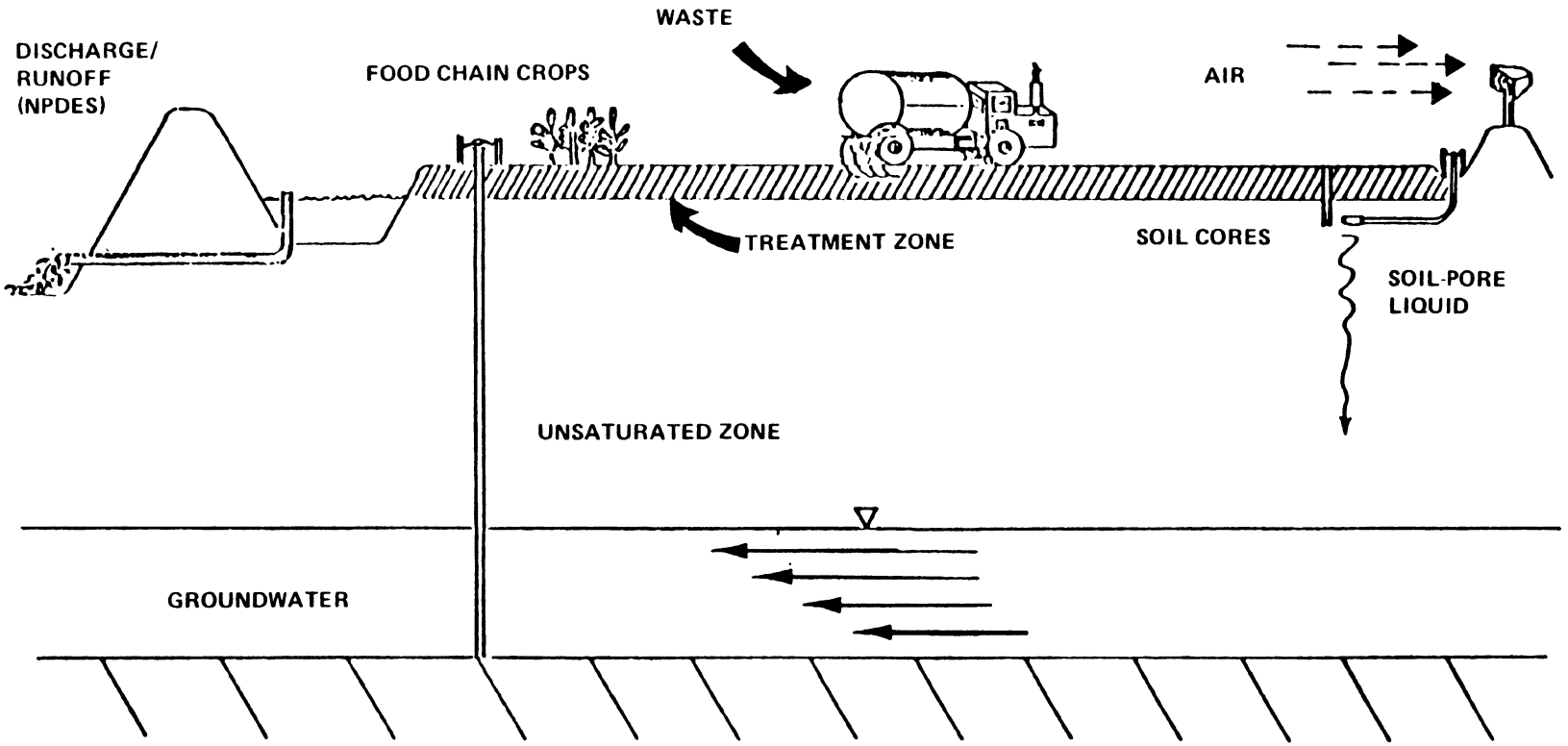

Figure 12-2. Various types of monitoring for land treatment units.

12.3 REGULATORY DEFINITION

The current regulations (U.S. EPA, 1982a) require the following types of monitoring:

1. Ground water detection monitoring to determine if a leachate plume has reached the edge of the waste management area (40 CFR 264.98).

2. Ground water compliance monitoring to determine if the facility is complying with ground water protection standards for hazardous constituents (40 CFR 264.99).

3. Monitoring of soil pH and concentration of cadmium in the waste when certain food-chain crops are grown on HWLT units where cadmium is disposed of (40 CFR 264.276).

4. Unsaturated zone monitoring, including soil cores and soil-pore liquid monitoring, to determine if hazardous constituents are migrating out of the treatment zone (40 CFR 246.278).

5. Waste analysis of all types of waste to be disposed at the HWLT unit (40 CFR 264.13).

12.4 MONITORING AND SAMPLING STRATEGY

As discussed earlier, the monitoring program centers around the treatment zone.

The frequency of sampling and the parameters to be analyzed depend on the characteristics of the waste being disposed, the physical layout of the unit, and the surface and subsurface characteristics of the site. Table 12-1 provides guidance for developing an operational monitoring program. Each of the types of monitoring is discussed below.

12.4.1 Waste Monitoring and Sampling Strategy

Waste streams need to be routinely sampled and tested to check for changes in composition. A detailed description of appropriate waste sampling techniques, tools, procedures, etc., is provided in Chapter Nine of this manual (in Part III, Sampling). These procedures should be followed during all waste sampling events. Waste analysis methods are provided in this manual. The analyst should choose the appropriate method, based on each waste and specific constituents to be tested for.

The frequency with which a waste needs to be sampled and the parameters to be analyzed depend greatly on the variables that influence the quantity and quality of the waste. When waste is generated in a batch, as would be expected from an annual or biannual cleanout of a lagoon or tank, the waste should be fully characterized prior to each application. When the waste is

TABLE 12-1 GUIDANCE FOR AN OPERATIONAL MONITORING PROGRAM AT HWLT UNITS

Media to be Monitored	Purpose	Sampling Frequency	Number of Samples	Parameters to be Analyzed
Waste	Quality Change.	Quarterly composites if continuous stream; each batch if intermittent generation.	One	At least rate and capacity limiting constituents, plus those within 25% of being limiting, principal hazardous constituents, pH and EC.
Soil cores (unsaturated zone)	Determine slow movement of hazardous constituents.	Quarterly	One composited from two per 1.5 ha (4 ac); minimum of 3 composited from 6 per uniform area.	All hazardous constituents in the waste or the principal hazardous constituents, metabolites of hazardous constituents, and nonhazardous constituents of concern.
Soil-pore liquid (unsaturated zone)	Determine highly mobile constituents.	Quarterly, preferably following leachate generating precipitation snowmelt.	One composited from two samplers per 1.5 ha (4 ac); minimum of 3 composited from 6 per uniform area.	All hazardous constituents in the waste or the principal hazardous constituents, mobile metabolites of hazardous constituents, and important mobile nonhazardous constituents.
Groundwater	Determine mobile constituents.	Semiannually	Minimum of four suggested--one upgradient, three downgradient.	Hazardous constituents and metabolites or select indicators.
Vegetation (if grown for food chain use)	Phytotoxic and hazardous transmitted constituents (food chain hazards).	Annually or at harvests.	One per 1.5 ha (4 ac) or three of processed crop before sale.	Hazardous metals and organics and their metabolites.
Runoff water	Soluble or suspended constituents.	As required for NPDES permit.	As permit requires, or one.	Discharge permit and background parameters plus hazardous organics.
Soil in the treatment zone	Determine degradation, pH, nutrients, and rate and capacity limiting constituents.	Quarterly	7-10 composited to one per 1.5 ha (4 ac).	
Air	Personnel and population health hazards.	Quarterly	Five	Particulates (adsorbed hazardous constituents) and hazardous volatiles.

generated more nearly continuously, samples should be collected and composited based on a statistical design over a period of time to ensure that the waste is of a uniform quality. For example, wastes that are generated continuously could be sampled weekly or daily on a flow-proportional basis and composited and analyzed quarterly or monthly. When no changes have been made in the operation of the plant or the treatment of the waste which could significantly alter concentration of waste constituents, the waste should, at a minimum, be analyzed for (1) the constituents that restrict the annual application rates (RLC) and the allowable cumulative applications (CLC), (2) the constituents that are within 25% of the level at which they would be limiting, and (3) all other hazardous constituents that have been shown to be present in the waste in the initial waste characterization. Because synergism and antagonism as well as unlisted waste metabolites can create hazards that cannot be described by chemical analysis alone, routine multigenicity testing may be performed if the treatment demonstration has indicated a possible problem. In addition, waste should be analyzed as soon as possible after a change in operations that could affect the waste characteristics.

12.4.2 Ground Water Monitoring and Sampling Strategy

To ensure that irreparable ground water damage does not occur as a result of HWLT, it is necessary that the ground water quality be monitored. Ground water monitoring supplements the unsaturated zone monitoring system but does not replace it. A contamination problem first detected in the leachate water may indicate the need to alter the management program, and ground water can then be observed for the same problem. It is through the successful combination of these two systems that accurate monitoring of vertically moving constituents can be achieved. Ground water monitoring requirements are discussed in Chapter Eleven of this manual.

12.4.3 Vegetation Monitoring and Sampling Strategy

Where food-chain crops are to be grown, analysis of the vegetation at the HWLT unit will aid in ensuring that harmful quantities of metals or other waste constituents are not being accumulated by, or adhering to surfaces of, the plants. Although a safety demonstration before planting is required (U.S. EPA, 1982a), operational monitoring is recommended to verify that crop contamination has not occurred. Vegetation monitoring is an important measurement during the post-closure period where the area may possibly be used for food or forage production. Sampling should be done annually or at each harvest. The concentrations of metals and other constituents in the vegetation will change with moisture content, stage of growth, and the part of the plant sampled, and thus results must be carefully interpreted. The number of samples to analyze is again based on a sliding scale similar to that used for sampling soils. Forage samples should include all aerial plant parts, and the edible parts of grain, fruit, or vegetation crops should be sampled separately.

12.4.4 Runoff Water Monitoring and Sampling Strategy

If runoff water analyses are needed to satisfy NPDES permit conditions (National Pollution Discharge Elimination System, U.S. EPA, 1981), a monitoring program should be instituted. This program would not be covered under RCRA hazardous waste land disposal requirements, but it would be an integral part of facility design. The sampling and monitoring approach will vary, depending on whether the water is released as a continuous discharge or as a batch discharge following treatment to reduce the hazardous nature of the water. Constituents to be analyzed should be specified in the NPDES permit.

When a relatively continuous flow is anticipated, sampling must be flow proportional. A means of flow measurement and an automated sampling device are a reasonable combination for this type of monitoring. Flow can be measured using a weir or flume (U.S.D.A., 1979) for overload flow-water pretreatment systems and packaged water treatment plants, and in-line flow measurement may be an additional option on the packaged treatment systems. The sampling device should be set up to obtain periodic grab samples as the water passes through the flow-rate measuring device. A number of programmable, automated samplers that can take discrete or composite samples are on the market.

For batch treatment, such as mere gravity separation or mechanically aerated systems, flow is not so important as is the hazardous constituent content of each batch. Sampling before discharge would, in this case, involve manual pond sampling, using multiple grab samples. The samples would preferably represent the entire water column to be discharged in each batch rather than a single depth increment. Statistical procedures should again be used for either treatment and discharge approach.

12.4.5 Unsaturated Zone Monitoring and Sampling Strategy

The unsaturated zone is described as the layer of soil or parent material separating the bottom of the treatment zone and the seasonal high-water table or ground water table and is usually found to have a moisture content less than saturation. In this zone, the movement of moisture may often be relatively slow in response to soil properties and prevailing climatic conditions; however, in some locations, soils and waste management practices may lead to periods of heavy hydraulic loading that could cause rapid downward flux of moisture.

An unsaturated zone monitoring plan should be developed for two purposes: (1) to detect any significant movement of hazardous constituents out of the system, and (2) to furnish information for management decisions. In light of the variability in soil-water flux and the mobility of hazardous waste constituents, the unsaturated zone monitoring plan should include sampling the soil to evaluate relatively slow-moving waste constituents (soil core monitoring) and sampling the soil-pore liquid to evaluate fast-moving waste constituents. Monitoring for hazardous constituents should be performed on a representative background plot(s) until background levels are established and

immediately below the treatment zone (active portion). The number, location, and depth of soil core and soil-pore liquid samples taken must allow an accurate indication of the quality of soil-pore liquid and soil below the treatment zone and in the background area. The frequency and timing of soil-pore liquid sampling must be based on the frequency, time, and rate of waste application; proximity of the treatment zone to ground water; soil permeability; and amount of precipitation. The data from this program must be sufficient to determine if statistically significant increases in hazardous constituents (or selected indicator constituents) have occurred below the treatment zone. Location and depth of soil core and soil-pore liquid samples follow the same reasoning, but the number, frequency, and timing of soil core sampling differs somewhat from that required for soil-pore liquid sampling. Thus, the unique aspects of these topics will be considered together with discussions of techniques for obtaining the two types of samples.

12.4.5.1 Location of Samples

Soil characteristics, waste type, and waste application rate are all important factors in determining the environmental impact of a particular land treatment unit or part of a unit on the environment. Therefore, areas of the land treatment unit for which these characteristics are similar (i.e., uniform areas) should be sampled as a single monitoring unit. A uniform area is defined as an area of the active portion of a land treatment unit which is composed of soils of the same soil series (U.S.D.A., 1975) and to which similar wastes or waste mixtures are applied at similar application rates. If, however, the texture of the surface soil differs significantly among soils of the same series classification, the phase classification of the soil should be considered in defining "uniform areas." A certified professional soil scientist should be consulted in designating uniform areas.

Based on that definition, it is recommended that the location of soil core sampling or soil-pore liquid monitoring devices within a given uniform area be randomly selected. Random selection of samples ensures a more accurate representation of conditions within a given uniform area. It is convenient to spot the field location for soil core and soil-pore liquid devices by selecting random distances on a coordinate system and using the intersection of the two random distances as the location at which a soil core should be taken or a soil-pore liquid monitoring device installed. This system works well for fields of both regular and irregular shape because the points outside the area of interest are merely discarded and only the points inside the area are used in the sample.

The location within a given uniform area of a land treatment unit (i.e., active portion monitoring) at which a soil core should be taken or a soil-pore liquid monitoring device installed should be determined using the following procedure:

1. Divide the land treatment unit into uniform areas under the direction of a certified professional soil scientist.

2. Set up coordinates for each uniform area by establishing two base lines at right angles to each other which intersect at an arbitrarily selected origin, for example, the southwest corner. Each baseline should extend far enough for all of the uniform area to fall within the quadrant.

3. Establish a scale interval along each base line. The units of this scale may be feet, yards, meters, or other units, depending on the size of the uniform area, but both base lines should have the same units.

4. Draw two random numbers from a random-number table (available in most basic statistics books). Use these numbers to locate one point along each of the base lines.

5. Locate the intersection of two lines drawn perpendicular to the base lines through these points. This intersection represents one randomly selected location for collection of one soil core, or for installation of one soil-pore liquid device. If this location at the intersection is outside the uniform area, disregard and repeat the above procedure.

6. For soil core monitoring, repeat the above procedure as many times as necessary to obtain the desired number of locations within each uniform area of the land treatment unit. This procedure for randomly selecting locations must be repeated for each soil core sampling event but will be needed only once in locating soil-pore liquid monitoring devices.

Locations for monitoring on background areas should also be randomly determined. Again, consult a certified professional soil scientist in determining an acceptable background area. The background area must have characteristics (including soil series classification) similar to those present in the uniform area of the land treatment unit it is representing, but it should be free from possible contamination from past or present activities that could have contributed to the concentrations of the hazardous constituents of concern. Establish coordinates for an arbitrarily selected portion of the background area and use the above procedure for randomly choosing sampling locations.

12.4.5.2 Depth of Samples

Because unsaturated zone monitoring is intended to detect pollutant migration from the treatment zone, samples should logically be obtained from immediately below this zone. Care should be taken to ensure that samples from active areas of the land treatment unit and background samples are monitoring similar horizons or layers of parent material. Because soils seldom consist of smooth, horizontal layers, but are often undulating, sloped, and sometimes discontinuous, it would be unwise to specify a single depth below the land surface to be used for comparative sampling. A convenient method for choosing

sampling depths is to define the bottom of the treatment zone as the bottom of a chosen diagnostic solid horizon and not as a rigid depth. Sampling depth would then be easily defined with respect to the bottom of the treatment zone. At a minimum, soil core and soil-pore liquid sampling should monitor within 30 cm (12 in.) of the bottom of the treatment zone. Additional sampling depths may be desirable, for instance, if analytical results are inconclusive or questionable. Core samples should include only the 0- to 15-cm increment below the treatment zone, whereas soil-pore liquid samplers should be placed so that they collect liquid from anywhere within this 30-cm zone.

12.4.5.3 Soil Core Sampling Techniques

Soil Cores

Waste constituents may move slowly through the soil profile for a number of reasons, such as the lack of sufficient soil moisture to leach through the system, a natural or artificially occurring layer or horizon of low hydraulic conductivity, or waste constituents that exhibit only a low to moderate mobility relative to water in soil. Any one or a combination of these effects can be observed by soil core monitoring. Based on the treatment zone concept, only the portions of soil cores collected below the treatment zone need to be analyzed. The intent is to demonstrate whether there are significantly higher concentrations of hazardous constituents in material below the treatment zone than in background soils or parent material.

Soil core sampling should proceed according to a definite plan with regard to number, frequency, and technique. Previous discussions of statistical considerations should provide guidance in choosing the number of samples required. Background values for soil core monitoring should be established by collecting at least eight randomly selected soil cores for each soil series present in the treatment zone. These samples can be composited in pairs (from immediately adjacent locations) to form four samples for analysis. For each soil series, a background arithmetic mean and variance should be calculated for each hazardous constituent. For monitoring the active portion of the land treatment facility, a minimum of six randomly selected soil cores should be obtained per uniform area and composited, as before, to yield three samples for analysis. If, however, a uniform area is >5 ha (12 ac), at least two randomly selected soil cores should be taken per 1.5 ha (4 ac) and composited in pairs based on location. Data from the samples in a given uniform area should be averaged and statistically compared. If analyses reveal a large variance from samples within a given uniform area, more samples may be necessary. Soil coring should be done at least semiannually, except for background sampling, which, after background values are established, may be performed as needed to determine if background levels are changing over time.

It is important to keep an accurate record of the locations from which soil core samples have been taken. Even when areas have been judged to be uniform, the best attempts at homogeneous waste application and management cannot achieve perfect uniformity. It is probable in many systems that small problem areas, or "hot spots," may occur, causing localized real or apparent

pollutant migration. Examples of "apparent" migration might include small areas where waste was applied too heavily or where the machinery on-site mixed waste too deeply. The sampling procedure itself is subject to error and so may indicate apparent pollutant migration. Therefore, anomalous data points can and should be resampled at the suspect location(s) to determine if a problem exists, even if the uniform area as a whole shows no statistically significant pollutant migration.

The methods used for soil sampling are variable and depend partially on the size and depth of the sample needed and the number and frequency of samples to be taken. Of the available equipment, oil field augers are useful if small samples need to be taken by hand, and bucket augers give larger samples. Powered coring or drilling equipment, if available, is the preferable choice because it can rapidly sample to the desired depths and provide a clean, minimally disturbed sample for analysis. Due to the time involved in coring to 1.5 m, and sometimes farther, powered equipment can often be less costly than hand sampling. In any case, extreme care must be taken to prevent cross contamination of samples. Loose soil or waste should be scraped away from the surface to prevent it from contaminating samples collected from lower layers. The material removed from the treatment zone portion of the borehole can be analyzed, if desired, to evaluate conditions in the treatment zone. It is advisable to record field observations of the treatment zone even if no analysis is done. Finally, boreholes absolutely must be backfilled carefully to prevent hazardous constituents from channeling down the hole. Native soil compacted to about field bulk density, clay slurry, or other suitable plug material may be used.

Sample handling, preservation, and shipment should follow a chain-of-custody procedure and a defined preservation method such as is found in Chapter Nine of this manual or in the analytical section of EPA document SW-874, Hazardous Waste Land Treatment (U.S. EPA, 1983). If more sample is collected than is needed for analysis, the volume should be reduced by either the quartering or riffle technique. (A riffle is a sample-splitting device designed for use with dried ground samples.)

The analysis of soil cores must include all hazardous constituents that are reasonably expected to leach or the principal hazardous constituents (PHCs) that generally indicate hazardous constituent movement (U.S. EPA, 1982a).

Soil-Pore Liquid

Percolating water added to the soil by precipitation, irrigation, or waste applications may pass through the treatment zone and may rapidly transport some mobile waste constituents or degradation products through the unsaturated zone to the ground water. Soil-pore liquid monitoring is intended to detect these rapid pulses of contaminants (often immediately after heavy precipitation events) that are not likely to be observed through the regularly scheduled analysis of soil cores. Therefore, the timing of soil-pore liquid

sampling is a key to the usefulness of this technique. Seasonability is the rule with soil-pore liquid sample timing (i.e., scheduled sampling cannot be on a preset date, but must be geared to precipitation events). Given that sampling is done soon after leachate-generating precipitation or snowmelt, the frequency also varies depending on site conditions. As a starting point, sampling should be done quarterly. More frequent sampling may be necessary at units located in areas with highly permeable soils or high rainfall, or at which wastes are applied very frequently. The timing of sampling should be geared to the waste application schedule as much as possible.

At land treatment units where wastes are applied infrequently (i.e., only once or twice a year) or where leachate-generating precipitation is highly seasonal, quarterly sampling and analysis of soil-pore liquid may be unnecessary. Because soil-pore liquid sampling is instituted primarily to detect fast-moving hazardous constituents, monitoring for these constituents many months after waste application may be useless. If fast-moving hazardous constituents are to migrate out of the treatment zone, they will usually migrate within at least 90 days following waste application, unless little precipitation or snowmelt has occurred. Therefore, where wastes are applied infrequently or leachate generation is seasonal, soil-pore liquid may be monitored less frequently (semiannually or annually). A final note about timing is that samples should be obtained as soon as liquid is present. The owner or operator should check the monitoring devices for liquid within 24 hr of any significant rainfall, snowmelt, or waste application.

The background concentrations of hazardous constituents in the soil-pore liquid should be established by installing two monitoring devices at random locations for each soil series present in the treatment zone. Samples should be taken on at least a quarterly basis for at least one year and can be composited to give one sample per quarter. Analysis of these samples should be used to calculate an arithmetic mean and variance for each hazardous constituent. After background values are established, additional soil-pore liquid samples should occasionally be taken to determine if the background values are changing over time.

The number of soil-pore liquid samplers needed is a function of site factors that influence the variability of leachate quality. Active, uniform areas should receive, in the beginning, a minimum of six samplers per uniform area. For uniform areas >5 ha, at least two samplers per 1.5 ha (4 ac) should be installed. Samples may be composited in pairs based on location to give three samples for analysis. The number of devices may have to be adjusted up (or down) as a function of the variability of results.

To date, most leachate collection has been conducted by scientists and researchers, and there is not an abundance of available field equipment and techniques. The U.S. EPA (1977) and Wilson (1980) have prepared reviews of pressure vacuum lysimeters and trench lysimeters. The pressure vacuum lysimeters are much better adapted to field use and have been used to monitor pollution from various sources (Manbeck, 1975; Nassau-Suffolk Research Task Group, 1969; The Resources Agency of California, 1963; James, 1974). These pressure vacuum samplers are readily available commercially and are the most

widely used, both for agricultural and waste monitoring uses. A third type of leachate sampler is the vacuum extractor as used in the field by Smith et al. (1977). A comparison of in situ extractors was presented by Levin and Jackson (1977).

These soil-pore liquid sampling devices are described in Chapter Nine of this manual (in Part III, Sampling).

12.4.6 Treatment Zone Monitoring and Sampling Strategy

Treatment zone monitoring of land treatment units is needed for two purposes. One main purpose is to monitor the degradation rate of the organic fraction of the waste material and parameters significantly affecting waste treatment. Samples are needed at periodic intervals after application to be analyzed for residual waste or waste constituents. Such measurements need to be taken routinely, as specified by a soil scientist. These intervals may vary from weekly to semiannual, depending on the nature of the waste, climatic conditions, and application scheduling. The second major function of treatment zone sampling is to measure the rate of accumulation of conserved waste constituents to provide some indication of the facility's life.

The sampling schedule and number of samples to be collected may depend on management factors, but a schedule may be conveniently chosen to coincide with unsaturated zone soil core sampling. For systems that will be loaded heavily in a short period, more (and more frequent) samples may be needed to ensure that the waste is being applied uniformly and that the system is not being overloaded. About seven to ten samples from each selected 1.5-ha (4-ac) area should be taken to represent the treatment zone, and these should be composited to obtain a single sample for analysis. In addition, if there are evidently anomalous "hot spots," these should be sampled and analyzed separately.

12.4.7 Air Monitoring and Sampling Strategy

The need for air monitoring at a land treatment unit is not necessarily dictated only by the chemical characteristics of the waste. Wind dispersal of particulates can mobilize even the most immobile, nonvolatile hazardous constituents. Therefore, it is suggested that land treatment air emissions be monitored at frequent intervals to ensure the health and safety of workers and adjacent residents. This effort may be relaxed if the air emissions are positively identified as innocuous compounds or too low in concentration to have any effect. Although air monitoring is not currently required, it is strongly recommended because wind dispersal is a likely pathway for pollutant losses from a land treatment unit.

Sampling generally involves drawing air over a known surface area at a known flow rate for a specified time interval. Low-molecular-weight volatiles may be trapped by solid sorbents, such as Tenax-GC. The high-molecular-weight compounds may be sampled by Florisil, glass-fiber filters, or polyurethane foam.

12.5 ANALYSIS

12.5.1 Analytical Considerations

Parameters to be measured include pH, soil fertility, residual concentrations of degradable rate-limiting constituents (RLC), and the concentrations of residuals that limit the life of the disposal site (CLC), plus those that, if increased in concentration by 25%, would become limiting. Hazardous constituents of concern should also be monitored. Based on the data obtained, the facility management or design can be adjusted or actions taken, as needed, to maintain treatment efficiency. Projections regarding facility life can also be made and compared with original design projections. Because the treatment zone acts as an integrator of all effects, the data can be invaluable to the unit operator.

The analyst should use specific methods in this manual for determining hazardous waste constituents.

12.5.2 Response to Detection of Pollutant Migration

If significant concentrations of hazardous constituents (or PHCs) are observed below the treatment zone, the following modifications to unit operations should be considered to maximize treatment within the treatment zone:

1. Alter the waste characteristics.

2. Reduce waste application rate.

3. Alter the method or timing of waste applications.

4. Cease application of one or more particular wastes at the unit.

5. Revise cultivation or management practices.

6. Alter the characteristics of the treatment zone, particularly soil pH or organic matter content.

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CHAPTER THIRTEEN

INCINERATION

13.1 INTRODUCTION

Environmental Protection Agency regulations require owners or operators of hazardous waste incinerators to perform specific testing prior to issuance of a final permit. These regulations are contained in 40 CFR Parts 264.340-264.347, 270.19, and 270.62.

The regulations require that incinerated hazardous wastes be destroyed with an efficiency of 99.99% or higher. In order to obtain a permit to incinerate hazardous wastes, owners or operators must demonstrate that their incinerator can operate at the required efficiency (usually referred to as destruction and removal efficiency, or DRE). This demonstration will most often involve a "trial" burn. Prior to the trial burn, the owner or operator must test the hazardous waste being evaluated for incineration and determine the presence and concentration of Appendix VIII constituents, along with other parameters. The analytical results obtained will allow the owner or operator to determine the principal organic hazardous constituents (POHCs) in the waste. These POHCs will usually be those compounds in the waste that are difficult to burn, toxic, and found at reasonably high concentrations in the waste. During the trial burn, the POHCs are monitored to determine whether the incinerator is meeting the required DRE.

The owner or operator will then prepare an incineration permit application, which is submitted to the appropriate state and EPA region. Contents of permits are listed in Sections 270.14, 270.19, and 270.62 of the RCRA regulations. As part of the permit application, the owner or operator will provide the waste analysis information, propose certain POHCs for the trial burn, and specify the sampling and analysis methods that will be used to obtain the trial burn data. This portion of the permit application is called the "trial burn plan." The regulatory agency(ies) will review the application and trial burn plan, make any necessary modifications, and authorize the owner to conduct the trial burn. After the trial burn, the results are submitted to the permit issuance authority and, assuming all requirements are met, a final incineration permit will be issued. The permit contains all the information pertaining to the licensed operation of the incinerator, and the owner or operator must comply with whatever conditions are specified in the permit. The rest of this chapter will explain the various sampling and analysis strategies that can be used during the trial burn and how analysis data can be used to obtain a final permit.

13.2 REGULATORY DEFINITION

As explained earlier, incinerator regulations are contained in 40 CFR Parts 264.340-.347, 270.19, and 270.62. Because Part 264 contains general requirements for hazardous waste incineration, it will not be discussed here.

Parts 270.19 and 270.62 describe actual sampling and analysis requirements and are summarized below. A summary of the major analytical requirements is given in this section and is followed by sections detailing acceptable sampling and analysis methods for meeting these requirements.

The trial burn plan must include the following items:

1. Heat value of the waste.

2. Viscosity or physical description.

3. A list of hazardous organic constituents that are listed in Appendix VIII and that are reasonably expected to be present in the waste.

4. Approximate concentration of those compounds.

5. A detailed description of sampling and analysis procedures that will be used.

During the trial burn (or as soon after as possible), the following determinations must be made:

1. The concentration of trial POHCs in the waste feed.

2. The concentration of trial POHCs, mass emissions, oxygen, and hydrogen chloride in the stack gases. (Determination of the oxygen and water concentration in the stack exhaust gas concentration is necessary for correction of measured particulate.)

3. The concentration of trial POHCs in any scrubber water, ash, or other residues that may be present as a result of the trial burn.

4. A computation of the DRE.

For routine operation, the only explicit sampling and analysis requirement is the determination of carbon monoxide in the stack gas. Although the permit writer or the state/local authorities may impose additional monitoring requirements in some instances, it is not anticipated that comprehensive sampling of the stack-gas effluent or specific analysis of POHCs will be required, except in trial burn situations.

13.3 WASTE CHARACTERIZATION STRATEGY

13.3.1 Sampling

Acquisition of a representative sample of hazardous waste for subsequent chemical analysis is accomplished by preparing a composite of several subsamples of the waste. Sampling equipment and tactics for collection of the subsamples are specified in Chapter Nine of this manual and generally involve grab sampling of liter- or kilogram-sized portions of waste materials. To

ensure that the bulk of the waste is represented by the composite sample, the sampling strategy requires collection of a minimum of four subsamples that provide integration over both the depth and the surface area of the waste as contained in drums, tanks, holding ponds, etc. The composite sample prepared in the field must be mixed thoroughly and split into at least three replicate samples prior to shipment to the analytical laboratory. This step is primarily a precaution against breakage or loss of sample, but it also provides the potential for a check on the homogeneity of the composite sample. To ensure that sampling and analysis results will withstand legal scrutiny, chain-of-custody procedures are incorporated into sampling protocols. The sampling protocols also include explicit provisions for ensuring the safety of the personnel collecting the samples.

13.3.2 Analysis of Hazardous Wastes

The overall strategy for waste characterization includes test procedures (to determine the characteristics of the waste) and analysis procedures (to determine the composition of the waste). The analysis procedures can be divided into three sections:

1. Characteristics (useful for storage, etc.; not required).

2. Proximate analysis (useful data but not required, except for heat value).

3. Specific analysis (required for determination of POHCs).

Figure 13-1 provides an overview of this analytical approach. The discussion below provides a capsule description of each major element of this scheme and the use of the resulting information in the hazardous waste incineration permitting process.

13.3.2.1 Characteristics

The characteristics of the waste sample, defined in terms of ignitability, corrosivity, reactivity (including explosivity and toxic gas generation), and extraction procedure toxicity, are determined according to the procedures presented in Chapter Eight of this manual. These tests are performed on a sample from each waste stream, unless there is sufficient information from an engineering analysis to indicate the waste meets any of these criteria. This information is relevant to the Part 264, Subpart B, General Waste Analysis requirement in that it affects procedures for safely storing, handling, and disposing of the waste at the facility. The data are also relevant to possible exclusion from the trial burn requirements of Part 122. The data on the characteristics of each hazardous waste may be available from the waste generator and from manifest or shipping papers received by the facility owner/operator.

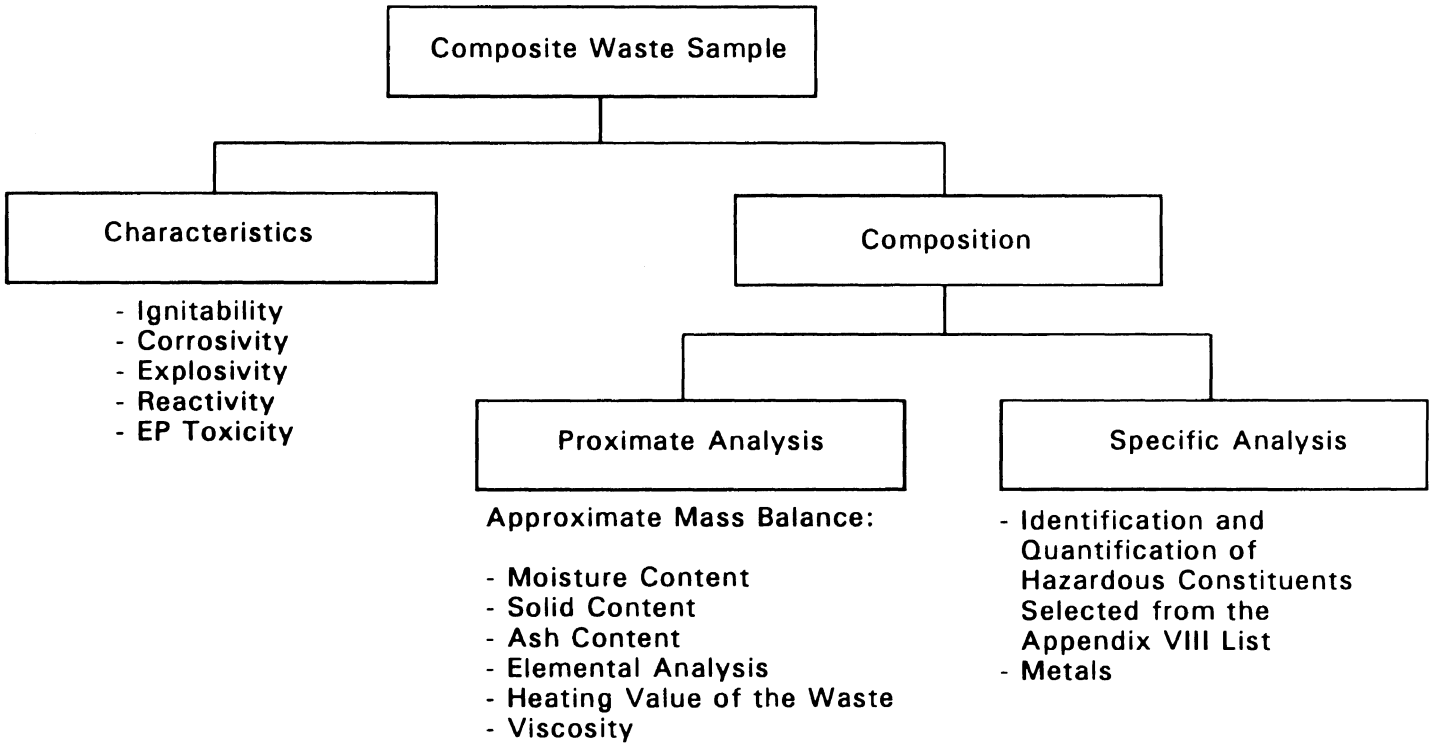


Figure 13-1. Overview of thhe analytical approach for waste characterization.

13.3.2.2 Proximate Analysis

The proximate analysis provides data relating to the physical form of the waste and an estimate of its total composition. This analysis includes determination of:

1. Moisture, solids, and ash content.

2. Elemental composition (carbon, nitrogen, sulfur, phosphorus, fluorine, chlorine, bromine, iodine to 0.1% level).

3. Heating value of the waste.

4. Viscosity.

Some or all of this information may satisfy the waste analysis requirements of the Part 264 regulations, as well as be responsive to the General Waste Analysis requirements of Subpart B. The elemental composition data allow one to predict if a high concentration of potentially significant combustion products (NO_x, SO_x, P_2O_5, hydrogen halides, and halogens) might be formed during incineration. These data also facilitate an informed selection of the Appendix VIII hazardous constituents that might be present in the waste by indicating whether the overall waste composition and hence the types of components present are consistent with expectations based on best professional judgment. For example, if bromine were not present in the waste, any organobromine compounds from Appendix VIII at levels of 1,000 mg/kg would be excluded from specific analysis.

13.3.2.3 Specific Analysis

The specific analysis portion of the waste characterization scheme provides qualitative confirmation of the presence and identity of the Appendix VIII constituents that might reasonably be expected to be present in the waste, based on professional judgment or on the results of proximate analysis. It is important to note that specific analysis does not involve screening every waste sample for all Appendix VIII hazardous components. A preliminary judgment is made as to the compounds or types of compounds that are actually present.

For the specific organic analyses, a high-resolution separation technique (fused-silica capillary gas chromatography) and a high-specificity detection technique (mass spectrometry) are used wherever possible. This approach ensures qualitative and quantitative analysis for a variety of waste types and process chemistries.

Specific analysis methods in this manual can be used for Appendix VIII constituents. Generally, the methods of choice for Appendix VIII components will be:

Method 6010	(Inductively Coupled Plasma Method)
Method 8270	(GC/MS Method for Semivolatile Organics: Capillary Column Technique)
Method 8240	(GC/MS Method for Volatile Organics)

Other more specific methods contained in this manual may be used; however, they cannot screen for a wide range of compounds. For example, Method 8010 can detect only those volatile compounds containing halogen.

13.3.3 Selection of POHCs

The criteria for selection of POHCs (typically one to six specific constituents per waste feed) include:

1. The expected difficulty of thermal degradation of the various hazardous organic constituents in the waste.

2. The concentration of those constituents in the waste.

It is anticipated that the designation of POHCs will be negotiated on a case-by-case basis for each permit application. It is important to note that it is not necessarily, or even generally, true that all Appendix VIII compounds present in the waste will be designated as POHCs. The intent is to select a few specific compounds as indicators of incinerator performance. The selected compounds should provide a sufficiently stringent test of the incinerator's performance to ensure that incineration of the waste can be carried out in an environmentally sound fashion. This criterion mandates selection of the more thermally stable constituents as POHCs.

At the same time, however, it is necessary that the designated POHCs be present in the waste in sufficiently high concentrations in order to be detected in the stack gas. This is a particularly important constraint for wastes that are to be incinerated with substantial quantities of auxiliary fuel, which effectively dilute the POHCs in the exhaust gas. Although the burning of auxiliary fuel might not affect the mass emission rate of POHCs, it would lead to an increased volumetric flow of stack gas and thus to a decreased concentration of POHCs at the stack. This lower concentration directly affects the detection limit achievable for a given stack-gas sample size (e.g., between 5 m^3 and 30 m^3).

It is recommended that, whenever possible, the permit writer select POHCs present in the waste at 1,000 mg/kg or higher. If it is considered desirable to designate as a POHC a thermally stable compound present at the hundreds-of-parts-per-million level, the trial burn permit application must include calculations and supporting data to indicate that 0.01% of the mass feed rate of that component in the waste could in fact be detected in the stack effluent. A waste concentration of 100 mg/kg probably represents a practical lower level below which determination of 99.99% DRE may require extraordinary

sampling analysis and quality control procedures, which may significantly increase the sampling and analysis costs for that trial burn.

For a waste material that is a listed hazardous waste under RCRA regulations (40 CFR Part 261, Subpart D), the constituents that caused the Administrator to list the waste as toxic (tabulated in Appendix VII of 40 CFR Part 261) would be logical candidates for designation as POHCs, if these constituents are organic chemicals.

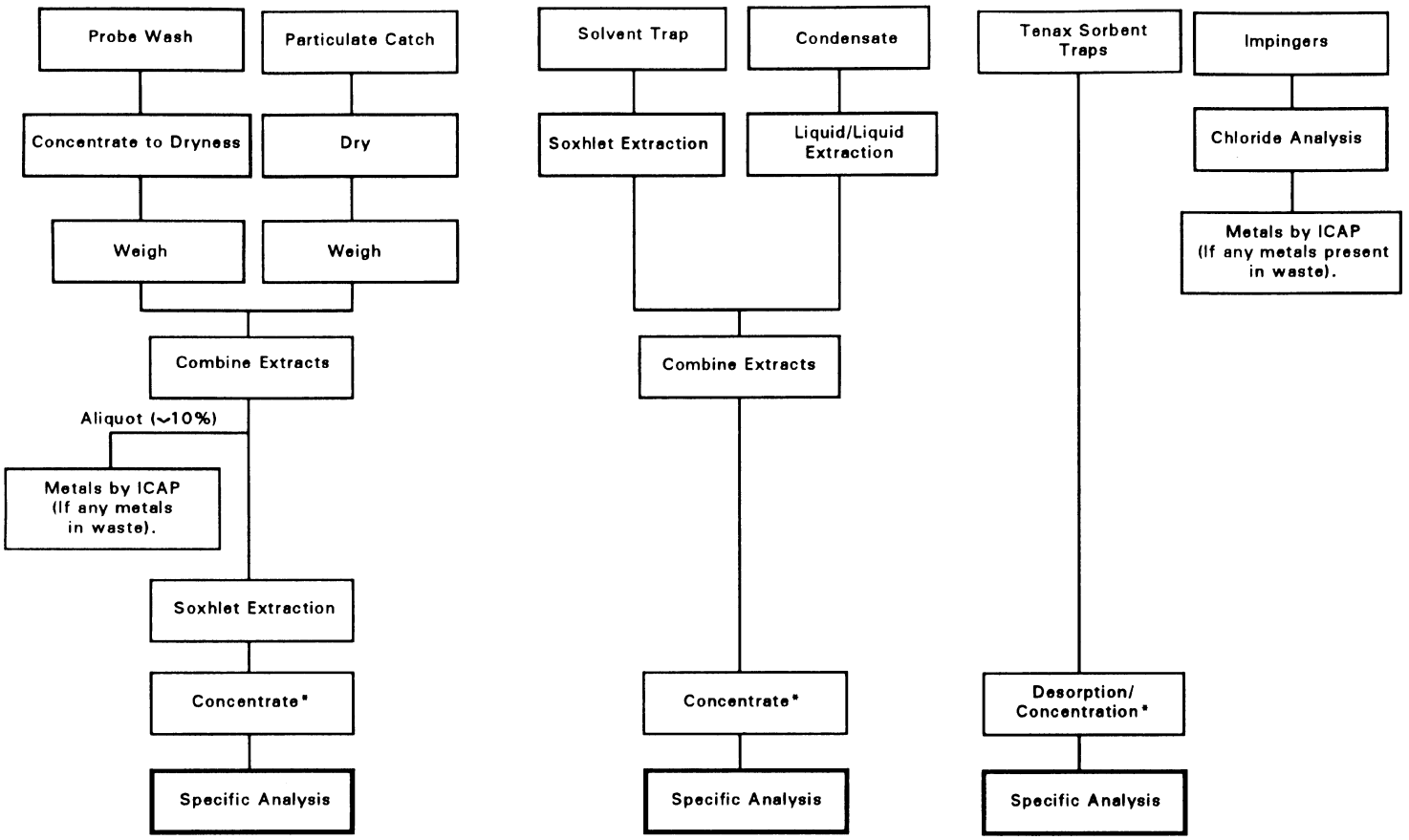
13.4 STACK-GAS EFFLUENT CHARACTERIZATION STRATEGY

The overall strategy for hazardous-waste-incinerator stack-gas effluent characterization to determine compliance with Part 264 performance standards is to collect replicate 3- to 6-hr, 5- to 30-m^3 samples of stack gas using a comprehensive sampling train, such as the EPA Modified Method 5 Sampling Train (MM5), the EPA/IERL-RTP Source Assessment Sampling System (SASS), or, for the volatile species, the Volatile Organic Sampling Train (VOST). These three strategies are described in detail in Chapter Ten (Methods 0010, 0020, and 0030). Any of the comprehensive sampling trains provides a sample sufficient for determination of particulate mass loading, concentrations of particulate and low-volatility vapor-phase organics, and concentrations of particulate and volatile metals. The VOST is used to collect the sample to be analyzed for volatile organic species. For burns of wastes that could also produce significant emissions of HCl, an MM5 type of train is used to collect and quantify HCl in the stack gas.

Figure 13-2 shows an overview of the analysis scheme for stack-gas samples. A separate sample (cyclone and particulate catch) will be used for determination of particulate mass loading and extraction of nonvolatile organic components. Heating during the particulate determination may drive off semivolatile organics. Volatile organic components of the stack gas will be collected using the VOST.

The directed analysis shown in Figure 13-2 is performed on triplicate samples. Although analysis of only two samples would allow an average level of a POHC to be determined, at least three samples should be analyzed so that an error bound for the measured values can be computed. The incremental cost of the replicate sampling and analysis is offset by increased confidence in the resulting data; quantitative results from a single sampling and analysis run should not generally be considered as an acceptable indicator of performance.

The survey analysis, which is a qualitative screen of the collected material to ensure that potentially hazardous but unexpected emissions do not go overlooked, need be performed on no more than one stack-gas sample. During a trial burn, the oxygen level in the stack gas must be measured using an Orsat or Fyrite analyzer, as detailed in 40 CFR Part 60, Appendix A, Method 3, so that the particulate loading may be corrected to a standard excess air level.



* As an alternative, the extracts from particulate and vapor portions of the train may be combined prior to analysis.

Figure 13-2. Overview of an analysis scheme for stack gas samples from a comprehensive sampling train.

For both trial and operating burns, on-line monitors (nondispersive infrared instruments) are used to provide continuous readings of carbon monoxide levels in the incinerator effluent.

13.5 ADDITIONAL EFFLUENT CHARACTERIZATION STRATEGY

The basic strategy for sampling scrubber water, ash, and other residue (if any) is to prepare composite samples from grab subsamples, collected using the same types of sampling devices and tactics as those used for waste characterization. This sampling is required only during trial burns, in accordance with 40 CFR Part 270.62. These additional effluent samples are analyzed for POHCs to determine appropriate disposal or subsequent treatment methods and to ensure that significant discharges of POHCs in other media do not go undetected.

13.6 SELECTION OF SPECIFIC SAMPLING AND ANALYSIS METHODS

The preceding discussion has briefly described the RCRA regulations that define sampling and analysis requirements for hazardous waste incineration and has presented an overview of the sampling and analysis procedures developed to meet these requirements.

This section will illustrate, by means of a hypothetical example, the transition from strategies, as described above, to methods, as described below. In the interest of clarity, the example is oversimplified, but should serve as a demonstration of how to develop and evaluate a hazardous waste incineration trial burn plan. The discussion will deal with sampling and analysis considerations only and will not address adequacy of design, operating conditions, or other engineering considerations.

13.6.1 Scenario

The owner/operator of an incineration facility seeks an RCRA permit to treat chlorinated organic waste material.

The facility is a liquid injection incinerator with a capacity of 10 x 10^6 Btu/hr and equipped with a wet scrubber for acid-gas removal. A waste oil (<0.1% chlorine) is burned as auxiliary fuel. The proposed operating conditions for hazardous waste incineration include a combustion zone temperature of 2000°F (1100°C) and a residence time of 2 sec with 150% excess air.

The waste is a still bottom from the production of perchloroethylene. Based on engineering analysis, it is expected to be a nonviscous organic liquid with a heating value >5,000 Btu/lb. The major components of the waste are expected to be highly chlorinated species such as hexachlorobenzene, hexachlorobutadiene, and other chlorinated aliphatic and aromatic compounds.

13.6.2 Strategy

There are insufficient data from other trial or operating burns to specify operating conditions under which this type of facility, when burning this type of waste, has been demonstrated to comply with the Part 264 performance criteria. Therefore, a trial burn will be required.

There are insufficient data to develop the trial burn plan available from the waste generator. Therefore, additional analyses of the waste will be necessary to support the trial burn permit application. The POHCs for which destruction and removal efficiencies are to be demonstrated in the trial burn must be designated, based on review of existing information and/or additional analysis of a representative sample of the waste.

Because the owner/operator plans to operate the facility under one set of temperature, residence time, and excess air conditions when treating hazardous waste, the trial burn will consist of three replicate tests under that set of operating conditions.

The trial burn sampling and analysis strategy must address:

1. The waste analysis requirements of 40 CFR Part 270.

2. The performance standards of 40 CFR Part 264, Subpart O.

3. The monitoring requirements of 40 CFR Part 264, Subpart O.

13.6.2.1 Sampling Strategy

During each of the three replicate tests, the following samples must be obtained:

1. One composite sample of the waste actually treated.

2. One time-averaged (3-4 hr) sample of stack gas.

3. One composite sample of spent scrubber water.

No bottom ash or fly ash streams (other than the stack particulate emissions) are expected to be generated as effluents from this facility.

13.6.2.2 Analysis Strategy

The waste must be analyzed to determine:

1. Quantity of designated trial burn POHCs.

2. Heating value of the waste.

3. Viscosity or physical form.

4. Quantity of organically bound chlorine. (This analysis is not mandatory; however, the data obtained may be helpful in determining a potential for HCl emissions.)

5. Identity and approximate quantity of known or suspected Appendix VIII constituents.

The stack gas must be analyzed to determine:

1. Quantity of designated trial burn POHCs.

2. Quantity of particulate matter emissions.

3. Quantity of hydrochloric acid emissions.

4. Carbon monoxide level.

5. Excess air level (oxygen/carbon dioxide level determination).

The scrubber water must be analyzed to determine quantities of designated trial burn POHCs.

13.6.3 Tactics and Methods

13.6.3.1 Selection of POHCs

The first step is to obtain a composite of the waste and to analyze it for Appendix VIII constituents. In this case the waste was sampled from a tank truck by taking a series of vertical cores at the available hatch location on the truck. The cores were obtained by using a Coliwasa (see Section 9.2.2.4 of Chapter Nine) and following the procedures. After the waste sample was collected, it was sent to the laboratory using chain-of-custody procedures (Section 9.2.2.7 of Chapter Nine) and was analyzed using Method 8270 (Chapter Four) (in this case the sample was directly injected with a split ratio of 100:1). The sample was also analyzed by Method 9020, Chapter Five. Table 13-1 summarizes the information that was obtained for the waste analysis. The major organic components that would appear to be candidates for selection as POHCs are listed in Table 13-2, along with relevant physical/chemical properties and recommended stack sampling and analysis methods.

The permit writer has designated hexachloro-butadiene, hexachlorobenzene, and hexachloroethane as POHCs. All three species are present in significant concentrations in the waste and will remain at >1,000 mg/kg concentration even if the waste were cut by as much as 1:10 with auxiliary fuel in order to limit the total chlorine feed rate and to maintain an adequate heating value in the total incinerator feed. Fully chlorinated species such as these are generally considered to be highly resistant to thermal degradation and thus provide an appropriate set of POHCs for DRE determination.

TABLE 13-1. INFORMATION ON COMPOSITION OF HYPOTHETICAL WASTE

Visual Inspection: The waste was a pitch-black, nonviscous liquid with obvious particulate loading. It had a pungent odor and fumed slightly when the cap was removed.

Loss on Ignition: Ignition at 900°C resulted in a 99.8% loss of mass.

Higher Heating Value: The waste would not burn in a bomb calorimeter; its higher heating value is estimated at approximately 2,000 Btu/lb.

TOX: 74.4% Cl.

GC/MS: This analysis indicates that hexachlorobutadiene is the major component (65%) and hexachlorobenzene is present at about 10% of the Total Organic Chlorine concentration. Other peaks in the chromatogram were identified as hexachloroethane (approx. 4%), tetrachloroethanes (approx. 3%), tetrachloroethylene (approx. 0.1%), plus four other chlorinated aliphatics at about 0.5% concentration of the CCl concentration.

Summary: All of the available evidence suggests that this waste contains essentially no perchloroethylene, that hexachlorobutadiene makes up about 65% of the waste, and that there are perhaps a dozen other components at 1-5% concentration. All of the minor components appear to be chlorinated, with hexachlorobenzene the most abundant.

TABLE 13-2

CANDIDATE POHCs FOR HYPOTHETICAL WASTE AND
RECOMMENDED STACK SAMPLING AND ANALYSIS METHODS
FOR HYPOTHETICAL TRIAL BURN

Compound (POHC)	Approx. concentration in waste (%)	B.P. (°C)	ΔH^a (kcal/mole)	MW (g/mole)	Stack Sampling Method		Analysis Method	
					Section number	Description	Method number	Description
Hexachlorobutadiene	65	215	N/A	260.76	1.2.1.8[b]	MM5 - Sorbent	8120, 8250, or 8270	GC/MS Extractables
Hexachlorobenzene	6	323	567.7	284.8	1.2.1.8[b]	MM5 - Particulate and Sorbents	8120, 8250, or 8270	GC/MS Extractables
Hexachloroethane	2	186.8	173.8	236.74	1.2.1.8[b]	MM5 - Sorbent	8120, 8250, or 8270	GC/MS Extractables
Tetrachloroethane[c]	1.5	130.5 (146.2)	230 (233)	167.84	1.2.1.13	VOST	8010 or 8240	GC/MS Volatiles
Tetrachloroethylene	0.1	121.0	197	165.85	1.2.1.13	VOST	8010 or 8240	GC/MS Volatiles

[a]The standard enthalpy of combustion.

[b]The SASS method (Chapter Nine, Method 0020) could also be selected. A specially fabricated glass-lined SASS train might be necessary to withstand the hydrochloric acid expected in the stack.

[c]Numbers given in parentheses refer only to 1,1,2,2-tetrachloroethane.

13.6.3.2 Selection of Sampling Methods

For sampling of wastes and liquid and solid effluents, the choice of method is based primarily on the nature of the medium. Review of available methods indicates that for dipper sampling (Chapter Nine) or sampling from the tap of the waste-feed pipe would be appropriate for collection of discrete subsamples of waste feed and of spent scrubber water at regular time intervals over the duration of each trial burn. These would then be combined to form the corresponding composite samples for each test.

For sampling of stack gas, both the nature of the medium and the nature (volatility, stability) of the POHC or other target species affect the choice of a sampling method. Table 13-2 summarizes these recommendations for the candidate POHCs in this example. Note that designation of tetrachloroethylene as a POHC in this instance would require use of VOST, although the MM5 or SASS approaches would collect all of the other candidate POHCs.

The MM5 train would also suffice to determine compliance with the two other performance standards of 40 CFR Part 264. The particulate matter emission rate can be determined from the mass of material collected in the probe wash, cyclone (if any), and filter of the MM5 train. The hydrochloric acid emission rate can be determined by using caustic scrubbing solution in the impinger portion of the MM5 train and determining the hydrochloric acid level as chloride.

In addition to the procedures chosen for the collection of POHCs, it would be necessary to specify procedures for the required monitoring for carbon monoxide and oxygen levels in the stack gas.

13.6.3.3 Selection of Analysis Methods

The analytical procedures used for qualitative identification and quantitative determination of POHCs and other target species are determined primarily by the nature (volatility, polarity) of the species sought.

This manual lists recommended analysis methods for each candidate POHC after the appropriate sample preparation steps in Methods 0010, 0020, and 0030 have been performed. Table 13-2 summarizes the recommendation for analysis of the candidate POHCs in this hypothetical example. Note that a single analytical method suffices to determine all of the hexachlorospecies of concern here although an additional method would be recommended if the analysis were to include the tetrachloroethanes and tetrachloroethylene.

13.6.4 Results and Calculations

This section illustrates the proper methods for calculating DRE, corrected particulate loading, and HCl emissions for the hypothetical example described above. Again, this example has been somewhat oversimplified for purposes of illustration.

According to 40 CFR Part 264, the DRE for each POHC is calculated as:

$$DRE = \frac{W_{in} - W_{out}}{W_{in}} \times 100\%$$

where:

W_{in} = mass feed rate of one POHC in the waste stream feeding the incinerator.

W_{out} = mass emission rate of the same POHC present in stack exhaust emissions.

13.6.4.1 Calculation of W_{in} (lb/hr):

$$W_{in} = \frac{C_w \times FR_w}{100}$$

where:

C_w = Concentration of one POHC in the waste, %.

FR_w = Mass feed rate of waste to the incinerator, lb/hr.

Assume that quantitative analysis of a representative aliquot drawn from the composite waste sample from test No. 1 gave the following concentrations:

hexachlorobutadiene	63 %
hexachlorobenzene	9.4%
hexachloroethane	1.1%

Further, assume that the thermal capacity of the facility (10×10^6 Btu/hr) was met by blending waste 1:10 with waste oil to give a feed mixture that was 8.2% chlorine and that had a heating value of 16,400 Btu/lb. The total mass feed rate to the incinerator was therefore 600 lb/hr, of which 540 lb/hr was auxiliary fuel (waste oil) and 60 lb/hr was chlorinated waste.

The W_{in} values for the three POHCs are therefore:

hexachlorobutadiene	(.63 x 60 lb/hr)	38 lb/hr
hexachlorobenzene	(.094 x 60 lb/hr)	5.6 lb/hr
hexachloroethane	(.011 x 60 lb/hr)	0.66 lb/hr

13.6.4.2 Calculation of W_{out} (lb/hr):

$$W_{out} = C_s \times ER_s \times 1.32 \times 10^{-4}$$

where:

C_s = Concentration of one POHC in the stack gas effluent, mg/dNm^3.

ER_s = Volumetric flow rate of stack gas, dNm^3/min.

1.32×10^{-4} = Conversion factor from mg/min to lb/hr.

Assume that quantitative analysis of the extract prepared from the time-integrated comprehensive sampling train sample from test No. 1 gave the following concentrations in the sampled gas:

hexachlorobutadiene	0.080 mg/m^3
hexachlorobenzene	0.020 mg/m^3
hexachloroethane	$\leq$0.004 mg/m^3

Further, assume that the average measured volumetric flow of stack gas during test No. 1 was 3,200 scfm or 90 dNm^3/min.

The W_{out} values for the three POHCs are therefore:

hexachlorobutadiene ($.080 \times 90 \times 1.32 \times 10^{-4}$)	9.5×10^{-4} lb/hr
hexachlorobenzene ($.020 \times 90 \times 1.32 \times 10^{-4}$)	2.4×10^{-4} lb/hr
hexachloroethane ($\leq 0.004 \times 90 \times 1.32 \times 10^{-4}$)	$< 0.48 \times 10^{-4}$ lb/hr

13.6.4.3 Calculation of DRE:

$$DRE = \frac{W_{in} - W_{out}}{W_{in}} \times 100$$

The DRE values for the three POHCs are therefore:

hexachlorobutadiene	99.997
hexachlorobenzene	99.996
hexachloroethane	>99.993

Note that compliance with a "four-9's" performance standard could not have been demonstrated in this particular example for a component present at <1% in the waste itself (or <1,000 mg/kg in the 1:10 waste:fuel blend fed to the incinerator) unless the detection limit for that component in the stack gas were <4 ug/m^3.

In this example, compliance with the 99.99% DRE performance standard has been demonstrated, in one test, for each of the three POHCs. If these results were supported by data from the other two replicate trial burn tests, the "four-9's" DRE could be considered to have been established.

13.6.4.4 Calculation of HCl Emissions

An incinerator burning highly chlorinated hazardous waste capable of producing significant stack-gas emissions of hydrogen chloride (HCl) must monitor and/or control HCl emissions.

The hypothetical waste in this example contains approximately 75% chlorine by weight (Table 13-1). At the proposed 60-lb/hr feed rate of waste that is blended 1:10 with auxiliary fuel for a total feed of 600 lb/hr (9.8×10^6 Btu/hr), the maximum HCl emission rate would be 45 lb/hr of chlorine basis or 46 lb/hr as HCl. This rate exceeds the regulatory limit of 4 lb/hr; therefore, the scrubber efficiency must be determined.

The stack emission rate of HCl can be calculated from measured values in the following manner:

$$HCl_{out} = C_{in} \times ER_S \times 1.32 \times 10^{-4}$$

where:

C_{in} = Concentration of HCl in the stack-gas sample (mg/m^3).

ER_S = Volumetric flow rate of the stack gas, m^3/min.

1.32×10^{-4} = Conversion factor from mg/min to lb/hr.

Assume that quantitative analysis of the impinger/condensate solution from the time-integrated comprehensive sampling train from test No. 1 gave 34 mg/m^3 HCl in the stack effluent.

The stack emission rate of HCl is calculated by:

$$HCl_{out} = 34\ mg/m^3\ (90\ m^3/min)\ (1.32 \times 10^{-4})$$

$$= 0.40\ lb/hr\ HCl.$$

This emission level is <1% of the 46 lb/hr of HCl potentially generated from the waste, an indication that the removal efficiency of the wet scrubber was >99%.

13.6.4.5 Calculation of Particulate Loading (mg/m^3)

An incinerator-burning hazardous waste must not emit particulate matter in excess of 180 mg/dscm when corrected to an oxygen concentration of 7% in the stack gas.

Assume that prior to chemical analysis, particulate samples from the stack effluent of the hypothetical waste (from probe washes and filter catches of the time-integrated comprehensive sample train) were dried and weighed. The hypothetical particulate loading from these measurements was calculated to be 80 mg/m^3 at the actual excess air level of the stack. The excess air level was determined to be 150%, based on hypothetical measured values of oxygen (12.8%) and carbon dioxide (6.7%). Correction to standard excess air level, as specified in the Part 264 regulations, leads to a particulate loading of 140 mg/m^3 (0.06 gr/scf). This total particulate emission is in compliance with the Part 264 performance standard that specifies $\leq$180 mg/m^3 ($\leq$0.08 gr/scf).

13.6.5 Summary

Incinerator performance in this example complies with the Part 264 Subpart O Incinerator Standards as they relate to:

1. Destruction and Removal Efficiency. All three POHCs showed compliance with the 99.99% DRE performance standard.

2. Limitation on HCl Emissions. The HCl emission rate of 0.40 lb/hr shows compliance with a 99% removal standard for HCl.

3. Limitation on Stack Emissions of Particulate Material. The corrected particulate loading of 140 mg/m^3 is less than the 180 mg/m^3 standard for particulate loading (corrected to a standard excess air level).

13.7 REFERENCES

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CHAPTER TWO

CHOOSING THE CORRECT PROCEDURE

SW-846 is not intended to be an analytical training manual. Therefore, method procedures are written based on the assumption that they will be performed by analysts who are formally trained in at least the basic principles of chemical analysis and in the use of the subject technology.

In addition, SW-846 methods, with the exception of required method use for the analysis of method-defined parameters, are intended to be guidance methods which contain general information on how to perform an analytical procedure or technique which a laboratory can use as a basic starting point for generating its own detailed Standard Operating Procedure (SOP), either for its own general use or for a specific project application. The performance data included in these methods are for guidance purposes only, and are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

2.0 INTRODUCTION

The purpose of this chapter is to aid the analyst in choosing the appropriate methods for sample analyses, based upon the sample matrix and the analytes to be determined. The ultimate responsibility for producing reliable analytical results lies with the entity subject to the regulation. Therefore, members of the regulated community are advised to refer to this chapter and to consult with knowledgeable laboratory personnel when choosing the most appropriate suite of analytical methods. In addition, analysts and data users are advised that, except where explicitly specified in a regulation, the use of SW-846 methods is not mandatory in response to Federal testing requirements.

SW-846 analytical methods are written as quantitative trace analytical methods to demonstrate that a waste does not contain analytes of concern that cause it to be managed as a hazardous waste. As such, these methods typically contain relatively stringent recommended quality control (QC) criteria appropriate to trace analyses. However, if a particular application does not require data of this quality, less stringent QC criteria may and should be used.

The choice of the appropriate sequence of analytical methods depends on the information sought and on the experience of the analyst. Appropriate selection is confirmed by the usability of data (i.e., adequate for its intended use). The use of the recommended procedures, whether they are approved or mandatory, does not release the analyst from demonstrating the correct execution of the method.

Sec. 2.1 provides guidance regarding the analytical flexibility inherent to SW-846 methods and the precedence of various QC criteria. Sec. 2.2 reviews the information required to choose the correct combination of methods for an analytical procedure. Sec. 2.3 provides useful information on implementing the method selection guidance for organic analyses. Sec. 2.4 provides guidance on choosing procedures for characteristic analyses. Sec. 2.5 provides guidance on the determination of analytes in groundwater. Finally, Sec. 2.6 provides information regarding choosing procedures for inorganic analyte analyses. Tables and figures referenced in this chapter are sequentially located after the last page chapter text.

2.1 GUIDANCE REGARDING FLEXIBILITY INHERENT TO SW-846 METHODS AND THE PRECEDENCE OF SW-846 QUALITY CONTROL CRITERIA

The specific products and instrument settings cited in SW-846 methods represent those products and settings used during method development or subsequently evaluated by the Agency for use in the method. Glassware, reagents, supplies, equipment and settings other than those listed in this manual may be employed, provided that method performance appropriate for the intended RCRA application has been documented. Such performance includes consideration of precision, accuracy (or bias), recovery, representativeness, comparability, and sensitivity (quantitation or reporting limits) relative to the data quality objectives for the intended use of the analytical results. In response to this inherent flexibility, if an alternative analytical procedure is employed, then EPA expects the laboratory to demonstrate and document that the procedure is capable of providing appropriate performance for its intended application. This demonstration must not be performed after the fact, but as part of the laboratory's initial demonstration of proficiency with the method. The documentation should be in writing, maintained in the laboratory, and available for inspection upon request by authorized representatives of the appropriate regulatory authorities. The documentation should include the performance data as well as a detailed description of the procedural steps as performed (i.e., a written standard operating procedure).

Given this allowance for flexibility, EPA wishes to emphasize that this manual also contains procedures for "method-defined parameters," where the analytical result is wholly dependant on the process used to make the measurement. Examples include the use of the toxicity characteristic leaching procedure (TCLP) to prepare a leachate, and the flash point, pH, paint filter liquids, and corrosivity tests. In these instances, changes to the specific methods may change the end result and incorrectly identify a waste as nonhazardous. Therefore, when the measurement of such method-defined parameters is required by regulation, those methods are <u>not</u> subject to the flexibility afforded in other methods.

Analysts and data users are advised that even for those analytes that are not method-defined, different procedures may produce some difference in results. Common examples include the differences in recoveries of phenolic compounds extracted from water by separatory funnel (Method 3510) and continuous liquid-liquid (Method 3520) extraction techniques, differences in recoveries of many compounds between Soxhlet (Method 3540) and ultrasonic (Method 3550) extraction techniques, and differences resulting from the choice of acid digestion of metals (Method 3050) or microwave digestion (Method 3051). Where practical, the Agency has included guidance in the individual methods regarding known potential problems, and analysts are advised to review this information carefully in choosing or modifying analytical procedures. Chapter One describes a variety of QC procedures that may be used to evaluate the quality of the analytical results. Additional QC procedures may be described in the individual methods. The results of these QC procedures should be used by the analyst to evaluate if the choice of the analytical procedures and/or any modifications are appropriate to generate data of the quality necessary to satisfy the data quality needs of the intended application.

The performance data included in the SW-846 methods are <u>not</u> intended to be used as absolute QC acceptance criteria for method performance. The data are intended to be guidance, by providing typical method performance in typical matrices, to assist the analyst in selection of the appropriate method for the intended application. In addition, it is the responsibility of the laboratory to establish actual operating parameters and in-house QC acceptance criteria, based on its own laboratory SOPs and in-house QC program, to demonstrate appropriate performance of the methods used in that laboratory for the RCRA analytical applications for which they are intended.

The regulated community is further advised that the methods here or from other sources need only be used for those specific analytes of concern that are subject to regulation or other monitoring requirements. The fact that a method provides a long list of analytes does not mean that each of those analytes is subject to any or all regulations, or that all of those analytes must be analyzed each time the method is employed, or that all of the analytes can be analyzed using a single sample preparation procedure. It is EPA's intention that the target analyte list for any procedure includes those analytes necessary to meet the data quality objectives of the project, i.e., those analytes subject to monitoring requirements and set out in a RCRA permit (or other applicable regulation), plus those analytes used in the methods for QC purposes, such as surrogates, internal standards, system performance check compounds, etc. Additional analytes, not included on the analyte list of a particular method(s) but needed for a specific project, may be analyzed by that particular method(s), if appropriate performance can be demonstrated for the analytes of concern in the matrices of concern at the levels of concern.

2.1.1 Trace analysis vs. macroanalysis

Through the choice of sample size and concentration procedures, the methods presented in SW-846 were designed to address the problem of "trace" analyses (<1000 ppm), and have been developed for an optimized working range. These methods are also applicable to "minor" (1000 ppm - 10,000 ppm) and "major" (>10,000 ppm) analyses, as well, through use of appropriate sample preparation techniques that result in analyte concentrations within that optimized range. Such sample preparation techniques include:

1. adjustment of size of sample prepared for analysis (for homogeneous samples),
2. adjustment of injection volumes,
3. dilution or concentration of sample,
4. elimination of concentration steps prescribed for "trace" analyses, and
5. direct injection (of samples to be analyzed for volatile constituents).

The performance data presented in each of these methods were generated from "trace" analyses, and may not be applicable to "minor" and "major" analyses. Generally, extraction efficiency improves as concentration increases.

CAUTION: Great care should be taken when performing trace analyses after the analysis of concentrated samples, given the possibility of contamination.

2.1.2 Choice of apparatus and preparation of reagents

Since many types and sizes of glassware and supplies are commercially available, and since it is possible to prepare reagents and standards in many different ways, the apparatus, reagents, and volumes included in these methods may be replaced by any similar types as long as this substitution does not affect the overall quality of the analyses.

2.1.3 Quality control criteria precedence

Chapter One contains general quality control (QC) guidance for analyses using SW-846 methods. QC guidance specific to a given analytical technique (e.g., extraction, cleanup, sample introduction, or analysis) may be found in Methods 3500, 3600, 5000, 7000, and 8000. Method-specific QC criteria may be found in Sec. 8.0 of most older individual methods, in Sec. 9.0 of newer methods, or in Sec. 11.0 of some air sampling methods. When inconsistencies exist between the information in these locations, method-specific QC criteria take precedence over both technique-specific criteria and those criteria given in Chapter One, and technique-specific QC criteria take precedence over the criteria in Chapter One.

2.2 INFORMATION NECESSARY FOR CHOOSING THE CORRECT PROCEDURE

In order to choose the correct combination of methods to comprise the appropriate analytical procedure, some basic information is necessary. This includes information on:

- The physical state of the sample
- The analytes of interest
- The sensitivity or quantitation limits needed
- The analytical objective
- Whether the purpose is quantitation or monitoring
- What sample containers and preservation will be used and what holding times may apply

2.2.1 Physical state(s) of sample

The phase characteristics of the sample must be known. There are several general categories of phases into which the sample may be categorized, including:

Aqueous	Oil or other Organic Liquid
Sludge	Stack Sampling (VOST) Condensate
TCLP or EP Extract	Multiphase Sample
Solid	
Groundwater	

There may be a substantial degree of overlap between the phases listed above and it may be useful to further divide these phases in certain instances. A multiphase sample may be a combination of aqueous, organic liquid, sludge, and/or solid phases, and generally must undergo a phase separation as the first step in the analytical procedure.

2.2.2 Analytes of interest

Analytes may be divided into various classes, based on the determinative methods which are used to identify and quantify them. The most basic differentiation is between organic (e.g., carbon-containing) analytes and inorganic (e.g., metals and anions) analytes.

Table 2-1 is an alphabetical list of analytes cited within the SW-846 organic determinative methods (excludes immunoassay and other screening methods). These analytes have been evaluated by those methods. The methods may also be applicable to other analytes that are similar to those listed. Tables 2-2 through 2-38 list the analytes for each organic determinative method. Table 2-39 indicates which methods are applicable to inorganic analytes.

NOTE: Analysts should review the discussion in Sec. 2.1 of this chapter with regard to the presence of an analyte in a method versus the need for its analysis for a given project.

2.2.3 Sensitivity or quantitation limits

Some regulations may require a specific sensitivity or quantitation limit for an analysis, as in the determination of analytes for the Toxicity Characteristic (TC). Drinking water quantitation limits, for those specific organic and metallic analytes covered by the National Primary Drinking Water Regulations, are desired in the analysis of groundwater.

2.2.4 Analytical objective

Knowledge of the analytical objective is essential in the choice of sample preparation procedures and in the selection of a determinative method. This is especially true when the

sample has more than one phase. Knowledge of the analytical objective may not be possible or desirable at all management levels, but that information should be included in the project planning document and transmitted to the analytical laboratory management to ensure that the correct techniques are used during the analytical effort.

2.2.5 Quantitation or monitoring

The strategy for quantitation of compounds in environmental or process samples may be contrasted with the strategy for collecting monitoring data. Quantitation samples define initial conditions. When there is little information available about the composition of the sample source, e.g., a well or process stream, mass spectral identification of organic analytes leads to fewer false positive results. Thus, the most practical form of quantitation for organic analytes is often mass spectral identification. However, where the sensitivity requirements exceed those that can be achieved using mass spectral methods (e.g., GC/MS or HPLC/MS), it may be necessary to employ a more sensitive quantitation method (e.g., electron capture). In these instances, the risk of false positive results may be minimized by confirming the results through a second analysis with a dissimilar detector or chromatographic column. Thus, the choice of technique for organic analytes may be governed by the quantitation limit requirements and potential interferants.

Similarly, the choice of technique for metals is governed by the quantitation limit requirements and potential interferants.

In contrast, monitoring samples are analyzed to confirm existing and on-going conditions, tracking the presence or absence of known constituents in an environmental or process matrix. In well-defined matrices and under stable analytical conditions, less compound-specific quantitation modes may be used, as the risk of false positive results is less.

2.2.6 Sample preservation and holding times

Table 2-40 provides information regarding recommended sample preservation techniques, sample holding times, and other information. Similar information may be found in Table 3-1 of Chapter Three (inorganic analytes) and Table 4-1 of Chapter Four (organic analytes). Samples need to be extracted and analyzed within the recommended holding times for the results to be considered reflective of native concentrations as collected. Analytical data generated outside of the recommended holding times should typically be considered as minimum values only. Such data may be used to demonstrate that a waste is hazardous where it shows the concentration of a constituent to be above the regulatory threshold, but cannot be used to demonstrate that a waste is <u>not</u> hazardous. However, regarding the information in Table 2-40, a longer holding time may be appropriate if it can be demonstrated that reported concentrations are not adversely affected from preservation, storage and analyses performed outside the recommended holding times.

2.3 CHOOSING PROCEDURES FOR ORGANIC ANALYSES

Figure 2-1 summarizes the organic analysis options available in SW-846.

2.3.1 Extraction and sample preparation procedures for organic analytes

SW-846 methods for preparing samples for organic analytes are shown in Table 2-41. Method 3500 and associated methods should be consulted for further details on preparing the sample for analysis.

2.3.1.1 Aqueous samples

Methods 3510, 3520, and 3535 may be used for extraction of the semivolatile organic compounds from aqueous samples. The choice of a preparative method depends on the sample. Method 3510, a separatory funnel liquid-liquid extraction technique, is appropriate for samples which will not form a persistent emulsion interface between the sample and the extraction solvent. The formation of an emulsion that cannot be broken up by mechanical techniques will prevent proper extraction of the sample. Method 3520, a continuous liquid-liquid extraction technique, may be used for any aqueous sample and will minimize emulsion formation.

Method 3535 is solid-phase extraction technique that has been tested for organochlorine pesticides, phthalate esters, polychlorinated biphenyls (PCBs), organophosphorus pesticides, nitroaromatics and nitramines, and some explosive compounds, and may be applicable to other semivolatile and extractable compounds as well. The aqueous sample is passed through a solid sorbent material which traps the analytes. They are then eluted from the solid-phase sorbent with a small volume of organic solvent. This technique may be used to minimize the volumes of organic solvents that are employed, but may not be appropriate for aqueous samples with high suspended solids contents.

2.3.1.1.1 Acidic extraction of phenols and acid analytes

The solvent extract obtained by performing Method 3510, 3520, or 3535 at a pH less than or equal to 2 will contain the phenols and acid/neutral extractable organics of interest, and may contain some mildly basic compounds. The particular pH extraction conditions needs to be defined during the project planning process based on the desired target analytes and performance goals.

2.3.1.1.2 Basic or neutral extraction of semivolatile analytes

The solvent extract obtained by performing Method 3510, 3520, or 3535 at a basic pH will contain the organic bases of interest, if acid extraction is performed first. It will also contain the neutral compounds of interest, if acid extraction is not performed. Refer to Table 1 in the extraction methods (3510 and/or 3520) for guidance on the requirements for pH adjustment prior to extraction and analysis.

2.3.1.2 Solid samples

Soxhlet extraction (Methods 3540, 3541 and 3542), pressurized fluid extraction (Method 3545), microwave extraction (Method 3546) and ultrasonic extraction (Method 3550) may be used with solid samples. Consolidated samples should be ground finely enough to pass through a 1-mm sieve. In limited applications, waste dilution (Methods 3580 and 3585) may be used if the entire sample is soluble in the specified solvent.

Methods 3540, 3541, 3542, 3545, 3546 and 3550 are neutral-pH extraction techniques and therefore, depending on the analysis requirements, acid-base partition cleanup (Method 3650) may be necessary. Method 3650 will only be needed if chromatographic interferences are severe enough to prevent quantitation of the analytes of interest. This separation will be most important if a GC method is chosen for analysis of the sample. If GC/MS is used, the ion selectivity of the technique may compensate for chromatographic interferences.

There are three extraction procedures for solid samples that employ supercritical fluid extraction (SFE). Method 3560 is a technique for the extraction of petroleum hydrocarbons from various solid matrices using carbon dioxide at elevated temperature and pressure. Method 3561 may be used to selectively extract polynuclear aromatic hydrocarbons (PAHs) from solid matrices using supercritical carbon dioxide and appropriate modifiers, based on the determinative procedure to be used. Method 3562 may be used to selectively extract organochlorine pesticides or PCBs from solid matrices using supercritical carbon dioxide.

2.3.1.3 Oils and organic liquids

Method 3580, waste dilution, may be used to prepare oils and organic liquid samples for analysis of semivolatile and extractable organic analytes by GC or GC/MS. Method 3585 may be employed for the preparation of these matrices for volatiles analysis by GC or GC/MS. To avoid overloading the analytical detection system, care must be exercised to ensure that proper dilutions are made. Methods 3580 and 3585 give guidance on performing waste dilutions.

To remove interferences for semivolatiles and extractables, Method 3611 (Alumina cleanup) may be performed on an oil sample directly, without prior sample preparation.

Method 3650 is the only other preparative procedure for oils and other organic liquids. This procedure is a back extraction into an aqueous phase. It is generally introduced as a cleanup procedure for extracts rather than as a preparative procedure. Oils generally have a high concentration of semivolatile compounds and, therefore, preparation by Method 3650 should be done on a relatively small aliquot of the sample. Generally, extraction of 1 mL of oil will be sufficient to obtain a saturated aqueous phase and avoid emulsions.

NOTE: The use of traditional extraction techniques, i.e., 3510, 3520, 3535, 3540, 3541, 3545, 3546, and 3550, is neither suitable nor recommended for use in these matrices due to a high potential for hydrocarbon interferences and decreased determinative method sensitivity, i.e., poor analytical performance.

2.3.1.4 Sludge samples

Determining the appropriate methods for analysis of sludges is complicated because of the lack of precise definitions of sludges with respect to the relative percent of liquid and solid components. There is no set ratio of liquid to solid which enables the analyst to determine which of the three extraction methods cited is the most appropriate. Sludges may be classified into three categories: liquid sludges, solid sludges, and emulsions, but with appreciable overlap.

If the sample is an organic sludge (solid material and organic liquid, as opposed to an aqueous sludge), the sample should be handled as a multiphase sample.

2.3.1.4.1 Liquid sludges

Method 3510 or Method 3520 may be applicable to sludges that behave like, and have the consistency of, aqueous liquids. Ultrasonic extraction (Method 3550) and Soxhlet-type (Method 3540 series) procedures will, most likely, be ineffective because of the overwhelming presence of the liquid aqueous phase.

2.3.1.4.2 Solid sludges

Soxhlet extraction (Methods 3540 and 3541), pressurized fluid (Method 3545) extraction, microwave extraction (Method 3546) and ultrasonic extraction (Method 3550) will be more effective when applied to sludge samples that resemble solids. Samples may be dried or centrifuged to form solid materials for subsequent determination of semivolatile compounds.

Using Method 3650, Acid-Base Partition Cleanup, on the extract may be necessary, depending on whether chromatographic interferences prevent determination of the analytes of interest.

2.3.1.4.3 Emulsions

Attempts should be made to break up and separate the phases of an emulsion. Several techniques are effective in breaking emulsions or separating the phases of emulsions, including:

1. Freezing/thawing -- Certain emulsions will separate if exposed to temperatures below 0 °C.

2. Salting out -- Addition of a salt to make the aqueous phase of an emulsion too polar to support a less polar phase promotes separation.

3. Centrifugation -- Centrifugal force may separate emulsion components by density.

4. Addition of water or ethanol -- Emulsion polymers may be destabilized when a preponderance of the aqueous phase is added.

5. Forced filtering through glass wool -- Many emulsions can be broken by forcing the emulsion through a pad of Pyrex glass wool in a drying column using a slight amount of air pressure (using a rubber bulb usually provides sufficient pressure).

If techniques for breaking emulsions fail, use Method 3520. If the emulsion can be broken, the different phases (aqueous, solid, or organic liquid) may then be analyzed separately.

2.3.1.5 Multiphase samples

Choice of the procedure for separating multiphase samples is highly dependent on the objective of the analysis. With a sample in which some of the phases tend to separate rapidly, the percent weight or volume of each phase should be calculated and each phase should be individually analyzed for the required analytes.

An alternate approach is to obtain a homogeneous sample and attempt a single analysis on the combination of phases. This approach will give no information on the abundance of the analytes in the individual phases other than what can be implied by solubility.

A third alternative is to select phases of interest and to analyze only those selected phases. This tactic must be consistent with the sampling/analysis objectives or it will yield

insufficient information for the time and resources expended. The phases selected should be compared with Figure 2-1 and Table 2-41 for further guidance.

2.3.2 Cleanup procedures

Cleanup procedure selection is determined by the analytes of interest within the extract. Each analyte type in Table 2-42, Cleanup Methods for Organic Analyte Extracts, corresponds to one or more of the possible determinative methods available in the manual. However, the necessity of performing cleanup may also depend upon the matrix from which the extract was developed. Cleanup of a sample may be done exactly as instructed in the cleanup method for some of the analytes. There are some instances when cleanup using one of the methods may only proceed after the procedure is modified to optimize recovery and separation. Several cleanup techniques may be possible for each analyte category. The information provided is not meant to imply that any or all of these methods must be used for the analysis to be acceptable. Extracts with components which interfere with spectral or chromatographic determinations are expected to be subjected to cleanup procedures.

The analyst in consultation with the regulator, customer and other project planning participants, as necessary, must determine the necessity for cleanup procedures, as there are no clear cut criteria for indicating their use. Method 3600 and associated methods should be consulted for further details on extract cleanup.

2.3.3 Determinative procedures

In Table 2-43. the determinative methods for organic analytes are divided into four categories, specifically: gas chromatography/mass spectrometry (GC/MS); gas chromatography (GC) with electromagnetic spectrometric (ES) detectors, i.e., Fourier Transform infrared (FT-IR) or atomic emission (AES); specific quantitation methods, i.e., gas chromatography (GC) with specific non-MS detectors; and high performance liquid chromatography (HPLC). This division is intended to help an analyst choose which determinative method will apply. Under each analyte column, SW-846 method numbers are indicated, if appropriate, for the determination of the analyte. A blank has been left if no chromatographic determinative method is available.

Generally, the MS procedures are more specific but less sensitive than the appropriate gas chromatographic/specific quantitation or ES method.

Method 8000 gives a general description of the techniques of gas chromatography and high performance liquid chromatography. Method 8000 should be consulted prior to application of any of the gas chromatographic methods.

Method 8081 (organochlorine pesticides), Method 8082 (polychlorinated biphenyls), Method 8141 (organophosphorus pesticides), and Method 8151 (chlorinated herbicides), are preferred over GC/MS because of the combination of selectivity and sensitivity of the flame photometric, nitrogen-phosphorus, and electron capture detectors.

Method 8260 is a GC/MS method for volatile analytes, which employs a capillary column. A variety of sample introduction techniques may be used with Method 8260, including Methods 5021, 5030, 5031, 5035, 5041, and 3585. A GC with a selective detector is also useful for the determination of volatile organic compounds in a monitoring scenario, as described in Sec. 2.2.5.

Method 8270 is a GC/MS method for semivolatile analytes, which employs a capillary column. Method 8410 is another capillary GC method for semivolatile analytes which uses a

Fourier Transform IR (FT-IR) detector. Method 8085 is a capillary GC method for pesticides which uses an atomic emission detector (AES).

Table 2-43 lists several GC and HPLC methods that apply to only a small number of analytes. Methods 8031 and 8033 are GC methods for acrolein, acrylonitrile, and acetonitrile. Methods 8315 and 8316 are HPLC methods for these three analytes. Method 8316 also addresses acrylamide, which may be analyzed by Method 8032.

HPLC methods have been developed for other types of analytes, most notably N-methyl carbamates (Method 8318); azo dyes, phenoxy acid herbicides, carbamates, and organophosphorus pesticides (Method 8321); PAHs (Method 8310); explosives (Methods 8330, 8331, and 8332); and some volatile organics (Methods 8315 and 8316).

Method 8430 utilizes a fourier transform infrared spectrometer (FT-IR) coupled to a gas chromatograph to determine bis(2-chloroethyl) ether and its hydrolysis products. The sample is introduced by direct aqueous injection. Method 8440 may be employed for the determination of total recoverable petroleum hydrocarbons (TRPH) in solid samples by infrared (IR) spectrophotometry. The samples may be extracted with supercritical carbon dioxide, using Method 3560.

2.4 CHOOSING PROCEDURES FOR CHARACTERISTIC ANALYSES

2.4.1 Figure 2-2 outlines a sequence for determining if a waste exhibits one or more of the characteristics of a hazardous waste.

2.4.2 EP and TCLP extracts

The leachate obtained from using either the EP (Figure 2-3A) or the TCLP (Figure 2-3B) is an aqueous sample, and therefore, requires further solvent extraction prior to the analysis of semivolatile compounds.

The TCLP leachate is solvent extracted with methylene chloride at a pH <2 and at a pH >11 by either Method 3510 or 3520. The leachate may also be extracted as received for organochlorine pesticides and semivolatiles and at pH <1.0 for phenoxyacid herbicides using the solid phase extraction (SPE) disk option in Method 3535. The best recoveries are usually obtained using either Method 3520 or Method 3535.

The solvent extract obtained by performing either Method 3510 or 3520 at an acidic pH will contain the acid/neutral compounds of interest. Refer to the specific determinative method for guidance on the pH requirements for extraction prior to analysis. Method 5031 (azeotropic distillation) may be used as an effective preparative method for pyridine.

Due to the high concentration of acetate in the TCLP extract, it is recommended that purge-and-trap be used to introduce the volatile sample into the gas chromatograph.

The EP and TCLP extracts can also be digested using acids (Method 3010, 3015, or 3020) and analyzed for metals using a 6000 or 7000 series method (Figures 2-3A and 2-3B).

2.5 CHOOSING PROCEDURES FOR GROUNDWATER ANALYSES

Appropriate analysis schemes for the determination of analytes in groundwater are presented in Figures 2-4A, 2-4B, and 2-4C. Quantitation limits for the inorganic analytes should correspond to the drinking water limits, where such limits are available.

2.5.1 Special techniques for inorganic analytes

All atomic absorption analyses should employ appropriate background correction systems whenever spectral interferences could be present. Several background correction techniques are employed in modern atomic absorption spectrometers. Matrix modification can complement background correction in some cases. Since no approach to interference correction is completely effective in all cases, the analyst should attempt to verify the adequacy of correction. If the interferant is known (e.g., high concentrations of iron in the determination of selenium), accurate analyses of synthetic solutions of the interferant (with and without analyte) could establish the efficacy of the background correction. If the nature of the interferant is not established, good agreement of analytical results using two substantially different wavelengths could substantiate the adequacy of the background correction.

To reduce matrix interferences, all graphite furnace atomic absorption (GFAA) analyses should be performed using techniques which maximize an isothermal environment within the furnace cell. Data indicate that two such techniques, L'vov platform and the delayed atomization cuvette (DAC), are equivalent in this respect, and produce high quality results.

All furnace atomic absorption analysis should be carried out using the best matrix modifier for the analysis. Some examples of modifiers are listed below. (See also the appropriate methods.)

Element(s)	Modifier(s)
As and Se	Nickel nitrate, palladium
Pb	Phosphoric acid, ammonium phosphate, palladium
Cd	Ammonium phosphate, palladium
Sb	Ammonium nitrate, palladium
Tl	Platinum, palladium

ICP, AA, and GFAA calibration standards need to match the acid composition and strength of the acids contained in the samples. Acid strengths of the calibration standards should be stated in the raw data. When using a method which permits the use of internal standardization, and the internal standardization option is being used, matrix matching is not required.

2.6 CHOOSING PROCEDURES FOR INORGANIC ANALYSES

Methods for preparing different sample matrices for inorganic analyses are shown in Table 2-44. Guidance regarding the use of leaching and digestive methods for inorganic analysis is provided in Table 2-45.

2.7 REFERENCES

1. M. J. Barcelona, "TOC Determinations in Ground Water," Ground Water 1984, 22(1), 18-24.

2. R. Riggin, et al.; Development and Evaluation of Methods for Total Organic Halide and Purgeable Organic Halide in Wastewater; U.S. Environmental Protection Agency; Office of Research and Development; Environmental Monitoring and Support Laboratory; ORD Publication Offices of Center for Environmental Research Information; Cincinnati, OH, 1984; EPA-600/4-84-008.

3. G. McKee, et al.; Determination of Inorganic Anions in Water by Ion Chromatography (Technical addition to Methods for Chemical Analysis of Water and Wastewater, EPA 600/4-79-020); U.S. Environmental Protection Agency; Environmental Monitoring and Support Laboratory; ORD Publication Offices of Center for Environmental Research Information; Cincinnati, OH, 1984; EPA-600/4-84-017.

TABLE 2-1

DETERMINATIVE METHODS FOR ORGANIC ANALYTES
Analytes are listed in alphabetical order and alternative analyte names are in parenthesis.
The applicable method listing does not include immunoassay or screening methods.

Analyte	Applicable Method
Abate (Temephos)	8085
Acenaphthene	8100, 8270, 8275, 8310, 8410
Acenaphthylene	8100, 8270, 8275, 8310, 8410
Acetaldehyde	8315
Acetone	8015, 8260, 8261, 8315
Acetonitrile	8015, 8033, 8260, 8261
Acetophenone	8261, 8270
2-Acetylaminofluorene	8270
1-Acetyl-2-thiourea	8270
Acifluorfen	8085, 8151
Acrolein (Propenal)	8015, 8260, 8261, 8315, 8316
Acrylamide	8032, 8316
Acrylonitrile	8015, 8031, 8260, 8261, 8316
Alachlor	8081,8085
Aldicarb (Temik)	8318, 8321
Aldicarb sulfone	8318, 8321
Aldicarb sulfoxide	8321
Aldrin	8081, 8085, 8270
Allyl alcohol	8015, 8260
Allyl chloride	8021, 8260, 8261
Ametryn	8085
2-Aminoanthraquinone	8270
Aminoazobenzene	8270
4-Aminobiphenyl	8270
Aminocarb	8321
2-Amino-4,6-dinitrotoluene (2-Am-DNT)	8095, 8330
4-Amino-2,6-dinitrotoluene (4-Am-DNT)	8095, 8330
3-Amino-9-ethylcarbazole	8270
t-Amyl alcohol (TAA)	8015
t-Amyl ethyl ether (TAEE, 4,4-Dimethyl-3-oxahexane)	8015, 8261
t-Amyl methyl ether (TAME)	8015, 8261
Anilazine	8270
Aniline	8131, 8261, 8270
o-Anisidine	8270
Anthracene	8100, 8270, 8275, 8310, 8410
Aramite	8270
Aroclor-1016 (PCB-1016)	8082, 8270
Aroclor-1221 (PCB-1221)	8082, 8270
Aroclor-1232 (PCB-1232)	8082, 8270
Aroclor-1242 (PCB-1242)	8082, 8270
Aroclor-1248 (PCB-1248)	8082, 8270
Aroclor-1254 (PCB-1254)	8082, 8270
Aroclor-1260 (PCB-1260)	8082, 8270
Aspon	8141
Asulam	8321

TABLE 2-1
(continued)

Analyte	Applicable Method(s)
Atraton	8085
Atrazine	8041, 8085, 8141
Azinphos-ethyl (Ethyl guthion)	8085, 8141
Azinphos-methyl (Guthion)	8085, 8141, 8270
Barban	8270, 8321
Baygon (Propoxur)	8318, 8321
Bendiocarb	8141, 8318, 8321
Benefin	8091
Benfluralin	8085
Benomyl	8321
Bentazon	8151
Benzal chloride	8121
Benzaldehyde	8315
Benz(a)anthracene	8100, 8270, 8275, 8310, 8410
Benzene	8015, 8021, 8260, 8261
Benzenethiol (Thiophenol)	8270
Benzidine	8270, 8325
Benzo(b)fluoranthene	8100, 8270, 8275, 8310
Benzo(j)fluoranthene	8100
Benzo(k)fluoranthene	8100, 8270, 8275, 8310
Benzoic acid	8270, 8410
Benzo(g,h,i)perylene	8100, 8270, 8275, 8310
Benzo(a)pyrene	8100, 8270, 8275, 8310, 8410
p-Benzoquinone	8270
Benzotrichloride	8121
Benzoylprop ethyl	8325
Benzyl alcohol	8270
Benzyl chloride	8021, 8121, 8260
α-BHC (α-Hexachlorocyclohexane)	8081, 8085, 8121, 8270
β-BHC (β-Hexachlorocyclohexane)	8081, 8085, 8121, 8270
δ-BHC (δ-Hexachlorocyclohexane)	8081, 8085, 8121, 8270
γ-BHC (Lindane, γ-Hexachlorocyclohexane)	8081, 8085, 8121, 8270
Bis(2-chloroethoxy)methane	8111, 8270, 8410
Bis(2-chloroethyl) ether	8111, 8270, 8410, 8430
Bis(2-chloroethyl)sulfide	8260
Bis(2-chloroisopropyl) ether	8021, 8111, 8270, 8410
Bis(2-n-butoxyethyl) phthalate	8061
Bis(2-ethoxyethyl) phthalate	8061
Bis(2-ethylhexyl) phthalate	8061, 8270, 8410
Bis(2-methoxyethyl) phthalate	8061
Bis(4-methyl-2-pentyl)-phthalate	8061
Bolstar (Sulprofos)	8085, 8141
Bromacil	8085, 8321
Brominal (Bromoxynil)	8085, 8270
Bromoacetone	8021, 8260
4-Bromoaniline	8131
Bromobenzene	8021, 8260
Bromochloromethane	8021, 8260, 8261

TABLE 2-1
(continued)

Analyte	Applicable Method(s)
2-Bromo-6-chloro-4-nitroaniline	8131
Bromodichloromethane	8021, 8260, 8261
2-Bromo-4,6-dinitroaniline	8131
Bromoform	8021, 8260, 8261
Bromomethane	8021, 8260, 8261
4-Bromophenyl phenyl ether	8111, 8270, 8275, 8410
Bromoxynil (Brominal)	8085, 8270
Butachlor	8085
Butanal	8315
1-Butanol (*n*-Butyl alcohol, *n*-Butanol)	8260
n-Butanol (1-Butanol, *n*-Butyl alcohol)	8260
2-Butanone (Methyl ethyl ketone, MEK)	8015, 8260, 8261
Butifos (DEF)	8085
Butralin	8091
n-Butyl alcohol (1-Butanol, *n*-Butanol)	8260
t-Butyl alcohol	8015, 8260
Butylate	8085, 8141, 8321
n-Butylbenzene	8021, 8260, 8261
sec-Butylbenzene	8021, 8260, 8261
tert-Butylbenzene	8021, 8260, 8261
Butyl benzyl phthalate	8061, 8270, 8410
2-*sec*-Butyl-4,6-dinitrophenol (DNBP, Dinoseb)	8041, 8085, 8151, 8270, 8321
Captafol	8081, 8085, 8270
Captan	8085, 8270
Carbaryl (Sevin)	8270, 8318, 8321, 8325
Carbendazim	8321
Carbofuran (Furaden)	8270, 8318, 8321
Carbofuran phenol	8321
Carbon disulfide	8260, 8261
Carbon tetrachloride	8021, 8260, 8261, 8535
Carbophenothion	8081, 8085, 8141, 8270
Carbosulfan	8321
Carboxin	8085
Casoron (Dichlobenil)	8085
Chloral hydrate	8260
Chloramben	8151
Chlordane (NOS)	8081, 8270
cis-Chlordane	8081
trans-Chlordane	8085, 8081
Chlorfenvinphos	8141, 8270
Chloroacetonitrile	8260
2-Chloroaniline	8131
3-Chloroaniline	8131
4-Chloroaniline	8131, 8270, 8410
Chlorobenzene	8021, 8260, 8261
Chlorobenzilate	8081, 8270
2-Chlorobiphenyl	8082, 8275
2-Chloro-1,3-butadiene (Chloroprene)	8021, 8260

Analyte	Applicable Method(s)
1-Chlorobutane	8260
Chlorodibromomethane (Dibromochloromethane)	8021, 8260, 8261
2-Chloro-4,6-dinitroaniline	8131
1-Chloro-2,4-dinitrobenzene	8091
1-Chloro-3,4-dinitrobenzene	8091
Chloroethane	8021, 8260, 8261
2-Chloroethanol	8021, 8260, 8430
2-(2-Chloroethoxy)ethanol	8430
2-Chloroethyl vinyl ether	8021, 8260
Chloroform	8021, 8260, 8261
1-Chlorohexane	8260
Chloromethane	8021, 8260, 8261
5-Chloro-2-methylaniline	8270
Chloromethyl methyl ether	8021
2-Chloro-5-methylphenol	8041
4-Chloro-2-methylphenol	8041
4-Chloro-3-methylphenol	8041, 8270, 8410
3-(Chloromethyl)pyridine hydrochloride	8270
1-Chloronaphthalene	8270, 8275
2-Chloronaphthalene	8121, 8270, 8410
Chloroneb	8081
2-Chloro-4-nitroaniline	8131
4-Chloro-2-nitroaniline	8131
1-Chloro-2-nitrobenzene	8091
1-Chloro-4-nitrobenzene	8091
2-Chloro-6-nitrotoluene	8091
4-Chloro-2-nitrotoluene	8091
4-Chloro-3-nitrotoluene	8091
2-Chlorophenol	8041, 8270, 8410
3-Chlorophenol	8041
4-Chlorophenol	8410
4-Chloro-1,2-phenylenediamine	8270
4-Chloro-1,3-phenylenediamine	8270
4-Chlorophenyl phenyl ether	8111, 8270, 8410
2-Chlorophenyl 4-nitrophenyl ether	8111
3-Chlorophenyl 4-nitrophenyl ether	8111
4-Chlorophenyl 4-nitrophenyl ether	8111
o-Chlorophenyl thiourea	8325
Chloroprene (2-Chloro-1,3-butadiene)	8021, 8260
3-Chloropropionitrile	8260
Chloropropham	8085, 8321
Chloropropylate	8081
Chlorothalonil	8081
2-Chlorotoluene	8021, 8260, 8261
4-Chlorotoluene	8021, 8260, 8261
Chloroxuron	8321
Chlorpyrifos	8085, 8141
Chlorpyrifos methyl	8141

TABLE 2-1
(continued)

Analyte	Applicable Method(s)
Chlorthalonil (Daconil)	8085
Chrysene	8100, 8270, 8275, 8310, 8410
Coumaphos	8085, 8141, 8270
p-Cresidine	8270
o-Cresol (2-Methylphenol)	8041, 8270, 8410
m-Cresol (3-Methylphenol)	8041, 8270
p-Cresol (4-Methylphenol)	8041, 8270, 8410
Crotonaldehyde	8015, 8260, 8315
Crotoxyphos	8141, 8270
m-Cumenyl methylcarbamate	8318, 8321
Cyanazine	8085
Cycloate	8085
Cyclohexanone	8315
2-Cyclohexyl-4,6-dinitrophenol	8041, 8270
2,4-D	8151, 8321
2,4-D (acid)	8085
2,4-D (butoxyethanol ester)	8321
2,4-D (ethylhexyl ester)	8321
Dacthal (DCPA)	8081, 8085
Daconil (Chlorthalonil)	8085
Dalapon	8151, 8321
2,4-DB	8151, 8321
2,4-DB (acid)	8085
DBCP (1,2-Dibromo-3-chloropropane)	8011, 8021, 8081, 8260, 8261, 8270
2,4-D, butoxyethanol ester	8321
DCM (Dichloromethane, Methylene chloride)	8021, 8260, 8261
DCPA (Dacthal)	8081, 8085
DCPA diacid	8151
2,4'-DDD	8085
4,4'-DDD	8081, 8085, 8270
2,4'-DDE	8085
4,4'-DDE	8081, 8085, 8270
2,4'-DDT	8085
4,4'-DDT	8081, 8085, 8270
DDVP (Dichlorvos, Dichlorovos)	8085, 8141, 8270, 8321
2,2',3,3'4,4'5,5',6,6'-Decachlorobiphenyl	8275
Decanal	8315
DEF (Butifos)	8085
Demeton-O, and Demeton-S	8085, 8141, 8270
2,4-D, ethylhexyl ester	8321
Diallate	8081, 8085, 8270
Diamyl phthalate	8061
2,4-Diaminotoluene	8270
Diazinon	8085, 8141
Dibenz(*a,h*)acridine	8100
Dibenz(*a,j*)acridine	8100, 8270
Dibenz(*a,h*)anthracene	8100, 8270, 8275, 8310
7H-Dibenzo(*c,g*)carbazole	8100

TABLE 2-1
(continued)

Analyte	Applicable Method(s)
Dibenzofuran	8270, 8275, 8410
Dibenzo(*a,e*)pyrene	8100, 8270
Dibenzo(*a,h*)pyrene	8100
Dibenzo(*a,i*)pyrene	8100
Dibenzothiophene	8275
Dibromochloromethane (Chlorodibromomethane)	8021, 8260, 8261
1,2-Dibromo-3-chloropropane (DBCP)	8011, 8021, 8081, 8260, 8261, 8270
Dibromofluoromethane	8260
Dibromomethane	8021, 8260, 8261
1,2-Dibromoethane (EDB, Ethylene dibromide)	8011, 8021, 8260
2,6-Dibromo-4-nitroaniline	8131
2,4-Dibromophenyl 4-nitrophenyl ether	8111
Di-*n*-butyl phthalate	8061, 8270, 8410
Dicamba	8085, 8151, 8321
Dichlobenil (Casoron)	8085
Dichlone	8081, 8270
Dichloran	8081
3,4-Dichloroaniline	8131
1,2-Dichlorobenzene	8021, 8121, 8260, 8261, 8270, 8410
1,3-Dichlorobenzene	8021, 8121, 8260, 8261, 8270, 8410
1,4-Dichlorobenzene	8021, 8121, 8260, 8261, 8270, 8410
3,3'-Dichlorobenzidine	8270,8325
3,5-Dichlorobenzoic acid	8085, 8151
2,3-Dichlorobiphenyl	8082
3,3'-Dichlorobiphenyl	8275
cis-1,4-Dichloro-2-butene	8260, 8261
trans-1,4-Dichloro-2-butene	8260, 8261
Dichlorodifluoromethane	8021, 8260, 8261
1,1-Dichloroethane	8021, 8260, 8261
1,2-Dichloroethane	8021, 8260, 8261
1,1-Dichloroethene (Vinylidene chloride)	8021, 8260, 8261
cis-1,2-Dichloroethene	8021, 8260, 8261
trans-1,2-Dichloroethene	8021, 8260, 8261
Dichlorofenthion	8141
Dichloromethane (DCM, Methylene chloride)	8021, 8260, 8261
2,6-Dichloro-4-nitroaniline	8131
2,3-Dichloronitrobenzene	8091
2,4-Dichloronitrobenzene	8091
3,5-Dichloronitrobenzene	8091
3,4-Dichloronitrobenzene	8091
2,5-Dichloronitrobenzene	8091
2,3-Dichlorophenol	8041
2,4-Dichlorophenol	8041, 8270, 8410
2,5-Dichlorophenol	8041
2,6-Dichlorophenol	8041, 8270
3,4-Dichlorophenol	8041
3,5-Dichlorophenol	8041
2,4-Dichlorophenol 3-methyl-4-nitrophenyl ether	8111

Analyte	Applicable Method(s)
2,3-Dichlorophenyl 4-nitrophenyl ether	8111
2,4-Dichlorophenyl 4-nitrophenyl ether	8111
2,5-Dichlorophenyl 4-nitrophenyl ether	8111
2,6-Dichlorophenyl 4-nitrophenyl ether	8111
3,4-Dichlorophenyl 4-nitrophenyl ether	8111
3,5-Dichlorophenyl 4-nitrophenyl ether	8111
Dichloroprop (Dichlorprop)	8085, 8151, 8321
1,2-Dichloropropane	8021, 8260, 8261
1,3-Dichloropropane	8021, 8260, 8261
2,2-Dichloropropane	8021, 8260, 8261
1,3-Dichloro-2-propanol	8021, 8260
1,1-Dichloropropene	8021, 8260, 8261
cis-1,3-Dichloropropene	8021, 8260, 8261
trans-1,3-Dichloropropene	8021, 8260, 8261
Dichlorovos (DDVP, Dichlorvos)	8085, 8141, 8270, 8321
Dichlorprop (Dichloroprop)	8085, 8151, 8321
Dichlorvos (DDVP, Dichlorovos)	8085, 8141, 8270, 8321
Dicrotophos	8141, 8270
Diclofol (Kelthane)	8085
Diclofop-methyl	8085
Dicofol	8081
Dicyclohexyl phthalate	8061
Dieldrin	8081, 8085, 8270
1,2,3,4-Diepoxybutane	8260
Diesel range organics (DRO)	8015
Diethylene glycol	8430
Diethyl ether	8015, 8260, 8261
Diethyl phthalate	8061, 8270, 8410
Diethylstilbestrol	8270
Diethyl sulfate	8270
Dihexyl phthalate	8061
Diisobutyl phthalate	8061
Diisopropyl ether (DIPE)	8015, 8261
Dimethoate	8141, 8270,8085, 8321
3,3'-Dimethoxybenzidine	8270, 8325
Dimethylaminoazobenzene	8270
2,5-Dimethylbenzaldehyde	8315
7,12-Dimethylbenz(a)anthracene	8270
3,3'-Dimethylbenzidine	8270, 8325
4,4-Dimethyl-3-oxahexane (*t*-Amyl ethyl ether, TAEE)	8015, 8261
α,α-Dimethylphenethylamine	8270
2,3-Dimethylphenol	8041
2,4-Dimethylphenol	8041, 8270
2,5-Dimethylphenol	8041
2,6-Dimethylphenol	8041
3,4-Dimethylphenol	8041
Dimethyl phthalate	8061, 8270, 8410
Dinitramine	8091

TABLE 2-1
(continued)

Analyte	Applicable Method(s)
2,4-Dinitroaniline	8131
3,5-Dinitroaniline	8095
1,2-Dinitrobenzene	8091, 8270
1,3-Dinitrobenzene (1,3-DNB)	8091, 8095, 8270, 8330
1,4-Dinitrobenzene	8091, 8270
4,6-Dinitro-2-methylphenol	8270, 8410
2,4-Dinitrophenol	8041, 8270, 8410
2,5-Dinitrophenol	8041
2,4-Dinitrotoluene (2,4-DNT)	8091, 8095, 8270, 8330, 8410
2,6-Dinitrotoluene (2,6-DNT)	8091, 8095, 8270, 8330, 8410
Dinocap	8270
Dinonyl phthalate	8061
Dinoseb (2-*sec*-Butyl-4,6-dinitrophenol, DNBP)	8041, 8085, 8151, 8270, 8321
Di-*n*-octyl phthalate	8061, 8270, 8410
Dioxacarb	8318
1,4-Dioxane	8260, 8261
Dioxathion	8085, 8141
Di-*n*-propyl phthalate	8410
DIPE (Diisopropyl ether)	8015, 8261
Diphenamid	8085
Diphenylamine	8270
5,5-Diphenylhydantoin	8270
1,2-Diphenylhydrazine	8270
Disperse Blue 3	8321
Disperse Blue 14	8321
Disperse Brown 1	8321
Disperse Orange 3	8321
Disperse Orange 30	8321
Disperse Red 1	8321
Disperse Red 5	8321
Disperse Red 13	8321
Disperse Red 60	8321
Disperse Yellow 5	8321
Disulfoton	8085, 8141, 8270, 8321
Diuron	8085, 8321, 8325
1,3-DNB (1,3-Dinitrobenzene)	8091, 8095, 8270, 8330
DNBP (2-*sec*-Butyl-4,6-dinitrophenol, Dinoseb)	8041, 8085, 8151, 8270, 8321
2,4-DNT (2,4-Dinitrotoluene)	8091, 8095, 8270, 8330, 8410
2,6-DNT (2,6-Dinitrotoluene)	8091, 8270, 8330, 8410
EDB (1,2-Dibromoethane, Ethylene dibromide)	8011, 8021, 8260
Endosulfan I	8081, 8085, 8270
Endosulfan II	8081, 8085, 8270
Endosulfan sulfate	8081, 8085, 8270
Endrin	8081, 8085, 8270
Endrin aldehyde	8081, 8085, 8270
Endrin ketone	8081, 8085, 8270
Epichlorohydrin	8021, 8260
EPN	8141, 8085, 8270

TABLE 2-1
(continued)

Analyte	Applicable Method(s)
Eptam (EPTC)	8085, 8141, 8321
EPTC (Eptam)	8085, 8141, 8321
ETBE (Ethyl *tert*-butyl ether)	8015, 8261
Ethalfluralin (Sonalan)	8085
Ethanol	8015, 8260, 8261
Ethion	8085, 8141, 8270
Ethoprop	8085, 8141
Ethyl acetate	8015, 8260, 8261
Ethyl benzene	8015, 8021, 8260, 8261
Ethyl carbamate	8270
Ethyl cyanide (Propionitrile)	8015, 8260, 8261
Ethylene dibromide (EDB, 1,2-Dibromoethane)	8011, 8021, 8260
Ethylene glycol	8430
Ethyl guthion (Azinphos-ethyl)	8085, 8141
Ethylene oxide	8015, 8260
Ethyl methacrylate	8260, 8261
Ethyl methanesulfonate	8270
Ethyl *tert*-butyl ether (ETBE)	8015, 8261
Etridiazole	8081
Famphur	8141, 8270, 8321
Fenamiphos	8085
Fenarimol	8085
Fenitrothion	8085, 8141
Fensulfothion	8085, 8141, 8270, 8321
Fenthion	8085, 8141, 8270
Fenuron	8321
Fluchloralin	8270
Fluometuron	8321
Fluoranthene	8100, 8270, 8275, 8310, 8410
Fluorene	8100, 8270, 8275, 8310, 8410
Fluridone	8085
Fonophos	8085, 8141
Formaldehyde	8315
Formetanate hydrochloride	8318, 8321
Furaden (Carbofuran)	8270, 8318, 8321
Gardona (Tetrachlovinphos, Stirophos)	80858141, 8270
Garlon (Triclopyr)	8085
Gasoline range organics (GRO)	8015
Guthion (Azinphos-methyl)	8085, 8141, 8270
Halowax-1000	8081
Halowax-1001	8081
Halowax-1013	8081
Halowax-1014	8081
Halowax-1051	8081
Halowax-1099	8081
Heptachlor	8081, 8085, 8270
2,2',3,3',4,4',5-Heptachlorobiphenyl	8082, 8275
2,2',3,4,4',5,5'-Heptachlorobiphenyl	8082, 8275

Analyte	Applicable Method(s)
2,2',3,4,4',5',6-Heptachlorobiphenyl	8082
2,2',3,4',5,5',6-Heptachlorobiphenyl	8082, 8275
Heptachlor epoxide	8081, 8085, 8270
Heptanal	8315
Hexachlorobenzene	8081, 8085, 8121, 8270, 8275, 8410
2,2',3,3,4,4'-Hexachlorobiphenyl	8275
2,2',3,4,4',5'-Hexachlorobiphenyl	8082, 8275
2,2',3,4,5,5'-Hexachlorobiphenyl	8082
2,2',3,5,5',6-Hexachlorobiphenyl	8082
2,2',4,4',5,5'-Hexachlorobiphenyl	8082
Hexachlorobutadiene (1,3-Hexachlorobutadiene)	8021, 8121, 8260, 8261, 8270, 8410
α-Hexachlorocyclohexane (α-BHC)	8081, 8085, 8121, 8270
β-Hexachlorocyclohexane (β-BHC)	8081, 8085, 8121, 8270
δ-Hexachlorocyclohexane (δ-BHC)	8081, 8085, 8121, 8270
γ-Hexachlorocyclohexane (γ-BHC, Lindane)	8081, 8085, 8121, 8270
Hexachlorocyclopentadiene	8081, 8085, 8121, 8270, 8410
Hexachloroethane	8121, 8260, 8270, 8410
Hexachlorophene	8270
Hexachloropropene	8141, 8270
Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)	8095, 8330, 8510
Hexamethyl phosphoramide (HMPA)	, 8270
Hexanal	8315
2-Hexanone	8260, 8261
Hexazinone	8085
Hexyl 2-ethylhexyl phthalate	8061
HMPA (Hexamethyl phosphoramide)	8141, 8270
HMX (Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine)	8095, 8330
1,2,3,4,6,7,8-HpCDD	8280, 8290
HpCDD, total	8280, 8290
1,2,3,4,6,7,8-HpCDF	8280, 8290
1,2,3,4,7,8,9-HpCDF	8280, 8290
HpCDF, total	8280, 8290
1,2,3,4,7,8-HxCDD	8280, 8290
1,2,3,6,7,8-HxCDD	8280, 8290
1,2,3,7,8,9-HxCDD	8280, 8290
HxCDD, total	8280, 8290
1,2,3,4,7,8-HxCDF	8280, 8290
1,2,3,6,7,8-HxCDF	8280, 8290
1,2,3,7,8,9-HxCDF	8280, 8290
2,3,4,6,7,8-HxCDF	8280, 8290
HxCDF	8280, 8290
Hydroquinone	8270
3-Hydroxycarbofuran	8318, 8321
5-Hydroxydicamba	8151
2-Hydroxypropionitrile	8260
Igran (Terbutryn)	8085
Imidan (Phosmet)	8085, 8141, 8270
Indeno(1,2,3-cd)pyrene	8100, 8270, 8275, 8310

TABLE 2-1
(continued)

Analyte	Applicable Method(s)
Iodomethane (Methyl iodide)	8260, 8261
Ioxynil	8085
Isobutyl alcohol (2-Methyl-1-propanol)	8260, 8261
Isodrin	8081, 8270
Isophorone	8270, 8410
Isopropalin	8091
Isopropyl alcohol (2-Propanol)	8015, 8260
Isopropylbenzene	8021, 8260
p-Isopropyltoluene	8021, 8260, 8261
Isosafrole	8270
Isovaleraldehyde	8315
Kelthane (Diclofol)	8085
Kepone	8270
Kerb (Pronamide)	8085, 8270
Lannate (Methomyl)	8318, 8321
Leptophos	8141, 8270
Lindane (γ-Hexachlorocyclohexane, γ-BHC)	8081, 8085, 8121, 8270
Linuron (Lorox)	8321, 8325
Lorox (Linuron)	8321, 8325
Malathion	8085, 8141, 8270
Maleic anhydride	8270
Malononitrile	8260
MCPA	8151, 8321
MCPA (acid)	8085
MCPP	8151, 8321
MCPP (acid)	8085
MEK (Methyl ethyl ketone, 2-Butanone)	8015, 8260, 8261
Merphos	8085, 8141, 8321
Mestranol	8270
Mesurol (Methiocarb)	8141, 8318, 8321
Methacrylonitrile	8260, 8261
Metalaxyl	8085
Methanol	8015, 8260
Methapyrilene	8270
Methiocarb (Mesurol)	8141, 8318, 8321
Methomyl (Lannate)	8318, 8321
Methoxychlor	8081, 8085, 8270
Methyl acrylate	8260
Methyl chlorpyrifos	8085
Methyl-*tert*-butyl ether (MTBE)	8015, 8260, 8261
3-Methylcholanthrene	8100, 8270
2-Methyl-4,6-dinitrophenol	8041
4,4'-Methylenebis(2-chloroaniline)	8270
4,4'-Methylenebis(*N,N*-dimethylaniline)	8270
Methyl ethyl ketone (MEK, 2-Butanone)	8015, 8260, 8261
Methylene chloride (Dichloromethane, DCM)	8021, 8260, 8261
Methyl iodide (Iodomethane)	8260, 8261
Methyl isobutyl ketone (MIBK, 4-Methyl-2-pentanone)	8260, 8261

TABLE 2-1
(continued)

Analyte	Applicable Method(s)
Methyl methacrylate	8260, 8261
Methyl methanesulfonate	8270
1-Methylnaphthalene	8261
2-Methylnaphthalene	8261, 8270, 8410
Methyl paraoxon	8085
Methyl parathion (Parathion, methyl)	8085, 8270, 8141, 8321
4-Methyl-2-pentanone (MIBK, Methyl isobutyl ketone)	8260, 8261
2-Methylphenol (*o*-Cresol)	8041, 8270, 8410
3-Methylphenol (*m*-Cresol)	8041, 8270
4-Methylphenol (*p*-Cresol)	8041, 8270, 8410
2-Methyl-1-propanol (Isobutyl alcohol)	8260, 8261
2-Methyl-2-propanol (*t*-Butyl alcohol)	8015, 8260
2-Methylpyridine (2-Picoline)	8015, 8260, 82618270
Methyl-2,4,6-trinitrophenyl-nitramine (Tetryl)	8330
Metolachlor	8085
Metolcarb	8318, 8321
Metribuzin	8085
Mevinphos	8085, 8141, 8270
Mexacarbate	8270, 8318, 8321
MGK-264	8085
MIBK (Methyl isobutyl ketone, 4-Methyl-2-pentanone)	8260, 8261
Mirex	8081, 8085, 8270
Molinate	8085, 8141, 8321
Monocrotophos	8141, 8270, 8321
Monuron	8321, 8325
MTBE (Methyl-*tert*-butyl ether)	8015, 8260, 8261
Naled	8141, 8270, 8321
Naphthalene	8021, 8100, 8260, 8261, 8270, 8275, 8310, 8410
Napropamide	8085
NB (Nitrobenzene)	8091, 8095, 8260, 8270, 8330, 8410
1,2-Naphthoquinone	8091
1,4-Naphthoquinone	8270, 8091
1-Naphthylamine	8270
2-Naphthylamine	8270
Neburon	8321
Nicotine	8270
5-Nitroacenaphthene	8270
2-Nitroaniline	8131, 8270, 8410
3-Nitroaniline	8131, 8270, 8410
4-Nitroaniline	8131, 8270, 8410
5-Nitro-*o*-anisidine	8270
Nitrobenzene (NB)	8091, 8095, 8260, 8270, 8330, 8410
4-Nitrobiphenyl	8270
Nitrofen	8081, 8270
Nitroglycerin	8095, 8332
2-Nitrophenol	8041, 8270, 8410
3-Nitrophenol	8041
4-Nitrophenol	8041, 8085, 8151, 8270, 8410

Analyte	Applicable Method(s)
4-Nitrophenyl phenyl ether	8111
2-Nitropropane	8260
Nitroquinoline-1-oxide	8270
N-Nitroso-di-*n*-butylamine (*N*-Nitrosodibutylamine)	8015, 8260, 8261, 8270
N-Nitrosodiethylamine	8261, 8270
N-Nitrosodimethylamine	8070, 8261, 8270, 8410
N-Nitrosodiphenylamine	8070, 8270, 8410
N-Nitroso-di-*n*-propylamine	8070, 8261, 8270, 8410
N-Nitrosomethylethylamine	8261, 8270
N-Nitrosomorpholine	8270
N-Nitrosopiperidine	8270
N-Nitrosopyrrolidine	8270
2-Nitrotoluene (*o*-Nitrotoluene, 2-NT)	8091, 8095, 8330
3-Nitrotoluene (*m*-Nitrotoluene, 3-NT)	8091, 8095, 8330
4-Nitrotoluene (*p*-Nitrotoluene, 4-NT)	8091, 8095, 8330
o-Nitrotoluene (2-Nitrotoluene, 2-NT)	8091, 8095, 8330
m-Nitrotoluene (3-Nitrotoluene, 3-NT)	8091, 8095, 8330
p-Nitrotoluene (4-Nitrotoluene, 4-NT)	8091, 8095, 8330
5-Nitro-*o*-toluidine	8270
trans-Nonachlor	8081
2,2'3,3'4,4'5,5'6-Nonachlorobiphenyl	8082, 8275
Nonanal	8315
Norflurazon	8085
2-NT (2-Nitrotoluene, *o*-Nitrotoluene)	8091, 8095, 8330
3-NT (3-Nitrotoluene, *m*-Nitrotoluene)	8091, 8095, 8330
4-NT (4-Nitrotoluene, *p*-Nitrotoluene)	8091, 8095, 8330
OCDD	8280, 8290
OCDF	8280, 8290
2,2',3,3',4,4'5,5'-Octachlorobiphenyl	8275
Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)	8095, 8330
Octamethyl pyrophosphoramide	8270
Octanal	8315
Oxamyl	8318, 8321
4,4'-Oxydianiline	8270
Oxyfluorfen	8085
Paraldehyde	8015, 8260
Parathion	8085, 8270
Parathion, ethyl	8141
Parathion, methyl	8085, 8270, 8141, 8321
PCB-1016 (Aroclor-1016)	8082, 8270
PCB-1221 (Aroclor-1221)	8082, 8270
PCB-1232 (Aroclor-1232)	8082, 8270
PCB-1242 (Aroclor-1242)	8082, 8270
PCB-1248 (Aroclor-1248)	8082, 8270
PCB-1254 (Aroclor-1254)	8082, 8270
PCB-1260 (Aroclor-1260)	8082, 8270
PCBs, as congeners	8082
PCNB (Pentachloronitrobenzene)	8081, 8091, 8270

TABLE 2-1
(continued)

Analyte	Applicable Method(s)
Pebulate	8085, 8141, 8321
1,2,3,7,8-PeCDD	8280, 8290
PeCDD, total	8280, 8290
1,2,3,7,8-PeCDF	8280, 8290
2,3,4,7,8-PeCDF	8280, 8290
PeCDF, total	8280, 8290
Pendimethaline (Penoxalin)	8085, 8091
Penoxalin (Pendimethaline)	8085, 8091
Pentachlorobenzene	8121, 8270
2,2',3,4,5'-Pentachlorobiphenyl	8082
2,3',4,4',5-Pentachlorobiphenyl	8275
2,2',4,5,5'-Pentachlorobiphenyl	8082, 8275
2,3,3',4',6-Pentachlorobiphenyl	8082
Pentachloroethane	8260, 8261
Pentachloronitrobenzene (PCNB)	8081, 8091, 8270
Pentachlorophenol	8041, 8085, 8151, 8270, 8410
Pentaerythritoltetranitrate	8095
Pentafluorobenzene	8260
Pentanal (Valeraldehyde)	8315
2-Pentanone	8015, 8260
Perchloroethylene (Tetrachloroethene, Tetrachloroethylene)	8021, 8260, 8261
Permethrin (*cis* + *trans*)	8081
Perthane	8081
Phenacetin	8270
Phenanthrene	8100, 8270, 8275, 8310, 8410
Phenobarbital	8270
Phenol	8041, 8270, 8410
1,4-Phenylenediamine	8270
1,2-Phenylenediamine (*o*-Phenylenediamine)	8141, 8321
Phorate	8085, 8141, 8270, 8321
Phosalone	8270
Phosmet (Imidan)	8085, 8141, 8270
Phosphamidon	8085, 8141, 8270
Phthalic anhydride	8270
Physostigmine	8321
Physostigmine salicylate	8321
Picloram	8085, 8151
2-Picoline (2-Methylpyridine)	8015, 8260, 8261, 8270
Piperonyl sulfoxide	8270
Polychlorinated biphenyls (PCBs), as Aroclors or congeners	8082, 8270
Profluralin	8085, 8091
Pramitol 5p (Prometon)	8085
Promecarb	8318, 8321
Prometon (Pramitol 5p)	8085
Prometryn	8085
Pronamide (Kerb)	8085, 8270
Propachlor (Ramrod)	8081, 8085
Propanal (Propionaldehyde)	8315

TABLE 2-1
(continued)

Analyte	Applicable Method(s)
1-Propanol (*n*-Propyl alcohol)	8015, 8260
2-Propanol (Isopropyl alcohol)	8015, 8260
Propargite (S-181)	8085
Propargyl alcohol	8260
Propazine	8085
Propenal (Acrolein)	8015, 8260, 8261, 8315, 8316
Propetamidophos	8085
Propham	8141, 8321
ß-Propiolactone	8260
Propionaldehyde (Propanal)	8315
Propionitrile (Ethyl cyanide)	8015, 8260, 8261
Propoxur (Baygon)	8318, 8321
n-Propylalcohol (1-Propanol)	8015, 8260
n-Propylamine	8260
n-Propylbenzene	8021, 8260, 8261
Propylthiouracil	8270
Prosulfocarb	8141, 8321
Prothiophos (Tokuthion)	8141
Pyrene	8100, 8270, 8275, 8310, 8410
Pyridine	8015, 8260, 8261
Ramrod (Propachlor)	8085
RDX (Hexahydro-1,3,5-trinitro-1,3,5-triazine)	8095, 8330
Resorcinol	8270
Ronnel	8085, 8141
Rotenone	8325
S-181 (Propargite)	8085
Safrole	8270
Sevin (Carbaryl)	8270, 8318, 8321, 8325
Siduron	8321, 8325
Simazine	8085, 8141
Silvex (2,4,5-TP)	8085, 8151, 8321
Solvent Red 3	8321
Solvent Red 23	8321
Sonalan (Ethalfluralin)	8085
Stirophos (Tetrachlorvinphos, Gardona)	8085, 8141, 8270
Strobane	8081
Strychnine	8270
Styrene	8021, 8260, 8261
Sulfallate	8270
Sulfotepp	8085, 8141
Sulprofos (Bolstar)	8085, 8141
2,4,5-T	8151, 8321
2,4,5-T (acid)	8085
2,4,5-TB	8085
TAA (t-Amyl alcohol)	8015
TAEE (t-Amyl ethyl ether, 4,4-Dimethyl-3-oxahexane)	8015, 8261
TAME (t-Amyl methyl ether)	8015, 8261
2,4,5-T, butoxyethanol ester	8321

TABLE 2-1
(continued)

Analyte	Applicable Method(s)
2,4,5-T, butyl ester	8321
2,3,7,8-TCDD	8280, 8290
TCDD, total	8280, 8290
2,3,7,8-TCDF	8280, 8290
TCDF, total	8280, 8290
Tebuthiuron	8085, 8321
Temephos (Abate)	8085
Temik (Aldicarb)	8318, 8321
TEPP (Tetraethyl pyrophosphate)	8141, 8270
Terbacil	8085
Terbufos	8141, 8270
Terbutryn (Igran)	8085
1,2,3,4-Tetrachlorobenzene	8121
1,2,3,5-Tetrachlorobenzene	8121
1,2,4,5-Tetrachlorobenzene	8121, 8270
2,2',3,5'-Tetrachlorobiphenyl	8082, 8275
2,2',4,5'-Tetrachlorobiphenyl	8275
2,2',5,5'-Tetrachlorobiphenyl	8082, 8275
2,3',4,4'-Tetrachlorobiphenyl	8082, 8275
1,1,1,2-Tetrachloroethane	8021, 8260
1,1,2,2-Tetrachloroethane	8021, 8260, 8261
Tetrachloroethene (Perchloroethylene, Tetrachloroethylene)	8021, 8260, 8261
2,3,4,5-Tetrachloronitrobenzene	8091
2,3,5,6-Tetrachloronitrobenzene	8091
2,3,4,5-Tetrachlorophenol	8041, 8085
2,3,4,6-Tetrachlorophenol	8041, 8085, 8270
2,3,5,6-Tetrachlorophenol	8041
Tetrachlorvinphos (Stirophos, Gardona)	8085, 8141, 8270
Tetraethyl dithiopyrophosphate	8270
Tetraethyl pyrophosphate (TEPP)	8141, 8270
Tetrahydrofuran (THF)	8261
THF (Tetrahydrofuran)	8261
Tetrazene	8331
Tetryl (Methyl-2,4,6-trinitrophenylnitramine)	8330
Thiodicarb	8318, 8321
Thiofanox	8321
Thiophanate-methyl	8321
Thionazin (Zinophos)	8141, 8270
Thiophenol (Benzenethiol)	8270
1,3,5-TNB (1,3,5-Trinitrobenzene)	8095, 8270, 8330
2,4,6-TNT (2,4,6-Trinitrotoluene)	8095, 8330
TOCP (Tri-*o*-cresylphosphate)	8141
Tokuthion (Prothiofos)	8141
m-Tolualdehyde	8315
o-Tolualdehyde	8315
p-Tolualdehyde	8315
Toluene	8015, 8021, 8260, 8261
Toluene diisocyanate	8270

TABLE 2-1
(continued)

Analyte	Applicable Method(s)
o-Toluidine	8015, 8260, 8261, 8270
Toxaphene	8081, 8270
2,4,5-TP (Silvex)	8085, 8151, 8321
Treflan (Trifluralin)	8081, 8085, 8091, 8270
Triademefon	8085
Triallate	8085, 8141, 8321
Triclopyr (Garlon)	8085
Trichlorfon	8141, 8321
2,4,6-Trichloroaniline	8131
2,4,5-Trichloroaniline	8131
1,2,3-Trichlorobenzene	8021, 8121, 8260, 8261
1,2,4-Trichlorobenzene	8021, 8121, 8260, 8261, 8270, 8275, 8410
1,3,5-Trichlorobenzene	8121
2,2',5-Trichlorobiphenyl	8082, 8275
2,3',5-Trichlorobiphenyl	8275
2,4',5-Trichlorobiphenyl	8082, 8275
1,1,1-Trichloroethane	8021, 8260, 8261
1,1,2-Trichloroethane	8021, 8260, 8261
Trichloroethene (Trichloroethylene)	8021, 8260, 8261, 8535
Trichlorofluoromethane	8021, 8260, 8261
Trichloronate	8141
1,2,3-Trichloro-4-nitrobenzene	8091
1,2,4-Trichloro-5-nitrobenzene	8091
2,4,6-Trichloronitrobenzene	8091
2,3,4-Trichlorophenol	8041
2,3,5-Trichlorophenol	8041
2,3,6-Trichlorophenol	8041
2,4,5-Trichlorophenol	8041, 8085, 8270, 8410
2,4,6-Trichlorophenol	8041, 8085, 8270, 8410
2,3,4-Trichlorophenyl 4-nitrophenyl ether	8111
2,3,5-Trichlorophenyl 4-nitrophenyl ether	8111
2,3,6-Trichlorophenyl 4-nitrophenyl ether	8111
2,4,5-Trichlorophenyl 4-nitrophenyl ether	8111
2,4,6-Trichlorophenyl 4-nitrophenyl ether	8111
3,4,5-Trichlorophenyl 4-nitrophenyl ether	8111
1,2,3-Trichloropropane	8021, 8260, 8261
Tri-*o*-cresylphosphate (TOCP)	8141
Triethylamine	8015
O,O,O-Triethyl phosphorothioate	8270
Trifluralin (Treflan)	8081, 8085, 8091, 8270
Trihalomethanes	8535
2,4,5-Trimethylaniline	8270
1,2,4-Trimethylbenzene	8021, 8260, 8261
1,3,5-Trimethylbenzene	8021, 8260, 8261
Trimethyl phosphate	8270
1,3,5-Trinitrobenzene (1,3,5-TNB)	8095, 8270, 8330
2,4,6-Trinitrophenylmethylnitramine	8095
2,4,6-Trinitrotoluene (2,4,6-TNT)	8095, 8330

TABLE 2-1
(continued)

Analyte	Applicable Method(s)
Tris-BP (Tris(2,3-dibromopropyl) phosphate)	8270, 8321
Tri-*p*-tolyl phosphate	8270
Tris(2,3-dibromopropyl) phosphate (Tris-BP)	8270, 8321
Valeraldehyde (Pentanal)	8315
Vernolate	8085
Vinyl acetate	8260
Vinyl chloride	8021, 8260, 8261
Vinylidene chloride (1,1-Dichloroethene)	8021, 8260, 8261
m-Xylene	8015, 8021, 8260, 8261
o-Xylene	8015, 8021, 8260, 8261
p-Xylene	8015, 8021, 8260, 8261
Zinophos (Thionazin)	8141, 8270

TABLE 2-2

METHOD 8011 (MICROEXTRACTION AND GAS CHROMATOGRAPHY)

1,2-Dibromo-3-chloropropane (DBCP)
1,2-Dibromoethane (EDB)

TABLE 2-3

METHOD 8015 (GC/FID) - NONHALOGENATED VOLATILES

Acetone	Ethyl *tert*-butyl ether (ETBE)
Acetonitrile	Gasoline range organics (GRO)
Acrolein	Isopropyl alcohol
Acrylonitrile	Methanol
Allyl alcohol	Methyl ethyl ketone (MEK, 2-Butanone)
t-Amyl alcohol (TAA)	*N*-Nitroso-di-*n*-butylamine
t-Amyl ethyl ether (TAEE)	Paraldehyde
t-Amyl methyl ether (TAME)	2-Pentanone
Benzene	2-Picoline
t-Butyl alcohol	1-Propanol (*n*-Propyl alcohol)
Crotonaldehyde	Propionitrile
Diesel range organics (DRO)	Pyridine
Diethyl ether	Toluene
Diisopropyl ether (DIPE)	*o*-Toluidine
Ethanol	*o*-Xylene
Ethyl acetate	*m*-Xylene
Ethyl benzene	*p*-Xylene
Ethylene oxide	Triethylamine

TABLE 2-4

METHOD 8021 (GC, PHOTOIONIZATION AND ELECTROLYTIC CONDUCTIVITY DETECTORS) - AROMATIC AND HALOGENATED VOLATILES

Allyl chloride	*cis*-1,2-Dichloroethene
Benzene	*trans*-1,2-Dichloroethene
Benzyl chloride	1,2-Dichloropropane
Bis(2-chloroisopropyl) ether	1,3-Dichloropropane
Bromoacetone	2,2-Dichloropropane
Bromobenzene	1,3-Dichloro-2-propanol
Bromochloromethane	1,1-Dichloropropene
Bromodichloromethane	*cis*-1,3-Dichloropropene
Bromoform	*trans*-1,3-Dichloropropene
Bromomethane	Epichlorhydrin
n-Butylbenzene	Ethylbenzene
sec-Butylbenzene	Hexachlorobutadiene
tert-Butylbenzene	Isopropylbenzene
Carbon tetrachloride	*p*-Isopropyltoluene
Chlorobenzene	Methylene chloride
Chlorodibromomethane	Naphthalene
Chloroethane	*n*-Propylbenzene
2-Chloroethanol	Styrene
2-Chloroethyl vinyl ether	1,1,1,2-Tetrachloroethane
Chloroform	1,1,2,2-Tetrachloroethane
Chloromethyl methyl ether	Tetrachloroethene
Chloroprene	Toluene
Chloromethane	1,2,3-Trichlorobenzene
2-Chlorotoluene	1,2,4-Trichlorobenzene
4-Chlorotoluene	1,1,1-Trichloroethane
1,2-Dibromo-3-chloropropane	1,1,2-Trichloroethane
1,2-Dibromoethane	Trichloroethene
Dibromomethane	Trichlorofluoromethane
1,2-Dichlorobenzene	1,2,3-Trichloropropane
1,3-Dichlorobenzene	1,2,4-Trimethylbenzene
1,4-Dichlorobenzene	1,3,5-Trimethylbenzene
Dichlorodifluoromethane	Vinyl chloride
1,1-Dichloroethane	*o*-Xylene
1,2-Dichloroethane	*m*-Xylene
1,1-Dichloroethene	*p*-Xylene

TABLE 2-5

METHODS 8031 AND 8033 (GC WITH NITROGEN-PHOSPHORUS DETECTION)
AND METHOD 8032 (GC WITH ELECTRON CAPTURE DETECTION)

Method 8031: Acrylonitrile
Method 8032: Acrylamide
Method 8033: Acetonitrile

TABLE 2-6

METHOD 8041 (GC) - PHENOLS

2-Chloro-5-methylphenol	2,5-Dinitrophenol
4-Chloro-2-methylphenol	Dinoseb (2-*sec*-butyl-4,6-dinitro phenol)
4-Chloro-3-methylphenol	2-Methyl-4,6-dinitrophenol
2-Chlorophenol	2-Methylphenol (*o*-Cresol)
3-Chlorophenol	4-Methylphenol (*p*-Cresol)
4-Chlorophenol	2-Nitrophenol
2-Cyclohexyl-4,6-dinitrophenol	3-Nitrophenol
2,3-Dichlorophenol	4-Nitrophenol
2,4-Dichlorophenol	Pentachlorophenol
2,5-Dichlorophenol	Phenol
2,6-Dichlorophenol	2,3,4,5-Tetrachlorophenol
3,4-Dichlorophenol	2,3,4,6-Tetrachlorophenol
3,5-Dichlorophenol	2,3,5,6-Tetrachlorophenol
2,3-Dimethylphenol	2,3,4-Trichlorophenol
2,4-Dimethylphenol	2,3,5-Trichlorophenol
2,5-Dimethylphenol	2,3,6-Trichlorophenol
2,6-Dimethylphenol	2,4,5-Trichlorophenol
3,4-Dimethylphenol	2,4,6-Trichlorophenol
2,4-Dinitrophenol	

TABLE 2-7

METHOD 8061 (GC/ECD) - PHTHALATE ESTERS

Benzyl benzoate	Dihexyl phthalate
Bis(2-*n*-butoxyethyl) phthalate	Diisobutyl phthalate
Bis(2-ethoxyethyl) phthalate	Di-*n*-butyl phthalate
Bis(2-ethylhexyl) phthalate	Diethyl phthalate
Bis(2-methoxyethyl) phthalate	Dinonyl phthalate
Bis(4-methyl-2-pentyl)-phthalate	Dimethyl phthalate
Butyl benzyl phthalate	Di-*n*-octyl phthalate
Diamyl phthalate	Hexyl 2-ethylhexyl phthalate
Dicyclohexyl phthalate	

TABLE 2-8

METHOD 8070 (GC) - NITROSAMINES

N-Nitrosodimethylamine
N-Nitrosodiphenylamine
N-Nitrosodi-*n*-propylamine

TABLE 2-9

METHOD 8081 (GC) - ORGANOCHLORINE PESTICIDES

Alachlor	Diallate	Hexachlorobenzene
Aldrin	Dichlone	Hexachlorocyclopentadiene
α-BHC	Dichloran	Isodrin
β-BHC	Dicofol	Methoxychlor
δ-BHC	Dieldrin	Mirex
γ-BHC (Lindane)	Endosulfan I	Nitrofen
Captafol	Endosulfan II	*trans*-Nonachlor
Carbophenothion	Endosulfan sulfate	Pentachloronitrobenzene (PCNB)
cis-Chlordane	Endrin	Permethrin (*cis* + *trans*)
trans-Chlordane	Endrin aldehyde	Perthane
Chlordane (NOS)	Endrin ketone	Propachlor
Chlorobenzilate	Etridiazole	Strobane
Chloroneb	Halowax-1000	Toxaphene
Chloropropylate	Halowax-1001	Trifluralin
Chlorothalonil	Halowax-1013	
DBCP	Halowax-1014	
Dacthal (DCPA)	Halowax-1051	
4,4'-DDD	Halowax-1099	
4,4'-DDE	Heptachlor	
4,4'-DDT	Heptachlor epoxide	

TABLE 2-10

METHOD 8082 (GC) - POLYCHLORINATED BIPHENYLS

Aroclor 1016	2,3',4,4'-Tetrachlorobiphenyl
Aroclor 1221	2,2',3,4,5'-Pentachlorobiphenyl
Aroclor 1232	2,2',4,5,5'-Pentachlorobiphenyl
Aroclor 1242	2,3,3',4',6-Pentachlorobiphenyl
Aroclor 1248	2,2',3,4,4',5'-Hexachlorobiphenyl
Aroclor 1254	2,2',3,4,5,5'-Hexachlorobiphenyl
Aroclor 1260	2,2',3,5,5',6-Hexachlorobiphenyl
PCBs as congeners	2,2',4,4',5,5'-Hexachlorobiphenyl
2-Chlorobiphenyl	2,2',3,3',4,4',5-Heptachlorobiphenyl
2,3-Dichlorobiphenyl	2,2',3,4,4',5,5'-Heptachlorobiphenyl
2,2',5-Trichlorobiphenyl	2,2',3,4,4',5',6-Heptachlorobiphenyl
2,4',5-Trichlorobiphenyl	2,2',3,4',5,5',6-Heptachlorobiphenyl
2,2',3,5'-Tetrachlorobiphenyl	2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl
2,2',5,5'-Tetrachlorobiphenyl	

TABLE 2-11

METHOD 8085 (GC/AED) - PESTICIDES

Abate (Temephos)	Dichlorprop	Metolachlor
Acifluorfen	Dichlorvos (DDVP)	Metribuzin
Alachlor	Diclofol (Kelthane)	Mevinphos
Aldrin	Diclofop-methyl	MGK-264
Ametryn	Dieldrin	Mirex
Atraton	Dimethoate	Molinate
Atrazine	Dinoseb	Napropamide
Azinphos ethyl (Ethyl guthion)	Dioxathion	Norflurazon
Azinphos methyl (Guthion)	Diphenamid	4-Nitrophenol
Benfluralin	Disulfoton (Disyston)	Oxyfluorfen
α-BHC	Diuron	Parathion
β-BHC	Endosulfan I	Pebulate
δ-BHC	Endosulfan II	Pendimethalin
γ-BHC (Lindane)	Endosulfan sulfate	Pentachlorophenol (PCP)
Bromacil	Endrin	Phorate
Bromoxynil (Brominal)	Endrin aldehyde	Phosphamidon
Butachlor	Endrin ketone	Picloram
Butylate	EPN	Profluralin
Captafol	Eptam (EPTC)	Prometon (Pramitol 5p)
Captan	Ethalfluralin (Sonalan)	Prometryn
Carbophenothion	Ethion	Pronamide (Kerb)
Carboxin	Ethoprop	Propachlor (Ramrod)
trans-Chlordane	Fenamiphos	Propargite (S-181)
Chlorpropham	Fenarimol	Propazine
Chlorpyrifos	Fenitrothion	Propetamidophos
Chlorthalonil (Daconil)	Fensulfothion	Ronnel
Cyanazine	Fluridone	Simazine
Cycloate	Fonofos	Sulfotepp
2,4-D acid	Gardona (Tetrachlovinphos)	Sulprofos (Bolstar)

TABLE 2-11
(continued)

Coumaphos	Fenthion	Silvex
2,4-DB acid	Heptachlor	2,4,5-T acid
DCPA (Dacthal)	Heptachlor epoxide	2,4,5-TB
2,4'-DDD	Hexachlorobenzene	Tebuthiuron
4,4'-DDD	Hexachlorocyclopentadiene	Terbacil
2,4'-DDE	Hexazinone	Terbutryn (Igran)
4,4'-DDE	Imidan (Phosmet)	2,3,4,5-Tetrachlorophenol
2,4'-DDT	Ioxynil	2,3,4,6-Tetrachlorophenol
4,4'-DDT	Malathion	Triademefon
DEF (Butifos)	MCPA acid	Triallate
Demeton-O	MCPP acid	Triclopyr (Garlon)
Demeton-S	Merphos	2,4,5-Trichlorophenol
Diallate	Metalaxyl	2,4,6-Trichlorophenol
Diazinon	Methoxychlor	Trifluralin (Treflan)
Dicamba	Methyl chlorpyrifos	Vernolate
Dichlobenil (Casoron)	Methyl paraoxon	
3,5-Dichlorobenzoic acid	Methyl parathion	

TABLE 2-12

METHOD 8091 (GC) - NITROAROMATICS AND CYCLIC KETONES

Benefin	2,4-Dinitrotoluene
Butralin	2,6-Dinitrotoluene
1-Chloro-2,4-dinitrobenzene	Isopropalin
1-Chloro-3,4-dinitrobenzene	1,2-Naphthoquinone
1-Chloro-2-nitrobenzene	1,4-Naphthoquinone
1-Chloro-4-nitrobenzene	Nitrobenzene
2-Chloro-6-nitrotoluene	2-Nitrotoluene
4-Chloro-2-nitrotoluene	3-Nitrotoluene
4-Chloro-3-nitrotoluene	4-Nitrotoluene
2,3-Dichloronitrobenzene	Penoxalin [Pendimethalin]
2,4-Dichloronitrobenzene	Pentachloronitrobenzene
3,5-Dichloronitrobenzene	Profluralin
3,4-Dichloronitrobenzene	2,3,4,5-Tetrachloronitrobenzene
2,5-Dichloronitrobenzene	2,3,5,6-Tetrachloronitrobenzene
Dinitramine	1,2,3-Trichloro-4-nitrobenzene
1,2-Dinitrobenzene	1,2,4-Trichloro-5-nitrobenzene
1,3-Dinitrobenzene	2,4,6-Trichloronitrobenzene
1,4-Dinitrobenzene	Trifluralin

TABLE 2-13

METHOD 8095 (GC) - EXPLOSIVES

2-Amino-4,6-dinitrotoluene	2-Nitrotoluene
4-Amino-2,6-dinitrotoluene	3-Nitrotoluene
3,5-Dinitroaniline	4-Nitrotoluene
1,3-Dinitrobenzene	Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
2,4-Dinitrotoluene	Pentaerythritoltetranitrate
2,6-Dinitrotoluene	1,3,5-Trinitrobenzene
Hexahydro-1,3,5-trinitro-1,3,5-triazine	2,4,6-Trinitrophenylmethylnitramine
Nitrobenzene	2,4,6-Trinitrotoluene
Nitroglycerine	

TABLE 2-14

METHOD 8100 - POLYNUCLEAR AROMATIC HYDROCARBONS

Acenaphthene	Dibenz(*a,h*)anthracene
Acenaphthylene	7H-Dibenzo(*c,g*)carbazole
Anthracene	Dibenzo(*a,e*)pyrene
Benz(*a*)anthracene	Dibenzo(*a,h*)pyrene
Benzo(*b*)fluoranthene	Dibenzo(*a,i*)pyrene
Benzo(*j*)fluoranthene	Fluoranthene
Benzo(*k*)fluoranthene	Fluorene
Benzo(*g,h,i*)perylene	Indeno(1,2,3-*cd*)pyrene
Benzo(*a*)pyrene	3-Methylcholanthrene
Chrysene	Naphthalene
Dibenz(*a,h*)acridine	Phenanthrene
Dibenz(*a,j*)acridine	Pyrene

TABLE 2-15

METHOD 8111 (GC) - HALOETHERS

Bis(2-chloroethoxy)methane	2,5-Dichlorophenyl 4-nitrophenyl ether
Bis(2-chloroethyl) ether	2,4-Dichlorophenyl 4-nitrophenyl ether
Bis(2-chloroisopropyl) ether	2,3-Dichlorophenyl 4-nitrophenyl ether
4-Bromophenyl phenyl ether	3,4-Dichlorophenyl 4-nitrophenyl ether
4-Chlorophenyl phenyl ether	4-Nitrophenyl phenyl ether
2-Chlorophenyl 4-nitrophenyl ether	2,4,6-Trichlorophenyl 4-nitrophenyl ether
3-Chlorophenyl 4-nitrophenyl ether	2,3,6-Trichlorophenyl 4-nitrophenyl ether
4-Chlorophenyl 4-nitrophenyl ether	2,3,5-Trichlorophenyl 4-nitrophenyl ether
2,4-Dibromophenyl 4-nitrophenyl ether	2,4,5-Trichlorophenyl 4-nitrophenyl ether
2,4-Dichlorophenyl 3-methyl-4-nitrophenyl ether	3,4,5-Trichlorophenyl 4-nitrophenyl ether
2,6-Dichlorophenyl 4-nitrophenyl ether	2,3,4-Trichlorophenyl 4-nitrophenyl ether
3,5-Dichlorophenyl 4-nitrophenyl ether	

TABLE 2-16

METHOD 8121 (GC) - CHLORINATED HYDROCARBONS

Benzal chloride	δ-Hexachlorocyclohexane (δ-BHC)
Benzotrichloride	γ-Hexachlorocyclohexane (γ-BHC)
Benzyl chloride	Hexachlorocyclopentadiene
2-Chloronaphthalene	Hexachloroethane
1,2-Dichlorobenzene	Pentachlorobenzene
1,3-Dichlorobenzene	1,2,3,4-Tetrachlorobenzene
1,4-Dichlorobenzene	1,2,3,5-Tetrachlorobenzene
Hexachlorobenzene	1,2,4,5-Tetrachlorobenzene
Hexachlorobutadiene	1,2,3-Trichlorobenzene
α-Hexachlorocyclohexane (α-BHC)	1,2,4-Trichlorobenzene
β-Hexachlorocyclohexane (β-BHC)	1,3,5-Trichlorobenzene

TABLE 2-17

METHOD 8131 (GC) - ANILINE AND SELECTED DERIVATIVES

Aniline	2,6-Dibromo-4-nitroaniline
4-Bromoaniline	3,4-Dichloroaniline
2-Bromo-6-chloro-4-nitroanilne	2,6-Dichloro-4-nitroaniline
2-Bromo-4,6-dintroaniline	2,4-Dinitroaniline
2-Chloroaniline	2-Nitroaniline
3-Chloroaniline	3-Nitroaniline
4-Chloroaniline	4-Nitroaniline
2-Chloro-4,6-dinitroaniline	2,4,6-Trichloroaniline
2-Chloro-4-nitroaniline	2,4,5-Trichloroaniline
4-Chloro-2-nitroaniline	

TABLE 2-18

METHOD 8141 (GC) - ORGANOPHOSPHORUS COMPOUNDS

Aspon	Disulfoton	Parathion, methyl
Atrazine	EPN	Pebulate
Azinphos-ethyl	EPTC	*o*-Phenylenediamine
Azinphos-methyl	Ethion	Phorate
Bendiocarb	Ethoprop	Phosmet
Bolstar (Sulprofos)	Famphur	Phosphamidon
Butylate	Fenitrothion	Propham
Carbophenothion	Fensulfothion	Prosulfocarb
Chlorfenvinphos	Fenthion	Ronnel
Chlorpyrifos	Fonophos	Simazine
Chlorpyrifos methyl	Hexamethyl phosphoramide (HMPA)	Stirophos (Tetrachlorvinphos, Gardona)
Coumaphos	Leptophos	Sulfotepp
Crotoxyphos	Malathion	Tetraethyl pyrophosphate (TEPP)
Demeton-O, and -S	Merphos	Terbufos
Diazinon	Methiocarb	Triallate
Dichlorofenthion	Mevinphos	Thionazin (Zinophos)
Dichlorvos (DDVP)	Molinate	Tokuthion (Prothiofos)
Dicrotophos	Monocrotophos	Trichlorfon
Dimethoate	Naled	Trichloronate
Dioxathion	Parathion, ethyl	Tri-*o*-cresyl phosphate (TOCP)

TABLE 2-19

METHOD 8151 (GC USING METHYLATION OR PENTAFLUOROBENZYLATION DERIVATIZATION) - CHLORINATED HERBICIDES

Acifluorfen	Dicamba	MCPP
Bentazon	3,5-Dichlorobenzoic acid	4-Nitrophenol
Chloramben	Dichloroprop	Pentachlorophenol
2,4-D	Dinoseb	Picloram
Dalapon	5-Hydroxydicamba	2,4,5-TP (Silvex)
2,4-DB	MCPA	2,4,5-T
DCPA diacid		

TABLE 2-20

METHOD 8260 (GC/MS) - VOLATILE ORGANIC COMPOUNDS

Acetone	Dibromofluoromethane	Methylene chloride
Acetonitrile	Dibromomethane	Methyl acrylate
Acrolein (Propenal)	1,2-Dichlorobenzene	Methyl methacrylate
Acrylonitrile	1,3-Dichlorobenzene	4-Methyl-2-pentanone (MIBK)
Allyl alcohol	1,4-Dichlorobenzene	Naphthalene
Allyl chloride	*cis*-1,4-Dichloro-2-butene	Nitrobenzene
Benzene	*trans*-1,4-Dichloro-2-butene	2-Nitropropane
Benzyl chloride	Dichlorodifluoromethane	*N*-Nitroso-di-*n*-butylamine
Bis(2-chloroethyl)-sulfide	1,1-Dichloroethane	Paraldehyde
Bromoacetone	1,2-Dichloroethane	Pentachloroethane
Bromobenzene	1,1-Dichloroethene	Pentafluorobenzene
Bromochloromethane	*cis*-1,2-Dichloroethene	2-Pentanone
Bromodichloromethane	*trans*-1,2-Dichloroethene	2-Picoline
Bromoform	1,2-Dichloropropane	1-Propanol
Bromomethane	1,3-Dichloropropane	2-Propanol
n-Butanol	2,2-Dichloropropane	Propargyl alcohol
2-Butanone (MEK)	1,3-Dichloro-2-propanol	ß-Propiolactone
t-Butyl alcohol	1,1-Dichloropropene	Propionitrile (Ethyl cyanide)
n-Butylbenzene	*cis*-1,3-Dichloropropene	*n*-Propylamine
sec-Butylbenzene	*trans*-1,3-Dichloropropene	*n*-Propylbenzene
tert-Butylbenzene	1,2,3,4-Diepoxybutane	Pyridine
Carbon disulfide	Diethyl ether	Styrene
Carbon tetrachloride	1,4-Dioxane	1,1,1,2-Tetrachloroethane
Chloral hydrate	Epichlorohydrin	1,1,2,2-Tetrachloroethane
Chloroacetonitrile	Ethanol	Tetrachloroethene
Chlorobenzene	Ethyl acetate	Toluene

TABLE 2-20
(continued)

1-Chlorobutane	Ethylbenzene	*o*-Toluidine
Chlorodibromomethane	Ethylene oxide	1,2,3-Trichlorobenzene
Chloroethane	Ethyl methacrylate	1,2,4-Trichlorobenzene
2-Chloroethanol	Hexachlorobutadiene	1,1,1-Trichloroethane
2-Chloroethyl vinyl ether	Hexachloroethane	1,1,2-Trichloroethane
Chloroform	2-Hexanone	Trichloroethene
1-Chlorohexane	2-Hydroxypropionitrile	Trichlorofluoromethane
Chloromethane	Iodomethane	1,2,3-Trichloropropane
Chloroprene	Isobutyl alcohol	1,2,4-Trimethylbenzene
3-Chloropropionitrile	Isopropylbenzene	1,3,5-Trimethylbenzene
2-Chlorotoluene	*p*-Isopropyltoluene	Vinyl acetate
4-Chlorotoluene	Malononitrile	Vinyl chloride
Crotonaldehyde	Methacrylonitrile	*o*-Xylene
1,2-Dibromo-3-chloropropane	Methanol	*m*-Xylene
1,2-Dibromoethane	Methyl-*t*-butyl ether	*p*-Xylene

TABLE 2-21

METHOD 8261 (VD/GC/MS) - VOLATILE ORGANIC COMPOUNDS

Acetone	1,3-Dichlorobenzene	Methacrylonitrile
Acetonitrile	1,4-Dichlorobenzene	Methyl *t*-butyl ether (MTBE)
Acetophenone	*cis*-1,4-Dichloro-2-butene	Methylene chloride
Acrolein	*trans*-1,4-Dichloro-2-butene	Methyl methacrylate
Acrylonitrile	Dichlorodifluoromethane	1-Methylnaphthalene
Allyl Chloride	1,1-Dichloroethane	2-Methylnaphthalene
t-Amyl ethyl ether (TAEE) (4,4-Dimethyl-3-oxahexane)	1,2-Dichloroethane	4-Methyl-2-pentanone
t-Amyl methyl ether (TAME)	1,1-Dichloroethene	Naphthalene
Aniline	*trans*-1,2-Dichloroethene	*N*-Nitrosodimethylamine
Benzene	*cis*-1,2-Dichloroethene	*N*-Nitrosodi-*n*-propylamine
Bromochloromethane	1,2-Dichloropropane	*N*-Nitrosomethylethylamine
Bromodichloromethane	1,3-Dichloropropane	*N*-Nitrosodibutylamine
Bromoform	2,2-Dichloropropane	*N*-Nitrosodiethylamine
Bromomethane	1,1-Dichloropropene	Pentachloroethane
2-Butanone	*cis*-1,3-Dichloropropene	2-Picoline
n-Butylbenzene	*trans*-1,3-Dichloropropene	Propionitrile
sec-Butylbenzene	Diethyl ether	*n*-Propylbenzene
tert-Butylbenzene	Diisopropyl ether (DIPE)	Pyridine
Carbon disulfide	1,4-Dioxane	Styrene
Carbon tetrachloride	Ethanol	1,1,2,2-Tetrachloroethane
Chlorobenzene	Ethyl acetate	Tetrachloroethene
Chlorodibromomethane	Ethylbenzene	Tetrahydrofuran
Chloroethane	Ethyl *t*-butyl ether (ETBE)	Toluene
Chloroform	Ethyl methacrylate	*o*-Toluidine
Chloromethane	Hexachlorobutadiene	1,2,3-Trichlorobenzene
2-Chlorotoluene	2-Hexanone	1,2,4-Trichlorobenzene
4-Chlorotoluene	Iodomethane	1,1,1-Trichloroethane
1,2-Dibromo-3-chloropropane	Isobutyl alcohol	1,1,2-Trichloroethane
Dibromomethane	Isopropylbenzene	Trichloroethene
1,2-Dichlorobenzene	*p*-Isopropyltoluene	Trichlorofluoromethane

TABLE 2-21
(continued)

1,2,3-Trichloropropane	*o*-Xylene
1,2,4-Trimethylbenzene	*m*-Xylene
1,3,5-Trimethylbenzene	*p*-Xylene
Vinyl chloride	

TABLE 2-22

METHOD 8270 (GC/MS) - SEMIVOLATILE ORGANIC COMPOUNDS

Acenaphthene	Endrin aldehyde
Acenaphthylene	Endrin ketone
Acetophenone	EPN
2-Acetylaminofluorene	Ethion
1-Acetyl-2-thiourea	Ethyl carbamate
Aldrin	Ethyl methanesulfonate
2-Aminoanthraquinone	Famphur
Aminoazobenzene	Fensulfothion
4-Aminobiphenyl	Fenthion
3-Amino-9-ethylcarbazole	Fluchloralin
Anilazine	Fluoranthene
Aniline	Fluorene
o-Anisidine	Heptachlor
Anthracene	Heptachlor epoxide
Aramite	Hexachlorobenzene
Aroclor-1016	Hexachlorobutadiene
Aroclor-1221	Hexachlorocyclopentadiene
Aroclor-1232	Hexachloroethane
Aroclor-1242	Hexachlorophene
Aroclor-1248	Hexachloropropene
Aroclor-1254	Hexamethylphosphoramide

TABLE 2-22
(continued)

Aroclor-1260	Hydroquinone
Azinphos-methyl	Indeno(1,2,3-cd)pyrene
Barban	Isodrin
Benz(a)anthracene	Isophorone
Benzidine	Isosafrole
Benzo(b)fluoranthene	Kepone
Benzo(k)fluoranthene	Leptophos
Benzoic acid	Malathion
Benzo(g,h,i)perylene	Maleic anhydride
Benzo(a)pyrene	Mestranol
p-Benzoquinone	Methapyrilene
Benzyl alcohol	Methoxychlor
α-BHC	3-Methylcholanthrene
β-BHC	4,4'-Methylenebis(2-chloroaniline)
δ-BHC	4,4'-Methylenebis(*N,N*-dimethylaniline)
γ-BHC (Lindane)	Methyl methanesulfonate
Bis(2-chloroethoxy)-methane	2-Methylnaphthalene
Bis(2-chloroethyl)ether	Methyl parathion
Bis(2-chloroisopropyl)ether	2-Methylphenol
Bis(2-ethylhexyl)phthalate	3-Methylphenol
4-Bromophenyl phenyl ether	4-Methylphenol
Bromoxynil	Mevinphos
Butyl benzyl phthalate	Mexacarbate
Captafol	Mirex
Captan	Monocrotophos
Carbaryl	Naled
Carbofuran	Naphthalene
Carbophenothion	1,4-Naphthoquinone
Chlordane (NOS)	1-Naphthylamine
Chlorfenvinphos	2-Naphthylamine

TABLE 2-22
(continued)

4-Chloroaniline	Nicotine
Chlorobenzilate	5-Nitroacenaphthene
5-Chloro-2-methylaniline	2-Nitroaniline
4-Chloro-3-methylphenol	3-Nitroaniline
3-(Chloromethyl)pyridine hydrochloride	4-Nitroaniline
1-Chloronaphthalene	5-Nitro-*o*-anisidine
2-Chloronaphthalene	Nitrobenzene
2-Chlorophenol	4-Nitrobiphenyl
4-Chloro-1,2-phenylenediamine	Nitrofen
4-Chloro-1,3-phenylenediamine	2-Nitrophenol
4-Chlorophenyl phenyl ether	4-Nitrophenol
Chrysene	Nitroquinoline-1-oxide
Coumaphos	*N*-Nitrosodi-*n*-butylamine
p-Cresidine	*N*-Nitrosodiethylamine
Crotoxyphos	*N*-Nitrosodimethylamine
2-Cyclohexyl-4,6-dinitrophenol	*N*-Nitrosodiphenylamine
4,4'-DDD	*N*-Nitrosodi-*n*-propylamine
4,4'-DDE	*N*-Nitrosomethylethylamine
4,4'-DDT	*N*-Nitrosomorpholine
Demeton-O	*N*-Nitrosopiperidine
Demeton-S	*N*-Nitrosopyrrolidine
Diallate (*cis* or *trans*)	5-Nitro-*o*-toluidine
2,4-Diaminotoluene	Octamethyl pyrophosphoramide
Dibenz(*a,j*)acridine	4,4'-Oxydianiline
Dibenz(*a,h*)anthracene	Parathion
Dibenzofuran	Pentachlorobenzene
Dibenzo(*a,e*)pyrene	Pentachloronitrobenzene
1,2-Dibromo-3-chloropropane	Pentachlorophenol
Di-*n*-butyl phthalate	Phenacetin
Dichlone	Phenanthrene

TABLE 2-22
(continued)

1,2-Dichlorobenzene
1,3-Dichlorobenzene
1,4-Dichlorobenzene
3,3'-Dichlorobenzidine
2,4-Dichlorophenol
2,6-Dichlorophenol
Dichlorovos
Dicrotophos
Dieldrin
Diethyl phthalate
Diethylstilbestrol
Diethyl sulfate
Dimethoate
3,3'-Dimethoxybenzidine
Dimethylaminoazobenzene
7,12-Dimethylbenz(*a*)anthracene
3,3'-Dimethylbenzidine
α,α-Dimethylphenethylamine
2,4-Dimethylphenol
Dimethyl phthalate
1,2-Dinitrobenzene
1,3-Dinitrobenzene
1,4-Dinitrobenzene
4,6-Dinitro-2-methylphenol
2,4-Dinitrophenol
2,4-Dinitrotoluene
2,6-Dinitrotoluene
Dinocap
Di-*n*-octyl phthalate
Diphenylamine
Phenobarbital
Phenol
1,4-Phenylenediamine
Phorate
Phosalone
Phosmet
Phosphamidion
Phthalic anhydride
2-Picoline (2-Methylpyridine)
Piperonyl sulfoxide
Pronamide
Propylthiouracil
Pyrene
Resorcinol
Safrole
Strychnine
Sulfallate
Terbufos
1,2,4,5-Tetrachlorobenzene
2,3,4,6-Tetrachlorophenol
Tetrachlorvinphos
Tetraethyl dithiopyrophosphate
Tetraethyl pyrophosphate
Thionazine
Thiophenol (Benzenethiol)
Toluene diisocyanate
o-Toluidine
Toxaphene
1,2,4-Trichlorobenzene
2,4,5-Trichlorophenol

TABLE 2-22
(continued)

5,5-Diphenylhydantoin	2,4,6-Trichlorophenol
1,2-Diphenylhydrazine	*O,O,O*-Triethylphosphorothioate
Dinoseb	Trifluralin
Disulfoton	2,4,5-Trimethylaniline
Endosulfan I	Trimethyl phosphate
Endosulfan II	1,3,5-Trinitrobenzene
Endosulfan sulfate	Tris(2,3-dibromopropyl)phosphate
Endrin	Tri-*p*-tolyl phosphate

TABLE 2-23

METHOD 8275 (TE/GC/MS) - SEMIVOLATILE ORGANIC COMPOUNDS

Acenaphthene	1,2,4-Trichlorobenzene
Acenaphthylene	2-Chlorobiphenyl
Anthracene	3,3'-Dichlorobiphenyl
Benz(*a*)anthracene	2,2',5-Trichlorobiphenyl
Benzo(*a*)pyrene	2,3',5-Trichlorobiphenyl
Benzo(*b*)fluoranthene	2,4',5-Trichlorobiphenyl
Benzo(*g,h,i*)perylene	2,2',5,5'-Tetrachlorobiphenyl
Benzo(*k*)fluoranthene	2,2'4,5'-Tetrachlorobiphenyl
4-Bromophenyl phenyl ether	2,2'3,5'-Tetrachlorobiphenyl
1-Chloronaphthalene	2,3',4,4'-Tetrachlorobiphenyl
Chrysene	2,2',4,5,5'-Pentachlorobiphenyl
Dibenzofuran	2,3',4,4',5-Pentachlorobiphenyl
Dibenz(*a,h*)anthracene	2,2',3,4,4',5'- Hexachlorobiphenyl
Dibenzothiophene	2,2',3,3',4,4'- Hexachlorobiphenyl
Fluoranthene	2,2',3,4',5,5',6- Heptachlorobiphenyl
Fluorene	2,2',3,4,4',5,5'- Heptachlorobiphenyl
Hexachlorobenzene	2,2',3,3',4,4',5- Heptachlorobiphenyl
Indeno(1,2,3-*cd*)pyrene	2,2',3,3',4,4',5,5'- Octachlorobiphenyl
Naphthalene	2,2',3,3'4,4',5,5',6- Nonachlorobiphenyl
Phenanthrene	2,2',3,3'4,4',5,5',6,6'- Decachlorobiphenyl
Pyrene	

TABLE 2-24

METHODS 8280 (HRGC/LRMS) AND 8290 (HRGC/HRMS) -
POLYCHLORINATED DIBENZO-*p*-DIOXINS (PCDDs)
AND POLYCHLORINATED DIBENZOFURANS (PCDFs)

2,3,7,8-TCDD	1,2,3,7,8-PeCDF
TCDD, total	2,3,4,7,8-PeCDF
1,2,3,7,8-PeCDD	PeCDF, total
PeCDD, total	1,2,3,4,7,8-HxCDF
1,2,3,4,7,8-HxCDD	1,2,3,6,7,8-HxCDF
1,2,3,6,7,8-HxCDD	1,2,3,7,8,9-HxCDF
1,2,3,7,8,9-HxCDD	2,3,4,6,7,8-HxCDF
HxCDD, total	HxCDF, total
1,2,3,4,6,7,8-HpCDD	1,2,3,4,6,7,8-HpCDF
HpCDD, total	1,2,3,4,7,8,9-HpCDF
OCDD	HpCDF, total
2,3,7,8-TCDF	OCDF
TCDF, total	

TABLE 2-25

METHOD 8310 (HPLC) - POLYNUCLEAR AROMATIC HYDROCARBONS

Acenaphthene	Chrysene
Acenaphthylene	Dibenzo(*a,h*)anthracene
Anthracene	Fluoranthene
Benz(*a*)anthracene	Fluorene
Benzo(*a*)pyrene	Indeno(1,2,3-*cd*)pyrene
Benzo(*b*)fluoranthene	Naphthalene
Benzo(*g,h,i*)perylene	Phenanthrene
Benzo(*k*)fluoranthene	Pyrene

TABLE 2-26

METHOD 8315 - CARBONYL COMPOUNDS

Acetaldehyde	Decanal	Octanal
Acetone	2,5-Dimethylbenzaldehyde	Pentanal (Valeraldehyde)
Acrolein	Formaldehyde	Propanal (Propionaldehyde)
Benzaldehyde	Heptanal	*m*-Tolualdehyde
Butanal (Butyraldehyde)	Hexanal (Hexaldehyde)	*o*-Tolualdehyde
Crotonaldehyde	Isovaleraldehyde	*p*-Tolualdehyde
Cyclohexanone	Nonanal	

TABLE 2-27

METHOD 8316 (HPLC)

Acrylamide
Acrylonitrile
Acrolein

TABLE 2-28

METHOD 8318 (HPLC) - *N*-METHYLCARBAMATES

Aldicarb (Temik)	Dioxacarb	Mexacarbate
Aldicarb sulfone	Formetanate hydrochloride	Oxamyl
Bendiocarb	3-Hydroxycarbofuran	Promecarb
Carbaryl (Sevin)	Methiocarb (Mesurol)	Propoxur (Baygon)
Carbofuran (Furadan)	Methomyl (Lannate)	Thiodicarb
m-Cumenyl methylcarbamate	Metolcarb	

TABLE 2-29

METHOD 8321 (HPLC/TS/MS) - NONVOLATILE ORGANIC COMPOUNDS

Azo Dyes	Carbamates
Disperse Red 1	Aldicarb
Disperse Red 5	Aldicarb sulfone
Disperse Red 13	Aldicarb sulfoxide
Disperse Yellow 5	Aminocarb
Disperse Orange 3	Barban
Disperse Orange 30	Benomyl
Disperse Brown 1	Bendiocarb
Solvent Red 3	Bromacil
Solvent Red 23	Butylate
	Carbaryl
	Carbendazim
Chlorinated Phenoxyacid Compounds	Carbofuran
2,4-D	Carbofuran phenol
2,4-D, butoxyethanol ester	Carbosulfan
2,4-D, ethylhexyl ester	Chloropropham
2,4-DB	Chloroxuron
Dalapon	*m*-Cumenyl methyl carbamate
Dicamba	Diuron
Dichlorprop	EPTC
Dinoseb	Fenuron
MCPA	Fluometuron
MCPP	Formetanate hydrochloride
Silvex (2,4,5-TP)	3-Hydroxycarbofuran
2,4,5-T	Linuron
2,4,5-T, butyl ester	Methiocarb
2,4,5-T, butoxyethanol ester	Methomyl
	Metolcarb

TABLE 2-29
(continued)

Organophosphorus Compounds	Carbamates (cont.)
Asulam	Mexacarbate
Fensulfothion	Molinate
Dichlorvos (DDVP)	Monuron
Dimethoate	Neburon
Disulfoton	Oxamyl
Parathion methyl	Pebulate
Merphos	*o*-Phenylenediamine
Methomyl	Physostigmine
Monocrotophos	Physostigmine salicylate
Famphur	Promecarb
Naled	Propham
Phorate	Propoxur
Trichlorfon	Prosulfocarb
Thiofanox	Siduron
Tris(2,3-dibromopropyl) phosphate (Tris-BP)	Tebuthiuron
	Thiodicarb
Anthraquinone Dyes	Thiophanate-methyl
Disperse Blue 3	Triallate
Disperse Blue 14	
Disperse Red 60	

TABLE 2-30

METHOD 8325 (HPLC/PB/MS) - NONVOLATILE ORGANIC COMPOUNDS

Benzidine	3,3'-Dimethylbenzidine
Benzoylprop ethyl	Diuron
Carbaryl	Linuron (Lorox)
o-Chlorophenyl thiourea	Monuron
3,3'-Dichlorobenzidine	Rotenone
3,3'-Dimethoxybenzidine	Siduron

TABLE 2-31

METHOD 8330 (HPLC) - NITROAROMATICS AND NITRAMINES

4-Amino-2,6-dinitrotoluene (4-Am-DNT)	Nitrobenzene (NB)
2-Amino-4,6-dinitrotoluene (2-Am-DNT)	2-Nitrotoluene (2-NT)
1,3-Dinitrobenzene (1,3-DNB)	3-Nitrotoluene (3-NT)
2,4-Dinitrotoluene (2,4-DNT)	4-Nitrotoluene (4-NT)
2,6-Dinitrotoluene (2,6-DNT)	Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)
Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)	1,3,5-Trinitrobenzene (1,3,5-TNB)
Methyl-2,4,6-trinitrophenyl-nitramine (Tetryl)	2,4,6-Trinitrotoluene (2,4,6-TNT)

TABLE 2-32

METHOD 8331 (HPLC)

Tetrazene

TABLE 2-33

METHOD 8332 (HPLC)

Nitroglycerine

TABLE 2-34

METHOD 8410 - SEMIVOLATILE ORGANIC COMPOUNDS

Acenaphthene	2,6-Dinitrotoluene
Acenaphthylene	Di-*n*-octyl phthalate
Anthracene	Di-*n*-propyl phthalate
Benzo(*a*)anthracene	Fluoranthene
Benzo(*a*)pyrene	Fluorene
Benzoic acid	Hexachlorobenzene
Bis(2-chloroethoxy)methane	1,3-Hexachlorobutadiene
Bis(2-chloroethyl) ether	Hexachlorocyclopentadiene
Bis(2-chloroisopropyl) ether	Hexachloroethane
Bis(2-ethylhexyl) phthalate	Isophorone
4-Bromophenyl phenyl ether	2-Methylnaphthalene
Butyl benzyl phthalate	2-Methylphenol
4-Chloroaniline	4-Methylphenol
4-Chloro-3-methylphenol	Naphthalene
2-Chloronaphthalene	2-Nitroaniline
2-Chlorophenol	3-Nitroaniline
4-Chlorophenol	4-Nitroaniline
4-Chlorophenyl phenyl ether	Nitrobenzene
Chrysene	2-Nitrophenol
Dibenzofuran	4-Nitrophenol
Di-*n*-butyl phthalate	*N*-Nitrosodimethylamine
1,2-Dichlorobenzene	*N*-Nitrosodiphenylamine
1,3-Dichlorobenzene	*N*-Nitroso-di-*n*-propylamine
1,4-Dichlorobenzene	Pentachlorophenol
2,4-Dichlorophenol	Phenanthrene
Diethyl phthalate	Phenol
Dimethyl phthalate	Pyrene
4,6-Dinitro-2-methylphenol	1,2,4-Trichlorobenzene
2,4-Dinitrophenol	2,4,5-Trichlorophenol
2,4-Dinitrotoluene	2,4,6-Trichlorophenol

TABLE 2-35

METHOD 8430 (GC/FT-IR) - BIS(2-CHLOROETHYL) ETHER
AND ITS HYDROLYSIS PRODUCTS

Bis(2-chloroethyl) ether
2-Chloroethanol
2-(2-Chloroethoxy)ethanol
Diethylene glycol
Ethylene glycol

TABLE 2-36

METHOD 8510 (COLORIMETRIC SCREENING) - RDX AND HMX

Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)
Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)

TABLE 2-37

METHOD 8535 (COLORIMETRIC SCREENING) - VOLATILE ORGANIC HALIDES

Trichloroethylene
Perchloroethylene (Tetrachloroethene)
Carbon tetrachloride
Trihalomethanes

TABLE 2-38

METHOD 8540 (UV-INDUCED COLORIMETRY) - PENTACHLOROPHENOL

Pentachlorophenol

TABLE 2-39

DETERMINATIVE METHODS FOR INORGANIC ANALYTES

Analyte	Applicable Methods
Aluminum	6010, 6020, 7000, 7010
Antimony	6010, 6020, 6200, 6800, 7000, 7062
Arsenic	6010, 6020, 6200, 7010, 7061, 7062, 7063
Barium	6010, 6020, 6200, 6800, 7000, 7010
Beryllium	6010, 6020, 7000, 7010
Boron	6010, 6800
Bromide	6500, 9056, 9211
Cadmium	6010, 6020, 6200, 6800, 7000, 7010
Calcium	6010, 6020, 6200, 6800, 7000
Chloride	6500, 9056, 9057, 9212, 9250, 9251, 9253
Chromium	6010, 6020, 6200, 6800, 7000, 7010
Chromium, hexavalent	6800, 7195, 7196, 7197, 7198, 7199
Cobalt	6010, 6020, 6200, 7000, 7010
Copper	6010, 6020, 6200, 6800, 7000, 7010
Cyanide	9010, 9012, 9013, 9213
Fluoride	6500, 9056, 9214
Iron	6010, 6020, 6200, 6800, 7000, 7010
Lead	6010, 6020, 6200, 6800, 7000, 7010
Lithium	6010, 7000
Magnesium	6010, 6020, 6800, 7000
Manganese	6010, 6020, 6200, 7000, 7010
Mercury	6010, 6020, 6200, 6800, 7470, 7471, 7472, 7473, 7474
Molybdenum	6010, 6200, 6800, 7000, 7010
Nickel	6010, 6020, 6200, 6800, 7000, 7010
Nitrate	6500, 9056, 9210
Nitrite	6500, 9056, 9216
Osmium	7000
Phosphate	6500, 9056
Phosphorus	6010
Phosphorus, white	7580
Potassium	6010, 6020, 6200, 6800, 7000
Rubidium	6200
Selenium	6010, 6020, 6200, 6800, 7010, 7741, 7742
Silver	6010, 6020, 6200, 6800, 7000, 7010
Silica	6010
Sodium	6010, 6020, 7000
Strontium	6010, 6200, 6800, 7000
Sulfate	6500, 9035, 9036, 9038, 9056
Sulfide	9030, 9031, 9215
Thallium	6010, 6020, 6200, 6800, 7000, 7010
Thorium	6200
Tin	6010, 6200, 7000
Titanium	6010, 6200
Vanadium	6010, 6020, 6200, 6800, 7000, 7010
Zinc	6010, 6020, 6200, 6800, 7000, 7010
Zirconium	6200

TABLE 2-40(A)

RECOMMENDED CONTAINERS, PRESERVATION TECHNIQUES, AND HOLDING TIMES FOR ORGANIC ANALYTES[a]
(Note: Footnotes are located on the last page of the table.)

VOLATILE ORGANICS

Sample Matrix	Container	Preservative[1]	Holding Time[2]
Concentrated waste samples	Method 5035: See method. Method 5021: See method. Methods 5031 and 5032: See methods. Use PTFE-lined lids for all procedures.	Cool to ≤6 °C.	14 days
Aqueous samples with no residual chlorine present	Methods 5030, 5031, and 5032: 2 x 40-mL vials with PTFE-lined septum caps	Cool to ≤6 °C and adjust pH to less than 2 with H_2SO_4, HCl, or solid $NaHSO_4$	14 days
		If carbonaceous materials are present, or if MTBE and other fuel oxygenate ethers are present and a high temperature sample preparative method is to be used, do not acid preserve the samples.	*7 days*
		If vinyl chloride, styrene, or 2-chloroethyl vinyl ether are analytes of interest, collect a second set of samples without acid preservatives and analyze as soon as possible.	*7 days*

VOLATILE ORGANICS (continued)			
Sample Matrix	Container	Preservative[1]	Holding Time[2]
Aqueous samples WITH residual chlorine present	Methods 5030, 5031, and 5032: 2 x 40-mL vials with PTFE-lined septum caps	Collect sample in a 125-mL container which has been pre-preserved with 4 drops of 10% sodium thiosulfate solution. Gently swirl to mix sample and transfer to a 40-mL VOA vial. Cool to ≤6 °C and adjust pH to less than 2 with H_2SO_4, HCl, or solid $NaHSO_4$.	14 days
		If carbonaceous materials are present, or if MTBE and other fuel oxygenate ethers are present and a high temperature sample preparative method is to be used, do not acid preserve the samples.	*7 days*
		If vinyl chloride, styrene, or 2-chloroethyl vinyl ether are analytes of interest, collect a second set of samples without acid preservatives and analyze as soon as possible.	*7 days*
Acrolein and acrylonitrile in aqueous samples	Methods 5030, 5031, and 5032: 2 x 40-mL vials with PTFE-lined septum caps	Adjust to pH 4-5. Cool to ≤6 °C. *These compounds are highly reactive and should be analyzed as soon as possible.*	7days
Solid samples (e.g. soils, sediments, sludges, ash)	Method 5035: See method. Method 5021: See method. Methods 5031 and 5032: See methods.	See the individual methods.	14 days
		If vinyl chloride, styrene, or 2-chloroethyl vinyl ether are analytes of interest, collect a second set of samples without acid preservatives and analyze as soon as possible.	7 days

SEMIVOLATILE ORGANICS/ORGANOCHLORINE PESTICIDES AND HERBICIDES

Sample Matrix	Container	Preservative[1]	Holding Time[2]
Concentrated waste samples	125-mL wide-mouth glass with PTFE-lined lid	None	Samples extracted within 14 days and extracts analyzed within 40 days following extraction.
Aqueous samples with no residual chlorine present	4 x 1-L amber glass container with PTFE-lined lid, or other size, as appropriate, to allow use of entire sample for analysis.	Cool to ≤6 °C.	Samples extracted within 7 days and extracts analyzed within 40 days following extraction.

SEMIVOLATILE ORGANICS/ORGANOCHLORINE PESTICIDES AND HERBICIDES (continued)

Sample Matrix	Container	Preservative[1]	Holding Time[2]
Aqueous samples WITH residual chlorine present	4 x 1-L amber glass container with PTFE-lined lid, or other size, as appropriate, to allow use of entire sample for analysis.	Add 3-mL 10% sodium thiosulfate solution per gallon (or 0.008%). Addition of sodium thiosulfate solution to sample container may be performed in the laboratory prior to field use. Cool to ≤6 °C.	Samples extracted within 7 days and extracts analyzed within 40 days following extraction.
Solid samples (e.g. soils, sediments, sludges, ash)	250-mL wide-mouth glass container with PTFE-lined lid	Cool to ≤6 °C.	Samples extracted within 14 days and extracts analyzed within 40 days following extraction.

POLYCHLORINATED BIPHENYLS, POLYCHLORINATED DIBENZO-*p*-DIOXINS, AND POLYCHLORINATED DIBENZOFURANS

Sample Matrix	Container	Preservative[1]	Holding Time[2]
Concentrated waste samples	125-mL wide-mouth glass with PTFE-lined lid	None	None
Aqueous samples with no residual chlorine present	4 x 1-L amber glass container with PTFE-lined lid, or other size, as appropriate, to allow use of entire sample for analysis.	Cool to ≤6 °C.	None

POLYCHLORINATED BIPHENYLS, POLYCHLORINATED DIBENZO-*p*-DIOXINS, AND POLYCHLORINATED DIBENZOFURANS (continued)

Sample Matrix	Container	Preservative[1]	Holding Time[2]
Aqueous samples WITH residual chlorine present	4 x 1-L amber glass container with PTFE-lined lid, or other size, as appropriate, to allow use of entire sample for analysis.	Add 3-mL 10% sodium thiosulfate solution per gallon (or 0.008%). Addition of sodium thiosulfate solution to sample container may be performed in the laboratory prior to field use. Cool to ≤6 °C.	None
Solid samples (e.g. soils, sediments, sludges, ash)	250-mL wide-mouth glass container with PTFE-lined lid.	Cool to ≤6 °C.	None

[a] The information presented in this table does not represent EPA requirements, but rather it is intended solely as guidance. Selection of containers, preservation techniques and applicable holding times should be based on the stated project-specific data quality objectives. See Chapter Three, Chapter Four, or the individual methods for more information.

[1] The exact sample, extract, and standard storage temperature should be based on project-specific requirements and/or manufacturer's recommendations for commercially available standards. Furthermore, alternative storage temperatures may be appropriate based on demonstrated analyte stability in a given matrix, provided the stated data quality objectives for a project-specific application are still attainable.

[2] A longer holding time may be appropriate if it can be demonstrated that the reported analyte concentrations are not adversely affected from preservation, storage and analyses performed outside the recommended holding times.

TABLE 2-40(B)

RECOMMENDED CONTAINERS, PRESERVATION TECHNIQUES, AND HOLDING TIMES FOR INORGANIC AND OTHER ANALYTES IN AQUEOUS MATRICES[a] (SEE CHAPTER THREE FOR MORE DETAILED GUIDANCE, INCLUDING REGARDING SOLID MATRICES)

Name	Container[1]	Preservation[2]	Holding Time[3]
Inorganic Tests:			
Chloride	P, G	None required	28 days
Cyanide, total and amenable to chlorination	P, G	Cool to ≤6 °C; if oxidizing agents present add 5 mL 0.1N $NaAsO_2$ per L or 0.06 g of ascorbic acid per L; adjust pH>12 with 50% NaOH. See Method 9010 for other interferences.	14 days
Hydrogen ion (pH)	P, G	None required	As soon as possible
Nitrate	P, G	Cool to ≤6 °C.	48 hours
Sulfate	P, G	Cool to ≤6 °C.	28 days
Sulfide	P, G	Cool to ≤6 °C , add zinc acetate NaOH to pH >9	7 days
Metals:			
Chromium VI	P, G	Cool to ≤6 °C.	24 hours
Mercury	P, G	HNO_3 to pH<2	28 days
All Other Metals	P, G	HNO_3 to pH<2	6 months
Hexane Extractable Material (HEM; Oil and grease)	G	Cool ≤6 °C, HCl or H_2SO_4 to pH<2	28 days
Organic carbon, total (TOC)	P, G	Cool to ≤6 °C, store in dark HCl or H_2SO_4 to pH<2	28 days
Radiological Tests:			
Alpha, beta and radium	P, G	HNO_3 to pH<2	6 months

[a] The information presented in this table does not represent EPA requirements, but rather it is intended solely as guidance. Selection of containers, preservation techniques and applicable holding times should be based on the stated project-specific data quality objectives. See Chapter Three, Chapter Four, or the individual methods for more information.

[1] Polyethylene (P) or glass (G)

[2] The exact sample, extract, and standard storage temperature should be based on project-specific requirements and/or manufacturer's recommendations for commercially available standards. Furthermore, alternative storage temperatures may be appropriate based on demonstrated analyte stability in a given matrix, provided the stated data quality objectives for a project-specific application are still attainable.

[3] A longer holding time may be appropriate if it can be demonstrated that the reported analyte concentrations are not adversely affected by preservation, storage and analyses performed outside the recommended holding times.

TABLE 2-41

PREPARATION METHODS FOR ORGANIC ANALYTES
(Note: Footnotes are located on the last page of the table.)

	Matrix			
Analyte Type	Aqueous[1]	Solids	Sludges and Emulsions[1,2]	Organic Liquids, Tars, Oils
Acid Extractable	3510 3520 (pH ≤ 2)	3540 3541 3542[13] 3545 3546 3550	3520 (pH ≤ 2)	3650 3580[3]
Acrolein[12], Acrylonitrile[12], and Acetonitrile	5031 5032[12]	5031 5032[12]	5031 5032[12]	3585
Acrylamide	8032[4]			
Aniline and Selected Derivatives	3510 3520 (pH >11) 5031[11]	3540 3541 3545 3550	3520 (pH >11)	3580[3]
Aromatic Volatiles	5021 5030 5032	5021 5032 5035	5030 5032	3585
Base/Neutral Extractable	3510 3520 (pH >11)	3540 3541 3542[13] 3545 3546 3550	3520 (pH >11)	3650 3580[3]
Carbamates	8318[5] 8321	8318[5] 8321	8318[5]	8318[5]
Chlorinated Herbicides	3535 (pH < 1) 8151[6] (pH ≤ 2) 8321	3545 3546 8151[6] 8321	8151[6] (pH ≤ 2)	3580[3]
Chlorinated Hydrocarbons	3510 3520 (pH as received)	3540 3541 3550	3520 (pH as received)	3580[3]
Dyes	3510 3520	3540 3541 3545 3550		
Explosives	3535 8330[7] 8331[8]	8330[7] 8331[8]		
Formaldehyde	8315[9]	8315[9]		

TABLE 2-41
(continued)

Analyte Type	Matrix: Aqueous[1]	Solids	Sludges and Emulsions[1,2]	Organic Liquids, Tars, Oils
Haloethers	3510 3520	3540 3541 3545 3550		
Halogenated Volatiles	5021 5030 5032	5021 5032 5035	5030	3585
Nitroaromatics and Cyclic Ketones	3510 3520 (pH 5-9) 3535	3540 3541 3545 3550	3520 (pH 5-9)	3580[3]
Nitrosamines	3510 3520	3540 3541 3545 3550		
Non-halogenated Volatiles	5021 5031 5032	5021 5031 5032	5021 5031 5032	5032 3585
Organochlorine Pesticides	3510 3520 3535 (pH 5-9)	3540 3541 3545 3546 3550 3562	3520 (pH 5-9)	3580[3]
Organophosphorus Pesticides	3510 3520 (pH 5-8) 3535	3540 3541 3545 3546	3520 (pH 5-8)	3580[3]
Phenols	3510 3520 (pH $\leq$ 2) 3535	3540 3541 3545 3546 3550 3562	3520 (pH $\leq$ 2)	3650 3580[3]
Phthalate Esters	3510 3520 3535 (pH 5-7)	3540 3541 3545 3546 3550	3520 (pH 5- 7)	3580[3]
Polychlorinated Biphenyls	3510 3520 3535 (pH 5-9)	3540 3541 3545 3546 3562	3520 (pH 5-9)	3580[3]

TABLE 2-41
(continued)

Analyte Type	Matrix			
	Aqueous[1]	Solids	Sludges and Emulsions[1,2]	Organic Liquids, Tars, Oils
PCDDs and PCDFs	8280[10] 8290[10]	3545 3546 8280[10] 8290[10]	8280[10] 8290[10]	8280[10] 8290[10]
Polynuclear Aromatic Hydrocarbons	3510 3520 (pH as received)	3540 3541 3545 3546 3550 3561	3520 (pH as received)	3580[3]
Volatile Organics	5021 5030 5031 5032	5021 5031 5032 5035	5021 5030 5031 5032	3585

1 The pH at which extraction should be performed is shown in parentheses.
2 If attempts to break an emulsion are unsuccessful, these methods may be used.
3 Method 3580 is only appropriate if the sample is soluble in the specified solvent.
4 Method 8032 contains the extraction, cleanup, and determinative procedures for this analyte.
5 Method 8318 contains the extraction, cleanup, and determinative procedures for these analytes.
6 Method 8151 contains the extraction, cleanup, and determinative procedures for these analytes.
7 Method 8330 contains the extraction, cleanup, and determinative procedures for these analytes.
8 Method 8331 is for Tetrazene only, and contains the extraction, cleanup, and determinative procedures for this analyte.
9 Method 8315 contains the extraction, cleanup, and determinative procedures for this analyte.
10 Methods 8280 and 8290 contain the extraction, cleanup, and determinative procedures for these analytes.
11 Method 5031 may be used when only aniline is to be determined.
12 Method 5032 may be used for acrolein and acrylonitrile.
13 Method 3542 is used for extraction of semivolatiles from stack samples collected using Method 0010.

TABLE 2-42

CLEANUP METHODS FOR ORGANIC ANALYTE EXTRACTS

Analyte Type	Method
Acid Extractable	3650, 3640
Base/Neutral Extractable	3650, 3640
Carbamates	8318[1]
Chlorinated Herbicides	8151[2]
Chlorinated Hydrocarbons	3620, 3640
Haloethers	3620, 3640
Nitroaromatics & Cyclic Ketones	3620, 3640
Nitrosamines	3610, 3620, 3640
Organochlorine Pesticides	3620, 3630, 3640 3660
Organophosphorus Pesticides	3620
Phenols	3630, 3640, 3650 8041[3]
Phthalate Esters	3610, 3611, 3620 3640
Polychlorinated Biphenyls	3620, 3630, 3640 3660, 3665
Polychlorinated Dibenzo-*p*-Dioxins and Polychlorinated Dibenzofurans	8280[4] 8290[4]
Polynuclear Aromatic Hydrocarbons	3610, 3611 3630, 3640, 3650

[1] Method 8318 contains the extraction, cleanup, and determinative procedures for these analytes.
[2] Method 8151 contains the extraction, cleanup, and determinative procedures for these analytes.
[3] Method 8041 includes a derivatization technique followed by GC/ECD analysis, if interferences are encountered using GC/FID.
[4] Methods 8280 and 8290 contain the extraction, cleanup, and determinative procedures for these analytes.

TABLE 2-43

DETERMINATIVE METHODS ORGANIC ANALYTES

Analyte Type	GC/MS Method	Specific GC Method[6]	HPLC Method
Acid Extractable	8270	8410[6]	
Acrolein, Acrylonitrile, Acetonitrile	8260, 8261	8015, 8031, 8033[1]	8315[2], 8316
Acrylamide	8260	8032	8316
Aniline and Selected Derivatives	8270	8131	
Aromatic Volatiles	8260, 8261	8021	
Base/Neutral Extractable	8270	8410[6]	8325[4]
Carbamates			8318, 8321
Chlorinated Herbicides	8270[3]	8151	8321
Chlorinated Hydrocarbons	8270	8121	
Diesel Range Organics (DRO)		8015, 8440[7]	
Dyes			8321
Explosives		8095	8330, 8331, 8332
Formaldehyde			8315
Gasoline Range Organics (GRO)		8015	
Haloethers	8270	8111	
Halogenated Volatiles	8260, 8261	8011, 8021	
Nitroaromatics and Cyclic Ketones	8270	8091	8330[5]
Nitrosoamines	8270	8070	
Non-halogenated Volatiles	8260	8015	8315
Organochlorine Pesticides	8270[3]	8081, 8085[6]	
Organophosphorus Pesticides	8270[3]	8141, 8085[6]	8321
Phenols	8270	8041, 8410[6]	
Phthalate Esters	8270	8061, 8410[6]	
Polychlorinated Biphenyls	8270[3]	8082	
PCDDs and PCDFs	8280, 8290		
Polynuclear Aromatic Hydrocarbons	8270	8100, 8410[6]	8310
Volatile Organics	8260, 8261	8011, 8015, 8021, 8031, 8032, 8033	8315, 8316

[1] Of these analytes, Method 8033 is for acetonitrile only.
[2] Of these analytes, Method 8315 is for acrolein only.
[3] This method is an alternative confirmation method, not the method of choice.
[4] Benzidines and related compounds.
[5] Nitroaromatics (see "Explosives").
[6] Includes GC/ES methods, e.g., Methods 8085 and 8410.
[7] FT-IR determinative method only. Does not use GC.

TABLE 2-44

PREPARATION METHODS FOR INORGANIC ANALYSES [1]

Matrix	Method
Surface water	3005, 3010, 3015, 3020
Groundwater	3005, 3010, 3015, 3020
Extracts	3010, 3015, 3020
Aqueous samples containing suspended solids	3010, 3015, 3020
Oils	3031, 3040, 3051, 3052[2]
Oil sludges	3031, 3052[2]
Tars	3031, 3052[2]
Waxes	3031, 3040, 3052[2]
Paints	3031, 3052[2]
Paint sludges	3031, 3052[2]
Petroleum products	3031, 3040, 3052[2]
Sediments	3050, 3051, 3052[2], 3060[3]
Sludges	3050, 3051, 3052[2], 3060[3]
Soil samples	3050, 3051, 3052[2], 3060[3]
Ashes	3052[2]
Biological tissues	3052[2]

[1]It is the responsibility of the analyst to refer to each analytical method to determine applicability of the chosen method to a specific waste type and target analyte.

[2]For total decomposition analysis ONLY.

[3]For the analysis of samples for hexavalent chromium ONLY.

TABLE 2-45

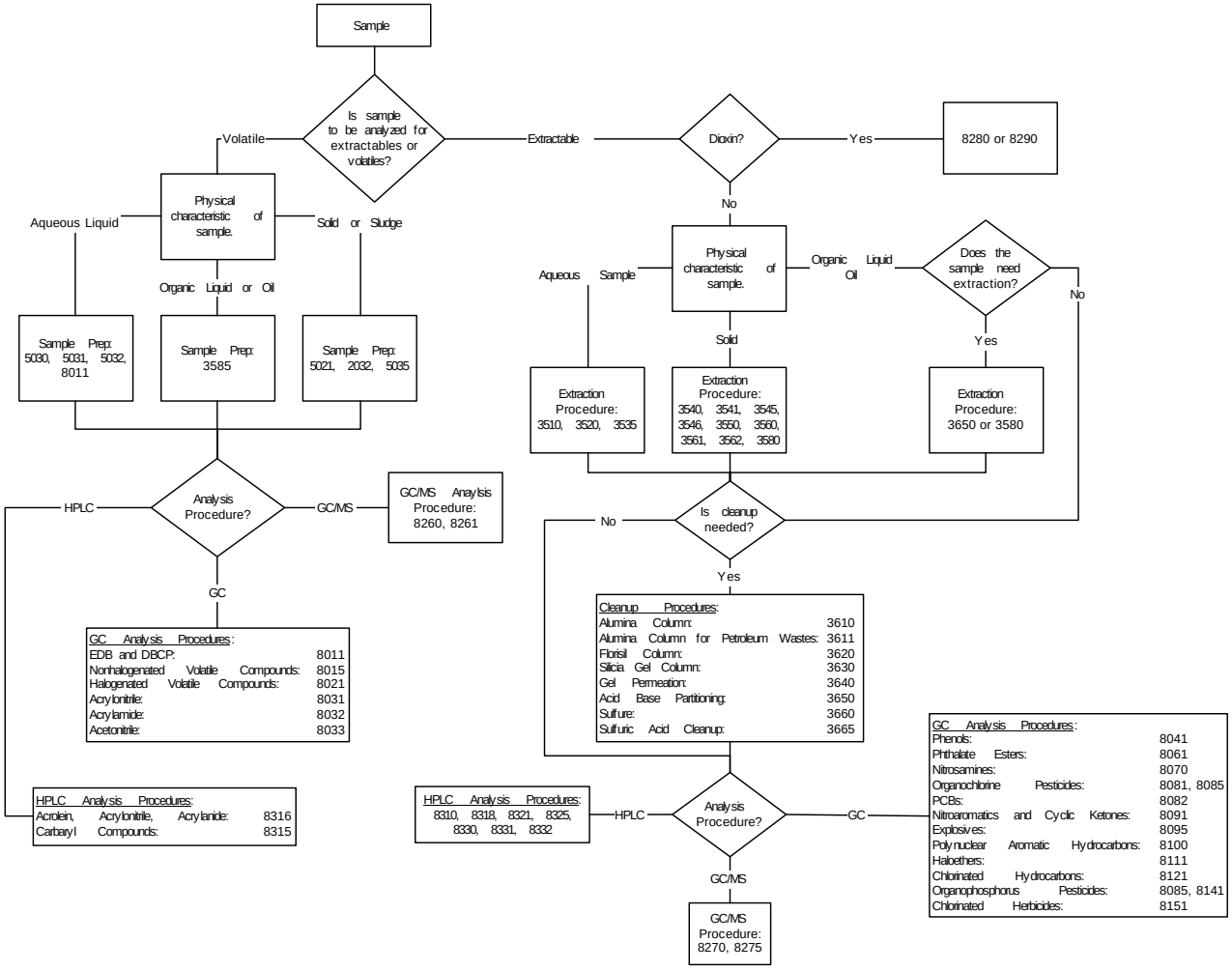
USE OF LEACHING, EXTRACTION AND DIGESTION METHODS
FOR INORGANIC ANALYSIS (In order of increasing strength)

Method	Reagents & Conditions	Use
1310	Dilute acetic acid	Simulate leaching that would result from codisposal of a solid waste and municipal waste in a sanitary landfill[1]
1311	Extraction Fluid # 1 -- Dilute glacial acetic acid and NaOH, pH 4.93 ± 0.05 Extraction Fluid # 2 -- Dilute glacial acetic acid, pH 2.88 ± 0.05	Simulate leaching that would result from codisposal of a solid waste and municipal waste in a sanitary landfill[1]
1312	Dilute H_2SO_4 and HNO_3 (synthetic acid rain)	Simulate acid rain leaching of a waste
1320	Dilute H_2SO_4 and HNO_3 (synthetic acid rain)	Simulate long-term acid rain leaching of a waste
3005	HNO_3, heat	Surface water and groundwater
3010	HNO_3, HCl, heat	Aqueous samples and extracts
3015	HNO_3 or alternatively HNO_3 and HCl, (pressure, heat)	Aqueous samples and extracts
3020	HNO_3, heat	Aqueous samples and extracts for GFAA work only
3031	Potassium permanganate, H_2SO_4, HNO_3, HCl, heat	Oils, oily sludges, tars, waxes, paint, paint sludge, and other viscous petroleum products
3040	Solvent (e.g., xylene, kerosene, or MIBK)	Dissolution of oils, oily wastes, greases and waxes
3050	HNO_3 and H_2O_2, heat (for GFAA or ICPMS) HNO_3, H_2O_2, and HCl, heat (for ICP-AES or FLAA)	Sediments, soils, and sludges
3051	HNO_3, or alternatively HNO_3 and HCl, microwave assisted (pressure, heat)	Sludges, sediments, soils and oils
3052	HNO_3, HF, HCl (optional) H_2O_2 (optional), heat, pressure	Siliceous, organic and other complex matrices for total sample decomposition
3060A	Na_2CO_3/NaOH, heat	Soils, sludges, sediments and some industrial wastes for the analysis of hexavalent chromium only.

[1] As described in the respective background documents developed in support of the rulemakings which added required use of these methods to the Toxicity Characteristic regulation (Method 1311 replaced Method 1310 for Toxicity Characteristic determinations on March 29, 1990, 55 FR 11862).

FIGURE 2-1

ORGANIC ANALYSIS OPTIONS FOR SOLID AND LIQUID MATRICES



For illustrative purposes only. See the disclaimer and Sec. 2.1 for information on the flexibility inherent in SW-846 methods.

FIGURE 2-2
SCHEMATIC OF SEQUENCE TO DETERMINE
IF A WASTE IS HAZARDOUS BY CHARACTERISTIC

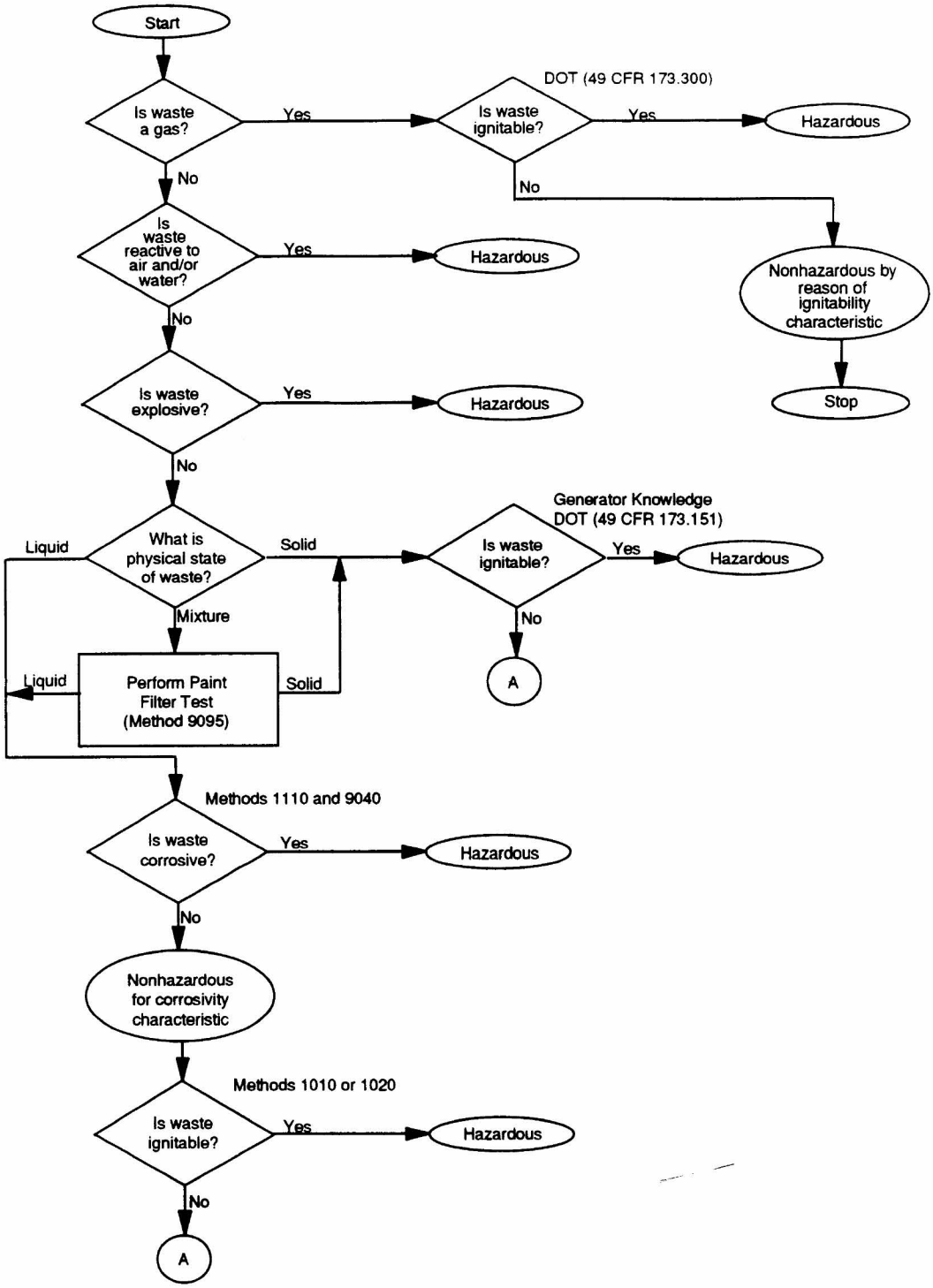


FIGURE 2-2
(continued)

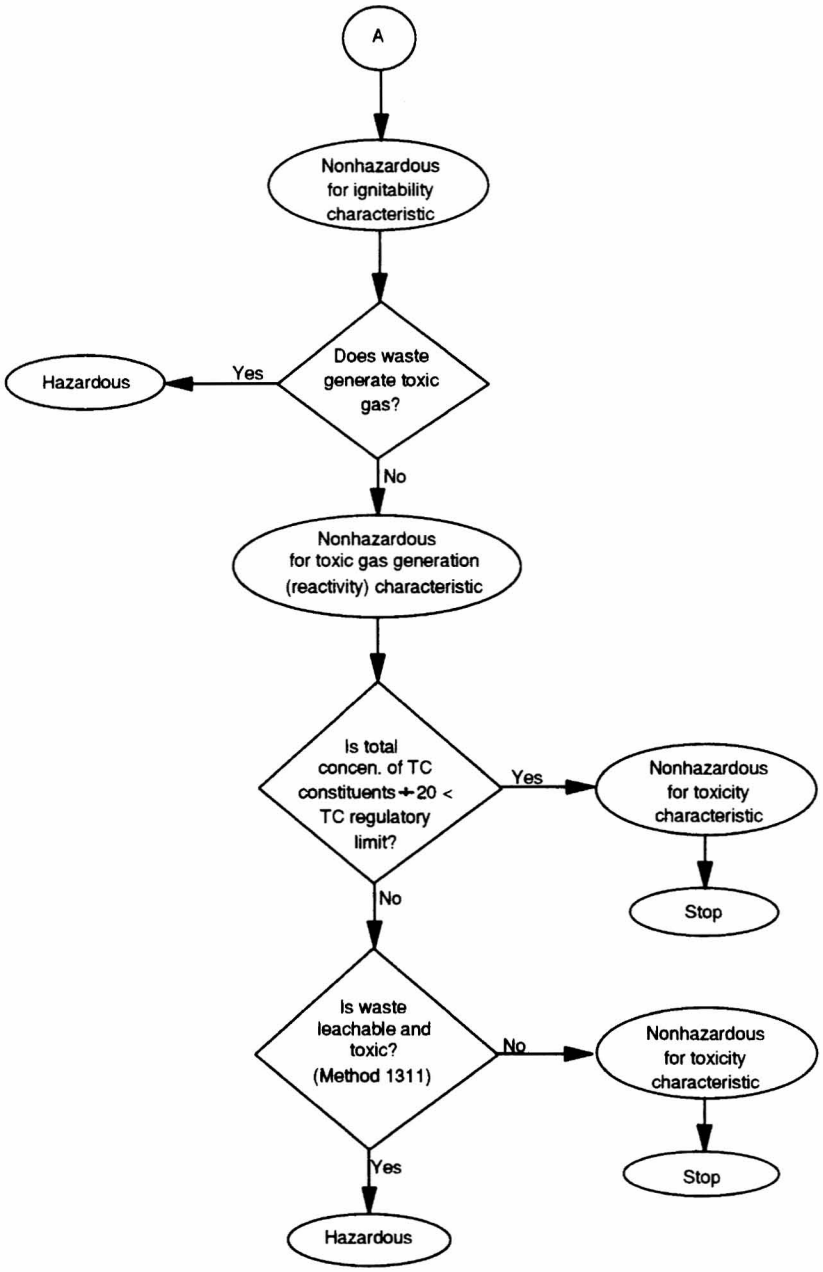


FIGURE 2-3A
RECOMMENDED SW-846 METHODS FOR ANALYSIS OF EP LEACHATES

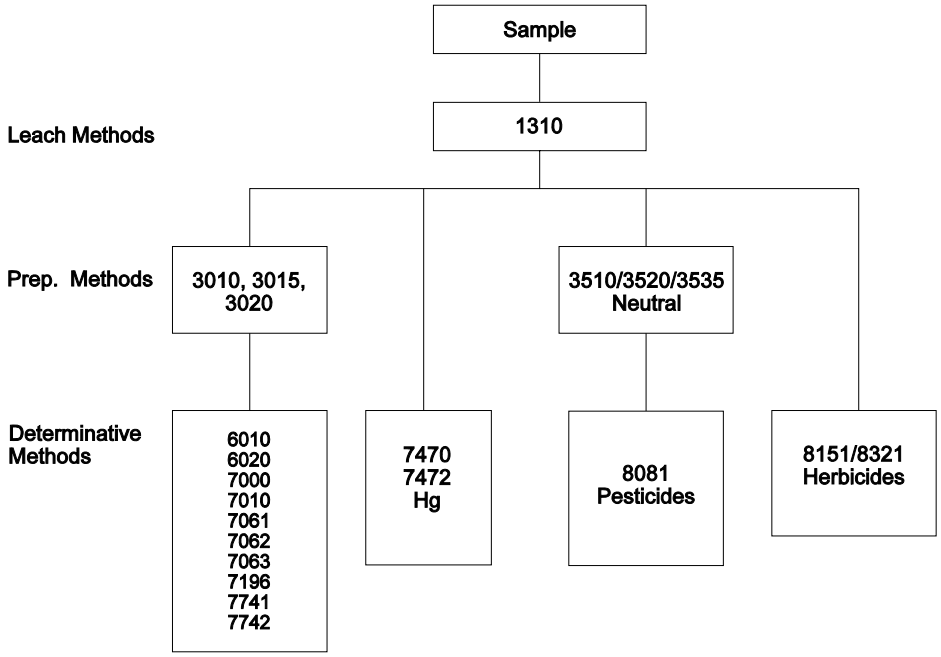


FIGURE 2-3B

RECOMMENDED SW-846 METHODS FOR ANALYSIS OF TCLP LEACHATES

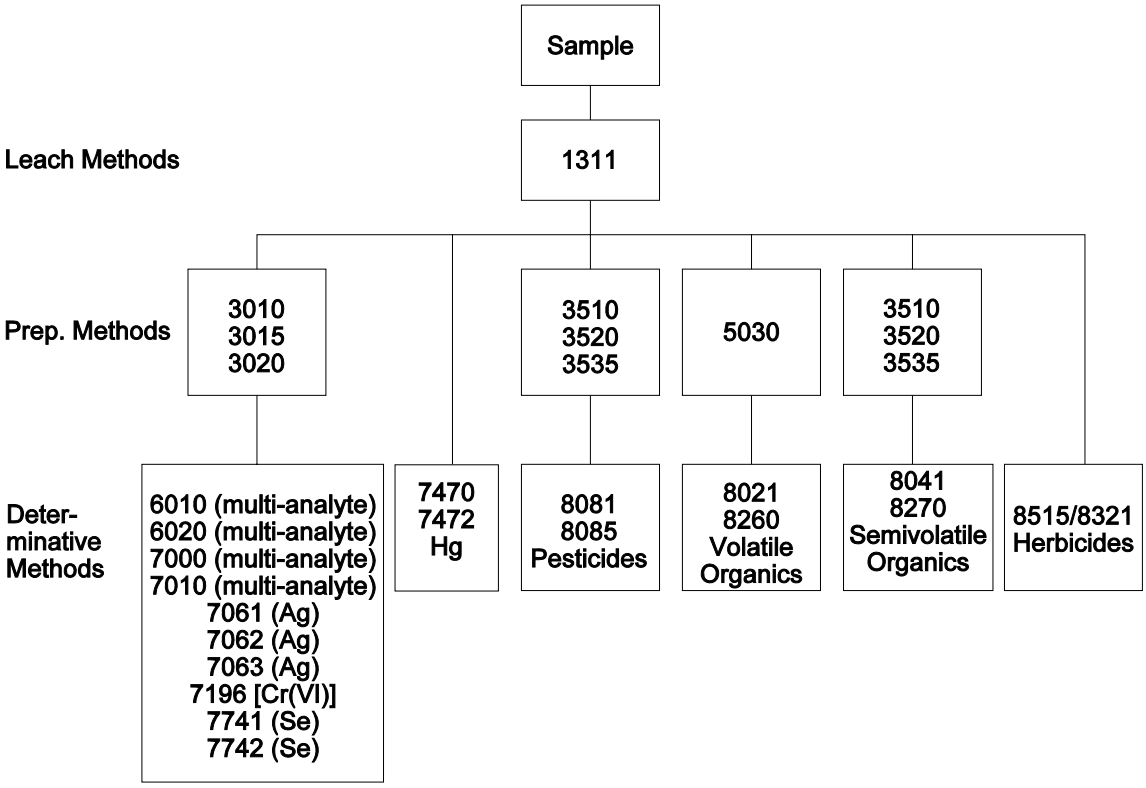
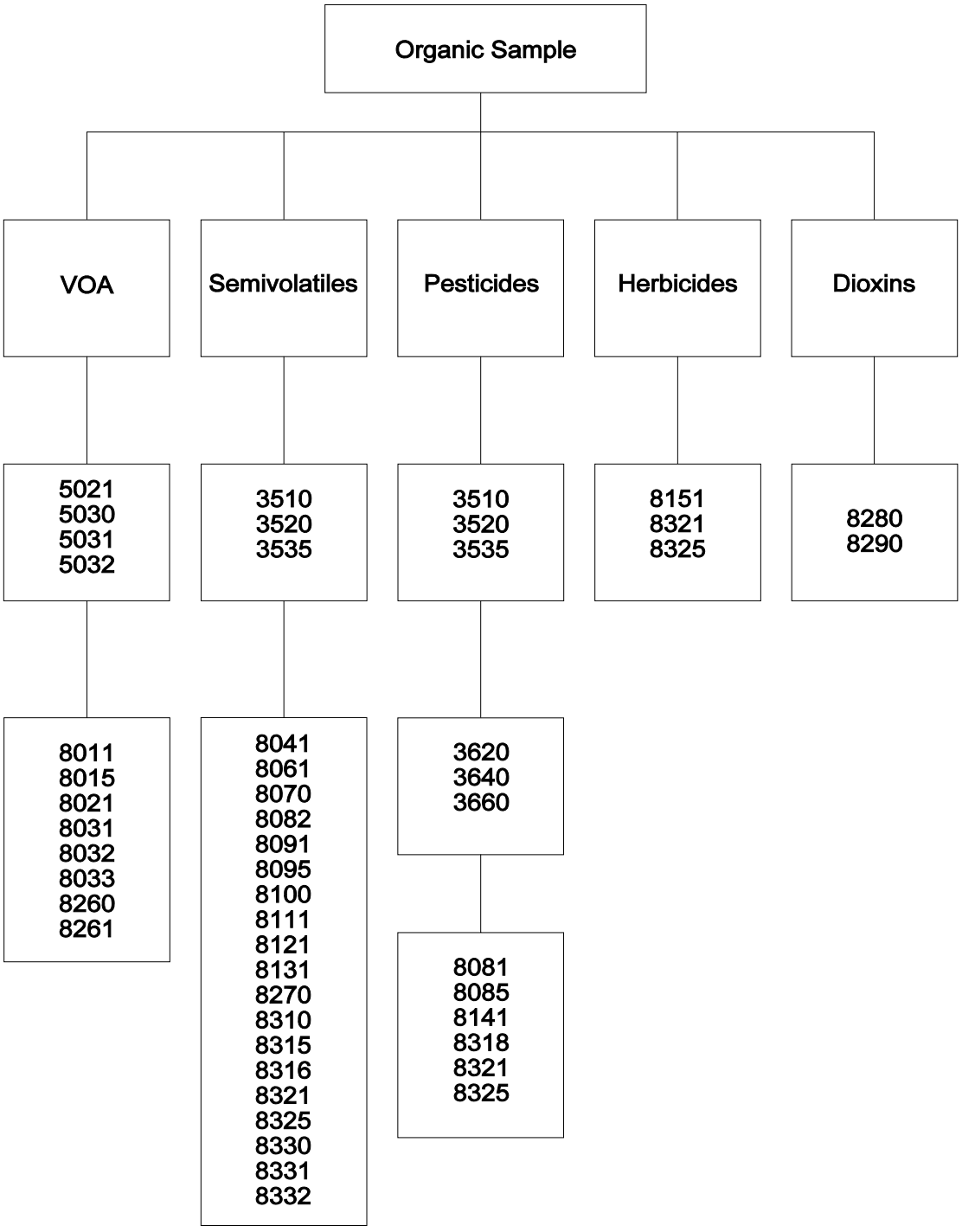
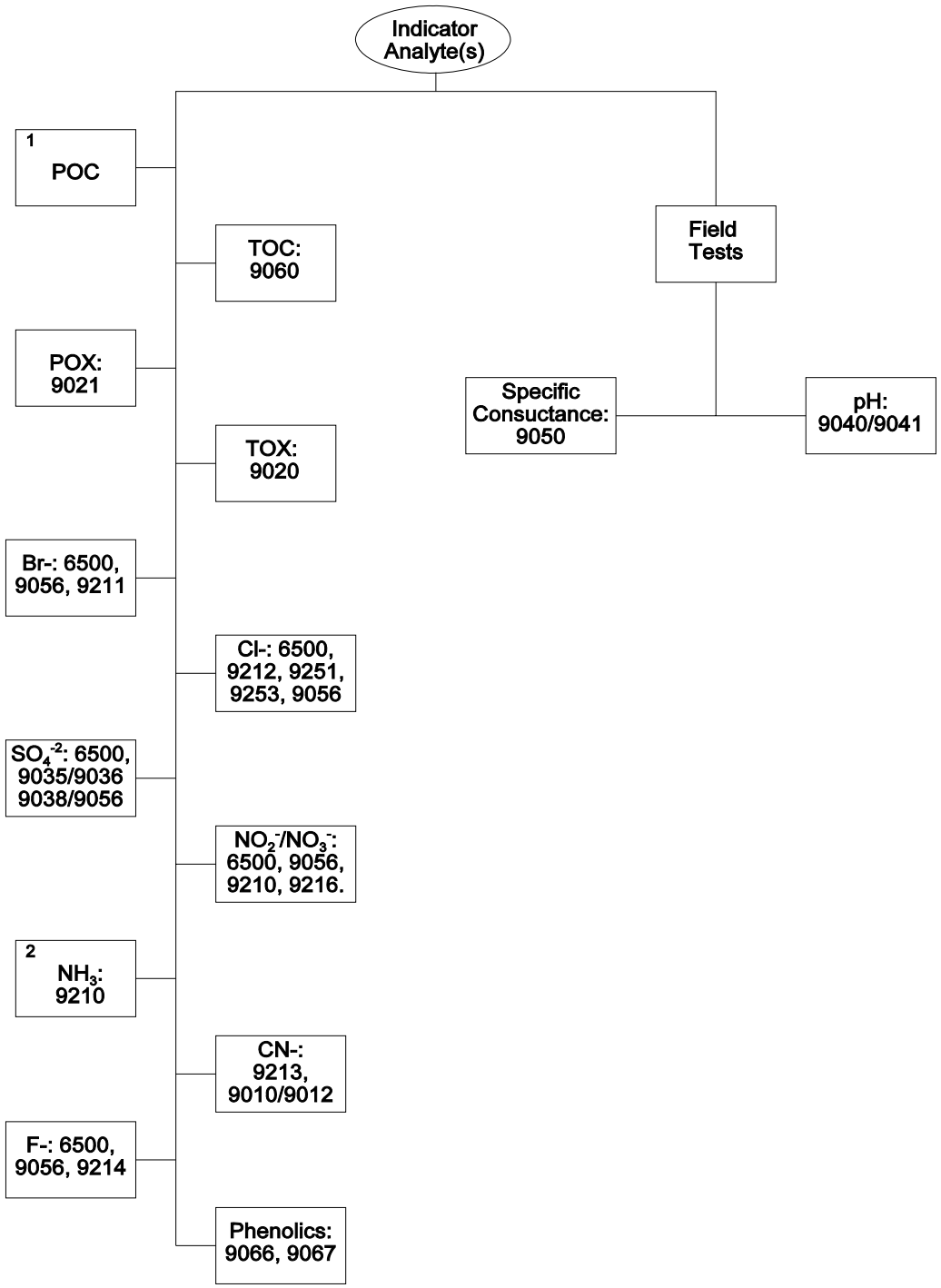


FIGURE 2-4A
GROUNDWATER ANALYSIS - ORGANIC ANALYTES



For illustrative purposes only. See the disclaimer and Sec. 2.1 for information on the flexibility inherent in SW-846 methods.

FIGURE 2-4B
GROUNDWATER ANALYSIS - INDICATOR ANALYTES

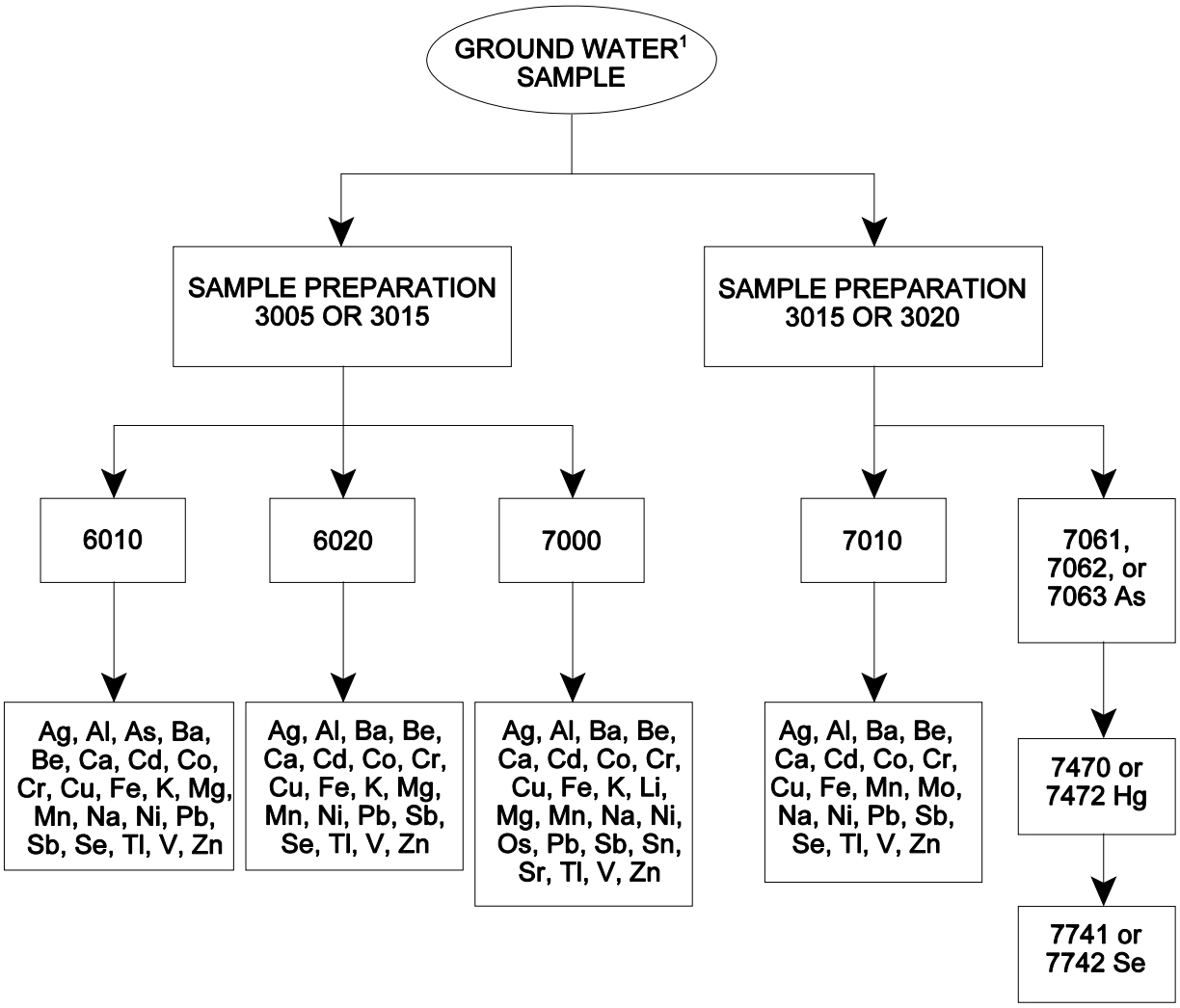


1- Barcelona 1984, (See Reference 1)
2- Riggin, 1984, (See Reference 2)

For illustrative purposes only. See the disclaimer and Sec. 2.1 regarding the flexibility inherent in SW-846 methods.

FIGURE 2-4C

GROUNDWATER ANALYSIS - INORGANIC ANALYTES



1. When analyzing for total dissolved metals, digestion is not necessary if the samples are filtered to the same concentration as the standards.

For illustrative purposes only. See the disclaimer and Sec. 2.1 regarding the flexibility inherent in SW-846 methods.

CHAPTER THREE

INORGANIC ANALYTES

Prior to employing the methods in this chapter, analysts are advised to consult the disclaimer statement at the front of this manual and the information in Chapter Two for guidance on the allowed flexibility in the choice of apparatus, reagents, and supplies. In addition, unless specified in a regulation, the use of SW-846 methods is not mandatory in response to Federal testing requirements. The information contained in each procedure is provided by EPA as guidance to be used by the analyst and the regulated community in making judgments necessary to meet the data quality objectives or needs for the intended use of the data.

3.1 INTRODUCTION

This chapter provides guidance for the analysis of inorganic analytes in a variety of matrices. The analytical methods are written as specific steps in the overall analysis scheme -- sample handling and preservation, sample digestion or preparation, and sample analysis for specific inorganic components. From these methods, the analyst should assemble a total analytical protocol which is appropriate for the sample to be analyzed and for the information required. This introduction discusses the options available in general terms, provides background information on the analytical techniques, and highlights some of the considerations to be made when selecting a total analysis protocol.

3.2 DEFINITIONS

The following terms are relevant for the determination of inorganic analytes:

Calibration blank: A volume of reagent water prepared with the same amounts of acids or other reagents as were the standards and samples.

Calibration curve: The functional relationship between analytical response and target analyte concentration determined for a series of calibration standards. The calibration curve is obtained by plotting the analytical response versus concentration and performing a regression analysis of the data.

Calibration standards: A series of solutions containing the target analyte at known and varying concentrations used by the analyst for instrument calibration (i.e., preparation of the calibration curve).

Continuing calibration verification (CCV): A solution containing a known concentration of analyte derived from the same source as the calibration standards. The CCV is used to assure calibration accuracy during each analysis run. It should be run for each analyte as described in the particular analytical method. At a minimum, it should be analyzed at the beginning of the run and after the last analytical sample. The CCV concentration should be at or near the mid-range levels of the calibration curve.

Dissolved metals: The concentration of metals determined in an aqueous sample after the sample is filtered through a 0.45-µm filter (see Method 3005).

Initial calibration verification (ICV) standard: A certified or independently-prepared solution from a source other than used for the calibration standards and used to

verify the accuracy of the initial calibration. For ICP analysis, it should be run at each wavelength used in the analysis.

Instrument detection limit (IDL): Typically used in metals analysis to evaluate the instrument noise level and response changes over time for analytes of interest. IDLs can be estimated by calculating the average of the standard deviations of three analytical runs performed on three non-consecutive days from the analysis of a reagent blank solution with seven consecutive measurements per day. Each measurement should be performed as though it were a separate analytical sample (i.e., each measurement must be followed by a rinse and/or any other procedure normally performed between the analysis of separate samples). IDLs should be determined at least once every three months or at a project-specific designated frequency and the associated documentation kept with the instrument log book.

Interference check sample (ICS): A solution containing both interfering and analyte elements of known concentration that can be used in metals ICP and ICP-MS analysis to verify background and inter-element correction factors.

Laboratory control sample (LCS): A volume of reagent water spiked with known concentrations of analytes and carried through the same preparation and analysis procedure as a sample. It is used to monitor analyte loss/recovery. The LCS may either be prepared from the same source as the calibration standards or independently of the calibration standards. An independently prepared LCS may either be obtained as or prepared from a certified reference solution or prepared from a certified reagent solid or from an alternate lot reagent solid relative to the calibration standards source. For each analytical batch, at least one LCS should be prepared from the same source as the calibration standards. In this way, if the recoveries of both the LCS and the matrix spike are outside the acceptance limits, the analyst will be able to determine whether the problem is due to a calibration error or a matrix interference.

Linear dynamic range: In either ICP-AES and ICP-MS analysis based on a one-point calibration, the concentration range above the highest calibration point over which the functional relationship between analyte signal and analyte concentration remains linear. A sample result that falls within the linear dynamic range is considered valid and may be reported, thus avoiding the need to dilute and reanalyze the sample.

Method blank: A volume of reagent water processed through each sample preparation procedure. Analysis of a method blank is used to assess contamination from the laboratory environment, sample processing equipment, and/or reagents.

Lower limit of quantitation (LLOQ): The lowest point of quantitation, or in most cases, the lowest point in the calibration curve which is less than or equal to the desired regulatory action levels based on the stated project requirements. Analysis of a standard prepared at the LLOQ concentration level or use of the LLOQ as the lowest point calibration standard provides confirmation of the established quantitation sensitivity of the method. The LLOQ recovery should be within 50% of the true value, or some other mutually agreed upon recovery based upon the project-specific data quality objectives, in order to verify the data reporting limit.
.
Method of standard addition (MSA): An alternative calibration procedure employed when the signal response of the analyte of interest is different in a particular matrix

than when it is in reagent water. The procedure is generally reserved for analyzing complex matrices. The standard addition technique involves the addition of known amounts of the target analyte to each of a series of replicate sample aliquots. The final concentrations of the sample replicates should span the calibration range of the method. The analytical responses versus the standard addition concentration for each of the replicates is plotted. After performing a linear regression, the curve is extrapolated to the x-axis. The analyte concentration in the original unspiked sample is equal to the inverse of the x-intercept. See Method 7000, for more information.

Optimum concentration range: In metals analysis, a concentration range, below which scale expansion should be used, and above which curve correction should be considered. This range will vary with the sensitivity of the instrument and the operating conditions employed.

Sample holding time: The storage time allowed between sample collection and sample analysis when the designated preservation and storage techniques are employed. Different times may be specified for holding field samples prior to extraction, digestion, or other such preparation procedures versus holding prepared samples (e.g. an extract or a solution resulting from a sample digestion) prior to analysis.

Sensitivity: The ability of an analytical technique or instrument to discriminate between small differences in analyte concentration (Reference 1). For metals analysis, the following methods are commonly employed to determine sensitivity.

(a) Atomic absorption (AA): The concentration of metal, in mg/L, that produces a transmission of 1%.

(b) Graphite furnace AA (GFAA): The mass of analyte required to give a response of 0.044 absorbance-seconds.

(c) Inductively coupled plasma (ICP): The average of the standard deviations of three runs of a reagent blank solution on three non-consecutive days with seven consecutive measurements per day.

Suspended metals: The concentration of metals determined in the portion of an aqueous sample that is retained by a 0.45-µm filter (Method 3005).

Total acid soluble/recoverable metals: The concentration of metals determined in an unfiltered sample following digestion using hot mineral acid by Methods 3005, 3010, 3015, 3020, 3050, or 3051.

Total metals: The concentration of metals determined in a sample following digestion by Method 3052.

3.3 SAFETY

The methods in this chapter do not address all safety issues associated with their use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses.

The toxicity or carcinogenicity of each reagent used in these methods has not been precisely defined. However, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals should be reduced to the lowest possible level by whatever means available. The following additional references to laboratory safety are available:

1. "Carcinogens - Working with Carcinogens," Department of Health, Education, and Welfare, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, Publication No. 77-206, August 1977.

2. "Handbook of Chemical Health and Safety," American Chemical Society, Oxford University Press, New York, 2001.

3. "NIOSH Pocket Guide to Chemical Hazards," Department of Health and Human Services, Centers for Disease Control, National Institute for Occupational Safety and Health, Publication No. 2005-149, September 2005.

4. "Occupational Safety and Health Standards," 29 CFR Part 1910, Occupational Safety and Health Administration, Department of Labor.

5. "Safety in Academic Chemistry Laboratories," 7th Edition, Volumes 1 and 2, American Chemical Society, Committee on Chemical Safety, Washington, D.C., 2003.

3.4 SAMPLING CONSIDERATIONS

3.4.1 Sample Collection

The fundamental goal of all field sampling activities is to collect samples that are representative of the water, soil or waste from which they were collected. Thus, representative sampling may be considered to be the sampling analog to analytical accuracy. Of equal importance is sampling precision for ensuring consistency both within a single sampling event and between sampling events conducted over time. Sampling imprecision can rival analytical imprecision as a source of measurement error. High quality field practices are, therefore, necessary for generating representative samples on a consistent basis. Sampling quality assurance includes the development of a quality assurance plan, data quality objectives and the generation of field quality control samples including equipment rinsates, trip blanks and field duplicates. Regardless of the specific program needs, the documentation of all relevant field and sample information is the final essential component of a sampling event for providing evidence that proper procedures and quality assurance were performed during sample collection. Use of inadequate field procedures and documentation can jeopardize an entire sampling program despite adequate planning, analytical facilities, and personnel.

While advances in analytical sensitivity are continuing to be made that allow for quantification of environmental contaminants at ultra-trace levels (i.e., < 0.1 ppb), clean sampling techniques are consequently being devised and practiced in order to minimize or eliminate sources of contamination during the collection of samples intended for ultra-trace contaminant testing. Such clean sampling and analysis techniques are not generally needed or required under the RCRA program and are beyond the scope of this chapter. However, as an introduction to this topic, Sec. 3.5 provides a more detailed discussion on the special category and requirements of clean analysis for determining constituents at ultra-trace levels.

3.4.2 Sample Containers

Sample container materials can introduce either positive or negative errors in measurement, particularly at low or ultra-trace levels, by contributing contaminants through leaching or surface desorption, or by depleting concentrations through adsorption. Additionally, the sample containers should be compatible with the reagents used for sample preservation. Thus, the collection and containment of the sample prior to analysis requires particular attention. Sample contamination introduced through field collection activities including sample containment and shipment can be assessed from the analysis of equipment rinsates and trip blanks. Guidelines on the selection of appropriate sample container materials for the collection of inorganic analytical samples are provided in Table 3-1.

3.4.3 Cleaning of Sample Containers

Sample containers should be scrupulously clean so as not to introduce contaminants that could interfere with quantification of the target analyte(s). This is of particular importance when determining trace or ultra-trace analyte concentration levels. The following cleaning sequence has been determined to be adequate to minimize contamination in the sample bottle, whether borosilicate glass, linear polyethylene, polypropylene, or PTFE:

- Detergent
- Tap water
- 1:1 HNO_3
- Tap water
- 1:1 HCl
- Tap water
- Reagent water

NOTE: **Chromic acid should not be used to clean glassware**, especially if chromium is to be included in the analytical scheme. Commercial, non-chromate products (e.g., Nochromix) may be used in place of chromic acid, if adequate cleaning is documented by an analytical quality control program. Chromic acid should also not be used with plastic bottles.

3.4.4 Sample Handling and Preservation

Sample holding times, recommended collection volumes or masses and recommended digestion volumes, and preservatives are listed in Table 3-1. The sample collection and digestion amounts depend on the combination of digestion or extraction and determinative procedures that will be employed for a given sample as well as the sensitivity that is required for a specific project. Likewise, the use of alternative preservatives to those indicated in Table 3-2 may be necessary depending on the objectives of the project. In all cases, the sample quantity that is collected should be representative of the bulk material whenever feasible.

3.4.5 Sample Preparation

For all non-speciated digestion methods, great reduction in analytical variability can be achieved through the use of appropriate sample preparation procedures. Generally, a reduction in subsampling variance can be accomplished by reducing the sample particle size, and homogeneously mixing the resulting fines. Under most circumstances, it is

recommended that the sample be analyzed without drying. If it is necessary to report the analytical data on a dry-weight basis, then a separate aliquot may be analyzed for moisture content and the wet-weight data corrected accordingly.

If the sample cannot be well-mixed and homogenized in the form in which it was received by the laboratory, then air- or oven-drying at 30 °C or less, crushing, sieving, grinding, and mixing should be performed as needed or feasible to homogenize the sample until the subsampling variance is less than the data quality objectives of the analysis. While proper sample preparation generally produces great reduction in analytical variability, it should be noted that in certain unusual circumstances there could be loss of volatile metals (e.g., Hg, organometallics) or irreversible chemical changes (e.g., precipitation of insoluble species, change in valence state) caused by inappropriate sample preparation procedures.

Variability due to sample heterogeneity is assessed by analyzing individually prepared sample replicates. Variability inherent in the analytical determinative procedure is assessed by matrix spiking of individually digested samples.

TABLE 3-1

MATERIALS FOR USE IN SAMPLE COLLECTION FOR
INORGANIC ANALYTE DETERMINATIONS

Analyte	Recommended Container Material
Metals	PTFE, plastic, glass
Chloride	PTFE, plastic, glass
Cyanide	PTFE, plastic
Fluoride	PTFE, plastic
Nitrate	PTFE, plastic, glass
pH	PTFE, plastic, glass
Specific Conductance	PTFE, plastic, glass
Sulfate	PTFE, plastic, glass
Sulfide	PTFE, plastic, glass

[a]These recommendations are intended as guidance only. The selection of sample container should be made based on the nature of the sample, the intended end use of the data and the project data quality objectives.

TABLE 3-2

RECOMMENDED SAMPLE HOLDING TIMES, PRESERVATION, COLLECTION QUANTITIES, AND DIGESTION VOLUMES FOR SELECTED INORGANIC ANALYTE DETERMINATIONS IN AQUEOUS AND SOLID SAMPLES [a,b]

Analyte	Matrix	Fraction	Minimum Collection Volume/Mass	Preservation [1]	Digestion Volume	Holding Time [2]
Metals (except Hg and Cr^{6+})	Aqueous	Total	600 mL	HNO_3 to pH<2	100 mL	6 months
		Dissolved	600 mL	Filter on site; HNO_3 to pH<2	100 mL	6 months
		Suspended	600 mL	Filter on site;	100 mL	6 months
	Solid	Total	200 g	None	2 g	6 months
Hexavalent chromium	Aqueous		400 mL	≤6 °C	100 mL	24 hours
	Solid		100 g	≤6 °C		30 days to extraction
				≤6 °C	2.5 g	7 days from extraction to analysis
Mercury	Aqueous	Total	400 mL	HNO_3 to pH<2	100 mL	28 days
		Dissolved	400 mL	Filter; HNO_3 to pH<2	100 mL	28 days
	Solid	Total	200 g	≤6 °C	0.2 g	28 days
Chloride	Aqueous		50 mL	≤6 °C	—	28 days
Cyanide	Aqueous		500 mL	≤6 °C; NaOH to pH>12	—	14 days
	Solid		5 g	≤6 °C	—	14 days
Fluoride	Aqueous		300 mL	≤6 °C	—	28 days

TABLE 3-2

RECOMMENDED SAMPLE HOLDING TIMES, PRESERVATION, COLLECTION QUANTITIES, AND DIGESTION VOLUMES FOR SELECTED INORGANIC ANALYTE DETERMINATIONS IN AQUEOUS AND SOLID SAMPLES [a,b]

Analyte	Matrix	Fraction	Minimum Collection Volume/Mass	Preservation [1]	Digestion Volume	Holding Time [2]
Nitrate	Aqueous		1000 mL	≤6 °C	—	28 days
Hexane Extractable Material (HEM; Oil & Grease)	Aqueous		1000 mL	≤6 °C HCl or H_2SO_4 to pH <2	—	28 days
	Solid		100 g	≤6 °C HCl or H_2SO_4 to pH <2; when practical		28 days
pH	Aqueous		25 mL	NA	—	Analyze immediately
	Solid		20 g	NA	—	Analyze immediately
Specific Conductance	Aqueous		100 mL	NA	—	Analyze immediately
Sulfate	Aqueous		50 mL	≤6 °C	—	28 days
Sulfide	Aqueous		100 mL	4 drops 2N zinc acetate/100 mL sample; NaOH to pH>9; Minimize aeration; Store headspace free at ≤6 °C	—	7 days
	Solid			Fill sample surface with 2N zinc acetate until moistened; Store headspace free at ≤6 °C	—	7 days

TABLE 3-2

RECOMMENDED SAMPLE HOLDING TIMES, PRESERVATION, COLLECTION QUANTITIES, AND DIGESTION VOLUMES FOR SELECTED INORGANIC ANALYTE DETERMINATIONS IN AQUEOUS AND SOLID SAMPLES [a,b]

Analyte	Matrix	Fraction	Minimum Collection Volume/Mass	Preservation [1]	Digestion Volume	Holding Time [2]
Organic Carbon, Total (TOC)	Aqueous		200 mL	≤6 °C store in dark HCl or H_2SO_4 to pH <2;	—	28 days
	Solid		100 g	≤6 °C	—	28 days

[a] These recommendations are intended as guidance only. The selection of sample and digestion volumes and preservation and holding times should be made based on the nature of the sample, the intended end use of the data and the data quality objectives.

[b] Additional sample quantities may need to be collected in order to allow for the preparation and analysis of QC samples, such as matrix spikes and duplicates.

[1] The exact sample extract, and standard storage temperature should be based on project-specific requirements and/or manufacturer's recommendations for standards. Alternative temperatures may be appropriate based on demonstrated analyte stability within a matrix, provided the data quality objectives for a specific project are still attainable.

[2] A longer holding time may be appropriate if it can be demonstrated that the reported analyte concentrations are not adversely affected by preservation, storage and analyses performed outside the recommended holding times.

3.5 SPECIAL CONSIDERATIONS FOR DETERMINING INORGANIC ANALYTES AT ULTRA-TRACE CONCENTRATION LEVELS

3.5.1 Clean Sampling Techniques

For the determination of ultra-trace analyte concentrations in environmental samples, it is essential that samples be collected and subsequently managed using techniques specifically designed to minimize sample contamination from field collection activities and to ensure target analyte stability. Such techniques represent a special category of sampling procedures designed specifically for ultra-trace analyses and are commonly referred to as clean or ultra-clean sampling procedures. Clean sampling methods are generally not intended for the determination of discharges from industrial facilities. Rather, they are primarily applicable for the determination of ambient element concentrations at levels of 0.1 ppb or less. At these concentrations, the opportunity for sample contamination during sample collection or analysis in the laboratory is significant and should be managed accordingly. Figure 3-1 provides a demonstration of the impact of clean sampling and analysis techniques on data obtained for estuarine waters. Clean sampling typically involves the following key steps:

- Special container pre-cleaning and pre-packaging requirements
- Specific sampling equipment and container materials selection
- Specific cleaning protocols for sampling equipment
- Equipment and container blank determinations prior to field use
- "Clean hands/dirty hands" sample collection techniques based on a 2-person sampling crew
    - Dirty hands sampler manages sampling equipment only
    - Clean hands sampler manages the sample container
- Special sample packaging prior to shipment
- Use of a laboratory trained and properly equipped to perform clean analysis of the analytes of interest

Given the laboratory resources required to perform clean analysis techniques, it is paramount that samples be collected using ultra-clean techniques and conditions in the field. Otherwise, subsequent analytical efforts become futile. The information provided in this section is intended only as an introduction to the topic of clean sampling. Specific guidelines for clean sampling may be found in Reference 2 and other sources.

3.5.2 Clean Analysis and the Analytical Blank

The significant role of the analytical blank in chemical analysis of trace metals cannot be overemphasized. Sensitive instrumentation such as ICP-MS, ICP-AES, and GFAA requires that sample preparation be at least as sophisticated as the instruments used for analysis. The analytical blank is normally a primary source of error in ultra-trace element analysis. Ultra-trace analysis is as dependent on control of the analytical blank as it is on the accuracy and precision of the instrument making the measurement. Inability to control contamination, is frequently the limiting factor in trace (parts per million (ppm) to parts per billion (ppb)) and ultra-trace (ppb to parts per trillion (ppt)) analysis. Analytical blank contributions occur from the following four major sources (References 3 through 7):

- The atmosphere in which the sample preparation and analysis are conducted
- The purity of the reagents used in sample preparation, including all reagents and the quantities added directly to the sample
- The materials and equipment used in digestion or extraction vessels that come in contact with the sample during the sample preparation and analysis

- The analyst's technique and skill in preparing the samples and performing the analyses

The four primary areas that affect the analytical blank can be demonstrated using standard reference materials in analysis. Table 3-3 illustrates and isolates the main blank influencing parameters: environment, reagents, materials, and analyst skills. The skill of the analyst was kept constant as the same analyst changed the environment, reagents, and combinations of these parameters in the analysis (see Reference 6). The trace elements in glass (TEG) standard reference material from the National Institute of Standards and Technology (NIST) was used to keep sample homogeneity constant and to permit removal of the sampling error by using sample sizes in which appropriate homogeneity had previously been demonstrated.

It is important to note that the relationship of the precision and measurement remained relatively constant. This relationship yields no information about the accuracy of the data. The significance of the first two major sources of contamination, environment and reagents, can be evaluated. In the example above, the contamination in the laboratory air and in the acid used for the reagent blank altered the accuracy of the example above by over two orders of magnitude for both lead and silver. The larger influence of the two sources in this example is the laboratory environment in which the samples were prepared.

3.5.2.1 Sample Preparation and Analysis Atmosphere

The atmosphere in which the sample is prepared is a major source of contamination for most target analytes when analyzing at ultra-trace levels. With the exception of some rare constituents, contamination from airborne sources represents the most significant of the four main contamination sources. To illustrate this point, Table 3-4 presents concentrations of lead found in samples of ambient air.

This contamination can also be seen in the comparison of 58,000 particles per liter of air measured in a normal laboratory in Pittsburgh, PA, and inside a clean chamber in an adjacent laboratory five meters away. Figure 3-2 demonstrates the dramatic difference between the two environments. Cost-effective methods of creating clean chambers for sample preparation are documented along with this data in Reference 4.

Any laboratory air that comes into contact with the sample may deposit some portion of its concentration into the sample. The sample is especially vulnerable to this transfer when it is being decomposed in acid. The acid will leach particles from the air, resulting in unwanted ions in solution, mixing with those of the sample.

To prevent air from contaminating a sample for ultra-trace analysis, the sample should be processed in a clean environment. This is much easier to accomplish than it may appear at first. These precautions are becoming state-of-the-art in many analytical and environmental laboratories. The prevention of airborne contamination is most frequently dealt with by employing a laminar flow clean bench or a clean laboratory facility. Instructions are referenced for the construction of both from component parts; both are relatively inexpensive and uncomplicated, once the concepts are understood (Reference 4).

There are many sources of airborne contamination. Several of the sources have been described and their particle size ranges are provided in Figure 3-3. These sources primarily provide particulates in discrete size ranges. Depending on whether the laboratory is located in an industrial, urban, or rural area, or near the sea, the distribution of these source particles will be different, as will their composition. The vertical dashed line in Figure 3 indicates the particle size cutoff, usually 0.5 µm, for the high efficiency particulate air (HEPA) filter used to prevent particulate contamination. Particles above this size cannot pass through a HEPA filter that is in good working order. These filters are in common use today (References 4 and 8.

The definition of clean air is derived from Federal Standard 209a, which defines cleanliness levels. Table 3-5 lists these conditions. "Laminar flow" is directed coherent air movement that does not contain any turbulence.

A dramatic reduction in airborne contaminants can be achieved by using HEPA-filtered air in laminar-flow clean hoods or entire clean laboratories. Table 3-6 demonstrates the dramatic differences in airborne contaminant concentrations in an ordinary laboratory, a clean laboratory, and a clean hood inside a clean laboratory.

3.5.2.2 Reagent Purity for Ultra-trace Analysis

The purity of the reagents used for acid decomposition, leaching, and extraction is extremely important to the overall level of the blank. Reagents have very different purities, depending on their processing grade and purpose. Frequently, the analyst should purchase special reagents, or purify lesser-grade reagents prior to use, in order to minimize the analytical blank.

In addition to the purity of the reagents, the reagent quantity that is added to the sample is also significant. When reagents are added, they bring with them elemental and molecular components that exist as contaminants. The more reagent that is used in excess of the stoichiometric reaction, the greater the potential for blank contamination. Reagents of high purity should either be purchased or produced in the laboratory.

In the preparation of high purity reagents, there is only one significant and practical choice for the method of purification, i.e., sub-boiling distillation (References 9 through 11). Different from normal distillation, sub-boiling distillation uses an infrared radiation source to heat the reagent to a temperature just below the boiling point. This use prevents the formation of bubbles that rise and burst at the surface of the liquid. Thus, the aerosolized solution particles are left in solution and prevented from physically transporting contaminants throughout the distillation apparatus. Sub-boiling distillation is a slower but very reliable method of purifying all of the common mineral acids and many organic reagents used in analytical methods. It relies exclusively on the vapor pressure of the reagent, and contaminant, and can therefore be specifically optimized for purification of the mineral acids if the object is to remove metal ions. Of all acids, nitric acid, for a variety of reasons, can be purified to excellent quality. Sources for sub-boiling apparatus equipment and methods for constructing one are provided in the references. Purchasing sub-boiling acids from commercial sources is also an option. Construction or purchase of sub-boiling reagent purification equipment may be cost effective for some laboratories depending on the quantity of reagents required for sample throughput.

3.5.2.3 Materials for Sample Preparation, Storage, and Analysis

For ultra-trace analyses, only certain materials are preferred for use in the construction of sample vessels and instrument components that come into contact with the sample. Over the past two decades, materials identified as being non-contaminating have become the top choices for bottles, beakers, reaction vessels, storage containers, nebulizers, and instrument components for trace and ultra-trace analysis. The materials are the same as those currently being used in many digestion vessels, bomb liners, and microwave vessels. The materials are characterized by being thermally durable, chemically resistant or inert, non-contaminating, and possessing appropriate compression and tensile strength. Table 3-7 lists, in order of preference, several types of, non-contaminating materials that are chemically inert to most acid reactions. These materials have been evaluated and tested extensively for their potential to contaminate (References 4, 6, 7, 12, and 13).

With the exception of polyethylene, the materials listed in Table 3-7 are those most commonly for sample preparation vessels, both atmospheric pressure vessels and closed vessel liners, that come into contact with the sample. These materials are the most stable to acid reactions (with the exception of quartz and glass if hydrofluoric acid is used). Fluoropolymers are the most common and were adapted from other chemical uses for application in pressure systems. The fluoropolymers, TFM, PFA and TFE or PTFE have the highest range of use temperatures for most plastics, ranging from 270-300 °C. They are also chemically inert to the majority of mineral acids and combinations thereof. Sulfuric acid has a boiling point of approximately 330 °C and can damage all fluoropolymers by melting them. Quartz and glass can safely contain sulfuric acid at these high temperatures, but borosilicate glass is not appropriate for ultra-trace elemental analysis (References 7 and 13). Glass actually forms a gel layer that hydrates and leaches, transferring contaminants from the glass to the sample solution. While these quantities may be considered minute, they would be detected in blanks and samples undergoing ultra-trace analyses.

Polyethylene is suitable for storage of diluted samples after decomposition, but it does not have a thermal-use temperature appropriate for decomposition. It is also not sufficiently inert to be useful as a decomposition vessel or vessel liner, similar to polycarbonate and polypropylene. The low cost of polyethylene and its relative inertness to cool, weakly acidic solutions make it an excellent storage container for trace element solutions (Reference 4).

3.5.2.4 Analytical Technique and Synergistic Equipment

The fourth significant source of analytical blank contamination is the skill of the analyst and the appropriateness of the technique being performed. Analytical blank control has been explained as the combination of atmosphere, reagent, material, and protocol being performed. Also, the skill and awareness of the analyst as well as the way in which the combinations of the aforementioned clean chemistry techniques are applied will have a significant effect on the final contamination error and analytical blank control. Sample preparation instrumentation may also assist in these protocols. For example, microwave sample preparation assists each of these parameters in synergistic ways, thus lowering the analytical blank, improving blank precision, and enhancing overall

quality control and transferability of methods. Some instrumentation and fundamental processes involved in specific sample preparation procedures assists the analyst by incorporating useful clean chemistry concepts into instrumentation and method structure. Such instrumentation is pertinent since microwave methods now exist that provide sample preparation for leaching or total analysis of many target analytes simultaneously. As an example, the skill of the analyst with regard to clean chemistry is assisted by the method structure and microwave equipment as indicated below:

- If a closed or controlled atmospheric microwave vessel is prepared in a clean hood and sealed before leaving the clean environment, the sample will not be affected by atmospheric contamination during the reaction, since it has not been removed from a clean environment.

- The vessel materials described previously might not normally be used by many laboratories, and therefore the advantages of the fluoropolymers would not be realized if they were not required in most microwave reaction vessels as they commonly are.

- The time that the sample spends in decomposition, leaching, or extraction may be reduced from hours to minutes, thus reducing the potential leaching of contaminants from the container walls.

- Because most microwave systems are sealed systems, evaporation of the reagent before it reacts productively is prevented and smaller quantities of reagents are used, thus preventing excess and unnecessary accumulation of contaminants in the blank.

By reducing the exposure variables, the blank is consequently reduced in size and is more consistent. An example of these components working together has been provided in the literature, where analysis under different conditions has verified these conclusions (References 4, 14 and 15). The example illustrates the isolation of the blank optimization areas: environment, reagents, materials, and analysis skills. The skill of the analyst is kept more constant as the instrument dictates more clean, chemically-appropriate procedures.

3.6 REAGENT PURITY

The purity of the reagents used for sample preservation, acid decomposition, leaching, extraction and analysis is extremely important relative to preventing or minimizing sample contamination. Reagents have very different purities, depending on their processing grade and purpose. Reagent grade, ACS grade or better are recommended for use with most SW-846 methods. Sample contamination introduced through sample preservation, handling, preparation and analysis is assessed from the analysis of method blanks.

TABLE 3-3

EXAMPLES OF THE ANALYTICAL BLANK INFLUENCE ON
ULTRA-TRACE ANALYSIS OF ELEMENTS IN GLASS

Conditions	Pb (ng)	Ag (ng)
Initial analysis of TEG* standard	330 ± 250	970 ± 500
Analysis using sub-boiled distilled acids	260 ± 200	--
Analysis in a Class 100 hood	20 ± 8	207 ± 200
Analysis using sub-boiled acids in a Class 100 hood	2 ± 1	3 ± 2

* TEG = Trace element in glass

Data are taken from Reference 6.

TABLE 3-4

EXAMPLES OF LEAD CONCENTRATIONS IN AIR

Site	Lead Concentration ($\mu g/m^3$)	Source
Downtown St. Louis, MO	18.84	Reference 16
Rural park, Southeastern MO	0.77	Reference 17
NIST Laboratory, MD	0.4	Reference 6

TABLE 3-5

CLEANLINESS LEVELS IN FEDERAL STANDARD 209A[a]

Class	Maximum Contamination in Work Area (particles/ft^{-3})
100	100 particles > 0.5 μm 0 particles > 5.0 μm
10,000	10,000 particles > 0.5 μm 65 particles > 5.0 μm
100,000	100,000 particles > 0.5 μm 700 particles > 5.0 μm

[a]The Federal standard required the use of laminar-flow equipment to attain this level of cleanliness. Since measurement of dust particles smaller than 0.5 μm introduces substantial errors, 0.5 μm has been adopted as the criterion of measurement.

Data are taken from Reference 8.

TABLE 3-6

PARTICULATE CONCENTRATIONS IN LABORATORY AIR

	Concentration ($\mu g/m^3$)			
Location	Iron	Copper	Lead	Cadmium
Ordinary laboratory	0.2	0.02	0.4	0.002
Clean room	0.001	0.002	0.0002	ND
Clean hood	0.0009	0.007	0.0003	0.0002

ND = Not Detected

Data are taken from Reference 17.

TABLE 3-7

NON-CONTAMINATING MATERIALS AND FOR USE AS DECOMPOSITION VESSELS AND SAMPLE CONTAINERS IN ULTRA-TRACE ANALYSES

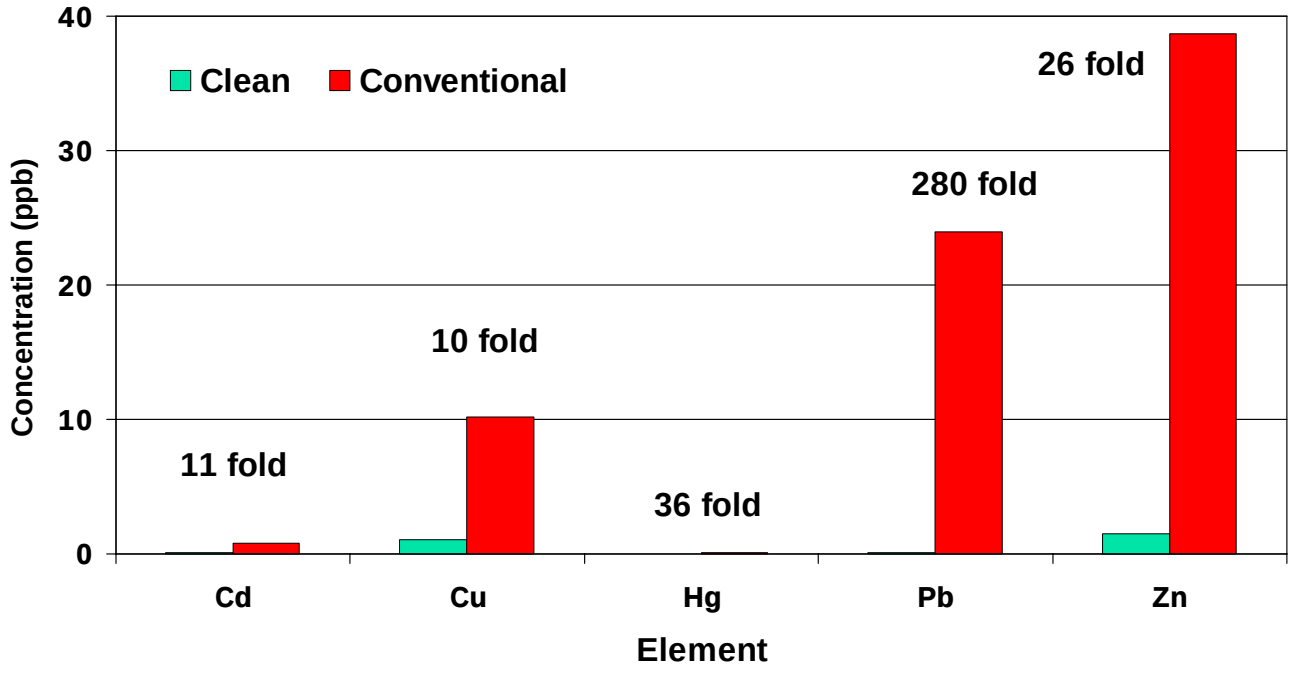
Listed from highest to lowest preference for use in sample containment
Fluoropolymers: PFA*, TFM, TFE*, FEP*, Tefzel*
Quartz - Synthetic
Polyethylene (suitable for storage only, not for acid digestion)
Quartz - Natural
Borosilicate Glass

* Various forms of PTFE

Data are taken from Reference 8.

FIGURE 3-1

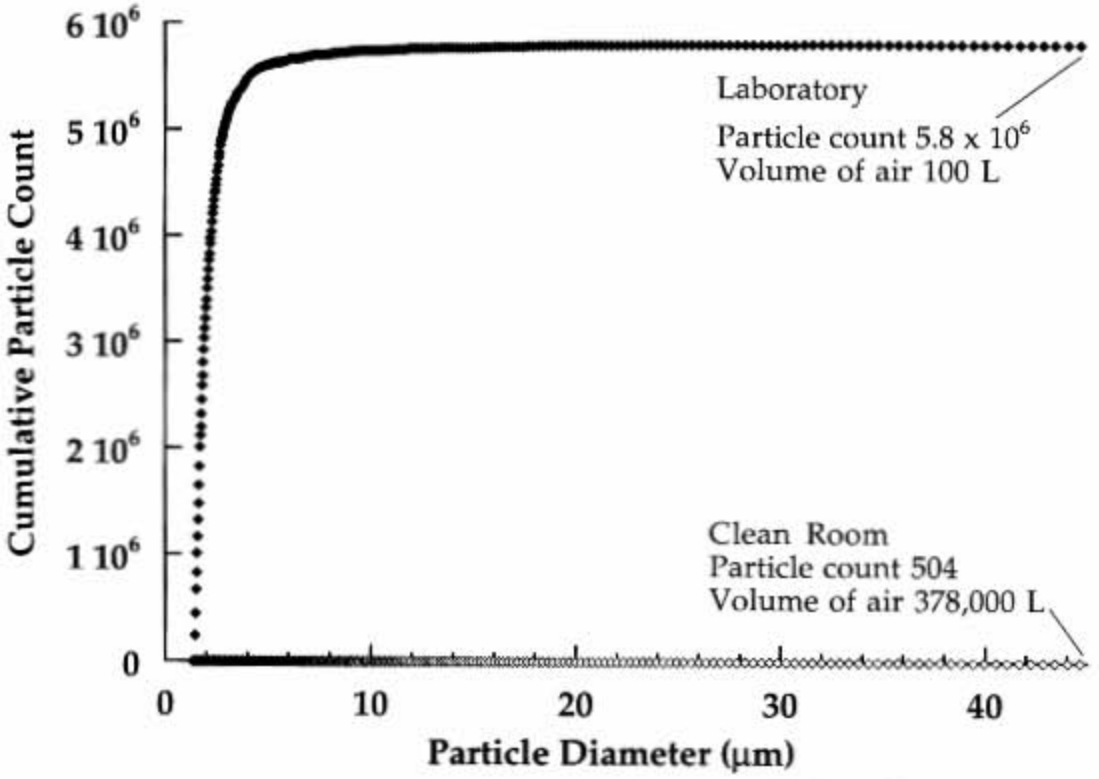
COMPARISON OF CLEAN VERSUS CONVENTIONAL SAMPLING AND ANALYSIS TECHNIQUES USED IN THE ANALYSIS OF SOUTH TEXAS ESTUARY WATERS



Taken from Reference 18.

FIGURE 3-2

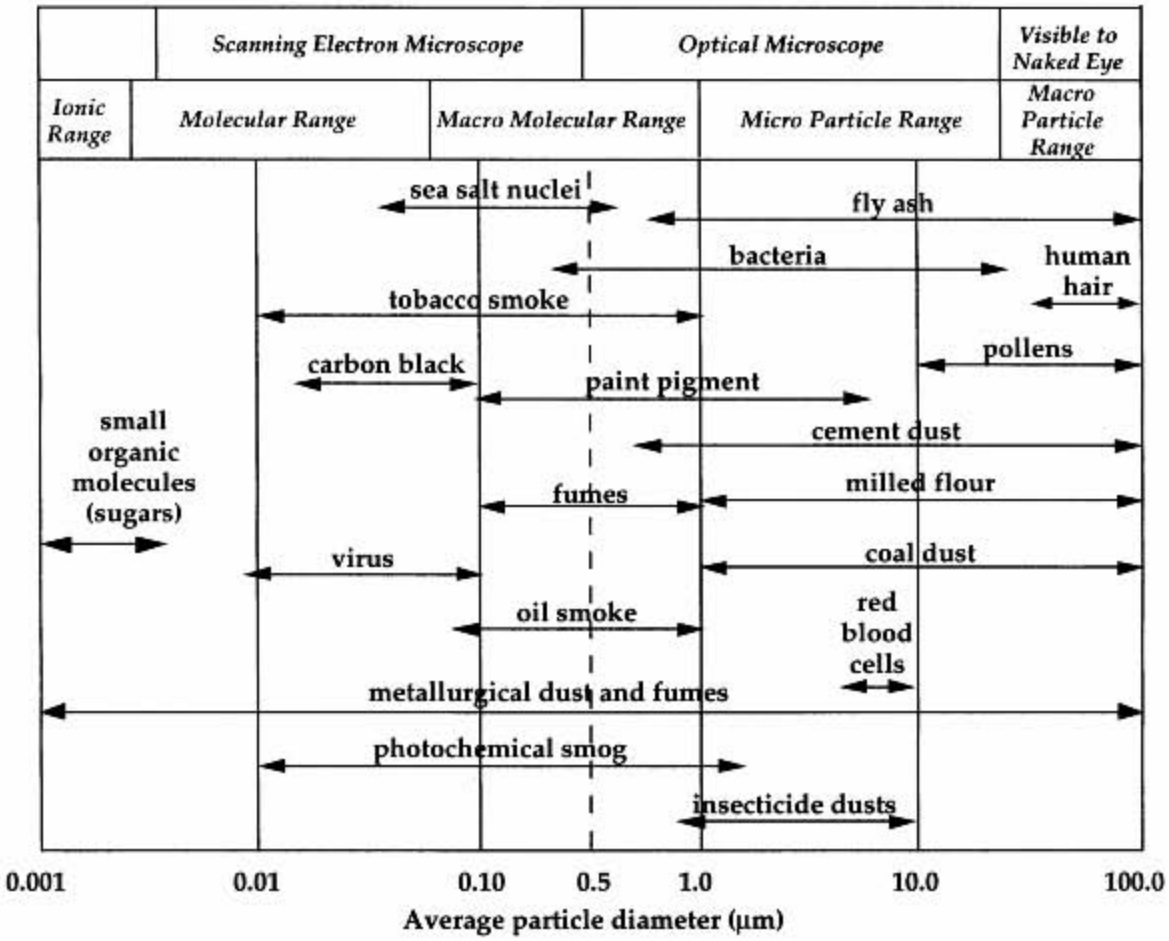
COMPARISON OF PARTICLE COUNT ANALYSIS OF A CLEAN ROOM AND
A STANDARD LABORATORY AT DUQUESNE UNIVERSITY IN PITTSBURGH, PA



Taken from Reference 4.

FIGURE 3-3

PARTICLE SIZE COMPARISON CHART FOR COMMON PARTICULATES



Taken from Reference 4, 19.

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3.8 SAMPLE DIGESTION METHODS

Prior to employing the methods in this chapter, analysts are advised to consult the disclaimer statement at the front of this manual and the information in Chapter Two for guidance on the allowed flexibility in the choice of apparatus, reagents, and supplies. In addition, unless specified in a regulation, the use of SW-846 methods is not mandatory in response to Federal testing requirements. The information contained in each procedure is provided by EPA as guidance to be used by the analyst and the regulated community in making judgments necessary to meet the data quality objectives or needs for the intended use of the data.

NOTE: Many of the methods listed below employ HCl in the digestion process. Chlorine is an interferant in ICP/MS analysis and its use in sample digestion is discouraged except when absolutely necessary or when the instrument manufacturer has indicated that the use of HCl will not adversely affect the equipment and accurate quantitation of the desired target analytes.

The methods in SW-846 for sample digestion or dissolution include:

Method 3005A: Acid Digestion of Waters for Total Recoverable or Dissolved Metals for Analysis by FLAA or ICP Spectroscopy

This method may be used for the preparation of ground water and surface water samples for total recoverable and dissolved metal determinations by FLAA, ICP-AES, or ICP-MS. The unfiltered or filtered sample is heated with dilute HCl and HNO_3 prior to metal determination.

Method 3010A: Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by FLAA or ICP Spectroscopy

This method may be used for the preparation of waste samples for total recoverable metal determinations by FLAA, ICP-AES, or ICP-MS. The samples are vigorously digested with nitric acid followed by dilution with hydrochloric acid. The method is applicable to aqueous samples, leachates, and mobility-procedure extracts.

Method 3015A: Microwave Assisted Acid Digestion of Aqueous Samples and Extracts

This method may be used for the preparation of aqueous samples, mobility-procedure extracts, and wastes that contain suspended solids for total recoverable metal determinations by FLAA, GFAA, ICP-AES, or ICP-MS. Nitric acid and hydrochloric acid are added to the sample in a PTFE digestion vessel and heated in a microwave unit prior to metals determination.

Method 3020A: Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by GFAA Spectroscopy

This method may be used for the preparation of waste samples for total recoverable metals determinations by GFAA or ICP-MS. The samples are vigorously digested with nitric acid followed by dilution with nitric acid. The method is applicable to aqueous samples, leachates, and mobility-procedure extracts.

Method 3031: Acid Digestion of Oils for Metals Analysis by Atomic Absorption or ICP Spectrometry

This method may be used for the preparation of waste oils, oil sludges, tars, waxes, paints, paint sludges and other viscous petroleum products for analysis by FLAA, GFAA, and

ICP-AES. The samples are vigorously digested with nitric acid, sulfuric acid, hydrochloric acid, and potassium permanganate prior to analysis.

Method 3040A: Dissolution Procedure for Oils, Greases, or Waxes

This method may be used for the preparation of oily waste samples for determination of soluble metals by FLAA, and ICP-AES methods. The samples are dissolved and diluted in organic solvent prior to analysis. The method is applicable to the organic extract in the oily waste EP procedure and other samples high in oil, grease, or wax content.

Method 3050B: Acid Digestion of Sediments, Sludges, and Soils

This method may be used for the preparation of waste samples for total recoverable metals determinations by FLAA and ICP-AES, or GFAA and ICP-MS depending on the options chosen. The samples are vigorously digested in nitric acid and hydrogen peroxide followed by dilution with either nitric or hydrochloric acid. The method is applicable to soils, sludges, and solid waste samples.

Method 3051A: Microwave Assisted Acid Digestion of Sediments, Sludges, Soils, and Oils

This method may be used for the preparation of sludges, sediments, soils and oils for total recoverable metal determinations by FLAA, GFAA, ICP-AES or ICP-MS. Nitric acid and hydrochloric acid are added to the representative sample in a fluorocarbon digestion vessel and heated in a microwave unit prior to metals determination.

Method 3052: Microwave Assisted Acid Digestion of Siliceous and Organically Based Matrices

This method may be used for the preparation of siliceous and organically based matrices including ash, biological tissue, oil, oil contaminated soil, sediment, sludge, and soil for total metals analysis by FLAA, CVAA, GFAA, ICP-AES, and ICP-MS. Nitric acid and hydrofluoric acid are added to a representative sample in a fluorocarbon digestion vessel and heated in a microwave unit prior to analysis.

Method 3060A: Alkaline Digestion for Hexavalent Chromium

This method may be used for the preparation of soils, sludges, sediments and similar waste materials for hexavalent chromium determination. The samples are digested and heated to dissolve the Cr(VI) and stabilize it against reduction to Cr(III).

3.9 METHODS FOR DETERMINATION OF INORGANIC ANALYTES

This section of the manual contains analytical techniques for trace inorganic analyte determinations. Instrumental techniques include:

- Inductively coupled argon plasma atomic emission spectrometry (ICP-AES),
- Inductively coupled plasma mass spectrometry (ICP-MS),
- Direct-aspiration or flame atomic absorption spectrophotometry (FLAA),
- Graphite furnace atomic absorption spectrophotometry (GFAA),
- Hydride-generation atomic absorption spectrometry (HGAA),
- Cold-vapor atomic absorption spectrometry (CVAA),
- X-ray fluorescence (XRF),
- Ion chromatography (IC)
- Capillary electrophoresis (CE)
- Speciated isotope dilution mass spectrometry (SIDMS) and
- Several procedures for hexavalent chromium analysis.

Each of these (except the individual hexavalent chromium analyses) is discussed briefly below. Some advantages, disadvantages, and cautions for the analysis of wastes are provided.

Prior to employing the above methods in this chapter, analysts are advised to consult the disclaimer statement at the front of this manual and the information in Chapter Two for guidance on the allowed flexibility in the choice of apparatus, reagents, and supplies. In addition, unless specified in a regulation, the use of SW-846 methods is not mandatory in response to Federal testing requirements. The information contained in each procedure is provided by EPA as guidance to be used by the analyst and the regulated community in making judgments necessary to meet the data quality objectives or needs for the intended use of the data.

ICP-AES allows simultaneous or rapid sequential determination of many elements in a short time. Aerosol samples are introduced into an extremely hot plasma source which vaporizes, atomizes, ionizes and electronically excites the sample components. Upon exiting the plasma, the electronically excited analytes emit characteristic photons that are detected via emission spectrometry. A primary disadvantage of ICP-AES is the occurrence of background radiation from other elements and the plasma gases. Although all ICP-AES instruments utilize high-resolution optics and background correction to minimize these interferences, analysis of trace levels of inorganic analytes in the presence of a large excess of a single analyte is difficult. Examples would be trace levels of inorganic analytes in an alloy or trace metals in a limed (high calcium) waste. ICP-AES and FLAA have comparable detection limits (within a factor of 4) except that ICP-AES exhibits greater sensitivity for refractories (Al, Ba, etc.). FLAA, in general, will exhibit lower detection limits than either ICP-AES or FLAA.

ICP-MS allows sensitive, simultaneous determination of many elements in a short time frame using MS detection in place of AES. In general ICP-MS exhibits greater sensitivity than either GFAA, FLAA or ICP-AES for most elements. The greatest disadvantage of ICP-MS is isobaric elemental interferences. These are caused by different elements forming atomic ions with the same nominal mass-to-charge ratio. Mathematical correction for interfering ions can minimize these interferences.

FLAA direct-aspiration determinations, as opposed to ICP-AES or ICP-MS, are normally completed as single-element analyses and are relatively free of interelement spectral interferences. Either a nitrous-oxide/acetylene or air/acetylene flame is used as an energy source for dissociating the aspirated sample into the free atomic state, making analyte atoms available for absorption of light and spectrophotometric detection. In the analysis of some

elements, the temperature or type of flame used is critical. If the proper flame and analytical conditions are not used, chemical and ionization interferences can occur.

GFAA replaces the flame with an electrically-heated graphite furnace. The furnace allows for gradual heating of the sample aliquot in several stages. Thus, the processes of dissolution, drying, decomposition of organic and inorganic molecules and salts, and formation of atoms, which should occur in a flame or ICP in a few milliseconds may be allowed to occur over a much longer time period and at controlled temperatures in the furnace. This allows an experienced analyst to remove unwanted matrix components by using temperature programming and/or matrix modifiers. The major advantage of this technique is that it affords extremely low detection limits. It is the easiest to perform on relatively clean samples. Because this technique is so sensitive, interferences can be a real problem; finding the optimum combination of digestion, heating times and temperatures, and matrix modifiers can be a challenge for complex matrices.

HGAA utilizes a chemical reduction to reduce and separate arsenic or selenium selectively from a sample digestate. The technique therefore has the advantage of being able to isolate these two elements from complex samples which may cause interferences for other analytical procedures. Significant interferences have been reported when any of the following is present: (1) easily reduced metals (Cu, Ag, Hg); (2) high concentrations of transition metals (>200 mg/L); (3) oxidizing agents (oxides of nitrogen) remaining following sample digestion.

CVAA uses a chemical reduction to reduce mercury selectively. The procedure is extremely sensitive, but is subject to interferences from some volatile organics, chlorine, and sulfur compounds.

XRF uses sealed radioisotope sources to irradiate samples with X-rays. When a sample is irradiated with X-rays, the source X-rays may undergo either scattering or absorption by sample atoms. This later process is known as the photoelectric effect. When an atom absorbs the source X-rays, the incident radiation dislodges electrons from the innermost shells of the atom, creating vacancies. The electron vacancies are filled by electrons cascading in from outer electron shells. Electrons in outer shells have higher energy states than inner shell electrons, and the outer shell electrons give off energy as they cascade down into the inner shell vacancies. This rearrangement of electrons results in emission of X-rays characteristic of the given atom. The emission of X-rays, in this manner, is termed X-ray fluorescence.

IC generally refers to the separation of ions through ion exchange chromatography. In this technique, an aqueous sample is injected into a mobile solution that is carried into a chromatography column. As the sample travels through the column, the sample analytes are temporarily retained on the column, the stationary phase, via electrostatic forces. The separated analytes are identified as they are released from the column based on their retention time. Detection and quantification in IC is most commonly performed using conductivity detection. IC is typically used for the determination of anionic analytes in waste samples.

CE refers to the electrophorectic separation of ions dissolved or suspended in an electrolyte. Samples are introduced into a capillary tube containing an electrolytic buffer. Under the application of an electric field the cations in the sample migrate toward the negatively charged electrode (cathode) and the anions migrate toward the positively charged electrode (anode). This technique may be coupled with a variety of determinative techniques for quantitative analysis. Inorganic anions can be determined in environmental samples using CE and indirect UV detection, in which analytes are detected and quantified based on proportional decreases in the absorbance of the buffer solution. CE is a complementary technique to IC and typically offers shorter analysis times than IC.

SIDMS is a quantitative method for determining elemental species based on the measurement of isotope ratio(s) in each species of a nuclide using mass spectrometry after speciated isotope dilution. Samples are mixed with one or more isotopic spikes which have different isotopic abundances and are artificially converted to chemical forms corresponding to the species to be analyzed. The spiked samples are then subjected to the separation of the species and the measurement of the altered isotope ratios in each species. Both species concentrations and species conversions can be mathematically derived.

The following methods are included in this section:

Method 6010C: Inductively Coupled Plasma-Atomic Emission Spectrometry
Method 6020A: Inductively Coupled Plasma-Mass Spectrometry
Method 6200: Field Portable X-Ray Fluorescence Spectrometry for the Determination of Elemental Concentrations in Soil and Sediment
Method 6500: Dissolved Inorganic Anions in Aqueous Matrices by Capillary Ion Electrophoresis
Method 6800: Elemental and Speciated Isotope Dilution Mass Spectrometry
Method 7000B: Flame Atomic Absorption Spectrophotometry
Method 7010: Graphite Furnace Atomic Absorption Spectrophotometry
Method 7061A: Arsenic (Atomic Absorption, Gaseous Hydride)
Method 7062: Antimony and Arsenic (Atomic Absorption, Borohydride Reduction)
Method 7063: Arsenic in Aqueous Samples and Extracts by Anodic Stripping Voltametry (ASV)
Method 7195: Chromium, Hexavalent (Coprecipitation)
Method 7196A: Chromium, Hexavalent (Colorimetric)
Method 7197: Chromium, Hexavalent (Chelation/Extraction)
Method 7198: Chromium, Hexavalent (Differential Pulse Polarography)
Method 7199: Determination of Hexavalent Chromium in Drinking Water, Groundwater and Industrial Wastewater Effluents by Ion Chromatography
Method 7470A: Mercury in Liquid Waste (Manual Cold-Vapor Technique)
Method 7471B: Mercury in Solid or Semisolid Waste (Manual Cold-Vapor Technique)
Method 7472: Mercury in Aqueous Samples and Extracts by Anodic Stripping Voltametry (ASV)
Method 7473: Mercury in Solids and Solutions by Thermal Decomposition, Amalgamation, and Atomic Absorption Spectrophotometry
Method 7474: Mercury in Sediment and Tissue Samples by Atomic Fluorescence Spectrometry
Method 7580: White Phosphorus (P_4) by Solvent Extraction and Gas Chromatography
Method 7741A: Selenium (Atomic Absorption, Gaseous Hydride)
Method 7742: Selenium (Atomic Absorption, Borohydride Reduction)

CHAPTER FOUR

ORGANIC ANALYTES

Prior to employing the methods in this chapter, analysts are advised to consult the disclaimer statement at the front of this manual and the information in Chapter Two for guidance on the allowed flexibility in the choice of apparatus, reagents, and supplies. In addition, unless specified in a regulation, the use of SW-846 methods is not mandatory in response to Federal testing requirements. The information contained in this chapter is provided by EPA as guidance to be used by the analyst and the regulated community in making judgements necessary to meet the data quality objectives or needs for the intended use of the data.

4.1 SAMPLING CONSIDERATIONS

4.1.1 Introduction

Following the initial and critical step of designing a sampling plan (Chapter Nine) is the implementation of that plan such that a representative sample of the solid waste is collected. Once the sample has been collected it must be stored and preserved to maintain the chemical and physical properties that it possessed at the time of collection. The sample type, type of containers and their preparation, possible forms of contamination, and preservation methods are all items which must be thoroughly examined in order to maintain the integrity of the samples. This section highlights considerations which must be addressed in order to maintain a sample's integrity and representativeness. This section is, however, applicable only to trace analyses.

Quality Control (QC) requirements need not be met for all compounds presented in the Table of Analytes for the method in use, rather, the requirements must be met for all compounds reported. A report of non-detect is considered a quantitative report, and must meet all applicable QC requirements for that compound and the method used.

4.1.2 Sample handling and preservation

This section deals separately with volatile and semivolatile organics. Refer to Chapter Two and Table 4-1 of this section for sample containers, sample preservation, and sample holding time information.

Volatile organics

Samples that contain analytes that are subject to biological degradation prior to analysis need to be preserved. Samples where aromatic hydrocarbons are target analytes, which are most subject to biological degradation, need to be preserved, unless they are to be analyzed immediately on-site, even if other VOA compound classes are present. Chemical preservation may be inappropriate for highly reactive compounds, e.g., styrene, vinyl chloride, 2-chloroethyl vinyl ether, acrylamide, etc., since it may accelerate loss by polymerization or other rapid chemical reaction. Samples for which chlorinated aliphatic hydrocarbons are the only target analytes generally do not need to be preserved. However, all aqueous samples containing free chlorine must be preserved with a dechlorinating agent in order to prevent formation of trihalomethanes and other possible chemical reactions.

Although VOA samples may be held for up to 7 days unpreserved or 14 days or longer preserved, it is not recommended as good laboratory practice to hold them that long. VOA samples should be run as soon as possible after receipt by the laboratory. Samples containing highly reactive compounds, e.g., styrene, vinyl chloride, 2-chloroethyl vinyl ether, acrylamide, etc., as target analytes should not be preserved and should be analyzed as soon as they are received in the laboratory.

Standard 40-mL glass screw-cap VOA vials with PTFE-lined silicone septa may be used for liquid matrices. Special 40-mL VOA vials for purge-and-trap of solid samples are described in Method 5035. VOA vials for headspace analysis of solid samples are described in Method 5021. Standard 125-mL wide-mouth glass containers may be used for Methods 5031 and 5032 for high concentration samples only. However, the sampling procedures described in Method 5035 may minimize sample preparation analyte loss better than the procedures described in Methods 5031 and 5032. The vials and septa should be washed with soap and water and rinsed with distilled deionized water. After thoroughly cleaning the vials and septa, they should be placed in an oven and dried at 100 °C for approximately one hour.

NOTE: Do not heat the septa for extended periods of time (i.e., more than one hour, because the silicone begins to slowly degrade at 105 °C).

When collecting the samples, liquids and solids should be introduced into the vials gently to reduce agitation which might drive off volatile compounds.

In general, liquid samples should be poured into the vial without introducing any air bubbles within the vial as it is being filled. Should bubbling occur as a result of violent pouring, the sample must be poured out and the vial refilled. The vials should be completely filled at the time of sampling, so that when the septum cap is fitted and sealed, and the vial inverted, no headspace is visible. The sample should be hermetically sealed in the vial at the time of sampling, and must not be opened prior to analysis to preserve their integrity.

- Due to differing solubility and diffusion properties of gases in LIQUID matrices at different temperatures, it is possible for the sample to generate some headspace during storage. This headspace will appear in the form of micro bubbles, and should not invalidate a sample for volatiles analysis.

- The presence of a macro bubble in a sample vial generally indicates either improper sampling technique or a source of gas evolution within the sample. The latter case is usually accompanied by a buildup of pressure within the vial, (e.g. carbonate-containing samples preserved with acid). Studies conducted by the USEPA (EMSL-Ci, unpublished data) indicate that "pea-sized" bubbles (i.e., bubbles not exceeding 1/4 inch or 6 mm in diameter) did not adversely affect volatiles data. These bubbles were generally encountered in wastewater samples, which are more susceptible to variations in gas solubility than are groundwater samples.

– Pre-testing of a representative soil or aqueous sample, prior to collection, with acid or bisulfate may show effervescence if carbonaceous materials are present. If bubbling occurs during chemical preservation, an increased potential for loss of volatile constituents exists and samples should therefore be collected without preserving with acid or bisulfate.

Immediately prior to analysis of liquid samples, the aliquot to be analyzed should be taken from the vial using the instructions from the appropriate sample introduction technique:

- For smaller analysis volumes, a gas-tight syringe may be inserted directly through the septum of the vial to withdraw the sample.

- For larger analysis volumes, (e.g. purge-and-trap analyses) the sample may be carefully poured into the syringe barrel. Opening a volatile sample to pour a sample into a syringe destroys the validity of the sample for future analysis. Therefore, if there is only one VOA vial, it is strongly recommended that the analyst fill a second syringe at this time to protect against possible loss of sample integrity. This second sample is maintained only until such time as the analyst has determined that the first sample has been analyzed properly.

If these guidelines are not followed, then the validity of the data generated from the samples may be suspect.

VOA vials for samples with solid or semi-solid matrices (e.g., sludges) should be filled according to the guidance given in the appropriate 5000 series sample introduction method (see Table 4-1) to be used. When 125-mL wide-mouth glass containers are used for high-concentration samples only, the containers should be filled as completely as possible. The 125-mL vials should be tapped slightly as they are filled to try and eliminate as much free air space as possible. A minimum of two vials should also be filled per sample location.

At least two VOA vials should be filled and labeled immediately at the point at which the sample is collected. They should NOT be filled near a running motor or any type of exhaust system because discharged fumes and vapors may contaminate the samples. The two vials from each sampling location should then be sealed in separate plastic bags to prevent cross-contamination between samples, particularly if the sampled waste is suspected of containing high levels of volatile organics. (Activated carbon may also be included in the bags to prevent cross-contamination from highly contaminated samples.) VOA samples may also be contaminated by diffusion of volatile organics through the septum during shipment and storage. To monitor possible contamination, a trip blank prepared from organic-free reagent water (as defined in Chapter One) should be carried throughout the sampling, storage, and shipping process. Reactive compounds such as 2-chloroethyl vinyl ether, vinyl chloride, and styrene can readily be lost under acidic conditions. If these types of compounds are analytes of interest, collect a second set of samples without acid preservatives and analyze as soon as possible.

Semivolatile organics (including pesticides, PCBs and herbicides)

Containers used to collect samples for the determination of semivolatile organic compounds should be soap and water washed followed by methanol (or isopropanol) rinsing (see Sec. 4.1.4 for specific instructions on glassware cleaning). The sample containers should be of glass, and have screw-caps with PTFE-lined septa. In situations where PTFE liners are not available, solvent-rinsed aluminum foil may be used as a liner. However, acidic or basic samples may react with the aluminum foil, causing eventual contamination of the sample. Plastic containers or lids may NOT be used for the storage of samples due to the possibility of sample contamination from the phthalate esters and other hydrocarbons within the plastic. Sample containers should be filled with care so as to prevent any portion of the collected sample coming in contact with the sampler's

gloves, thus causing contamination. Samples should not be collected or stored in the presence of exhaust fumes. If the sample comes in contact with the sampler (e.g., if an automatic sampler is used), run organic-free reagent water through the sampler and use as a field blank.

4.1.3 Safety

The methods in this chapter do not address all safety issues associated with their use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals used in these methods. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses.

Safety should always be the primary consideration in the collection of samples. A thorough understanding of the waste production process, as well as all of the potential hazards making up the waste, should be investigated whenever possible. The site should be evaluated just prior to sampling to determine additional safety measures. Minimum protection of gloves and safety glasses should be worn to prevent sample contact with the skin and eyes. A respirator should be worn even when working outdoors if organic vapors are present. More hazardous sampling missions may require the use of supplied air and special clothing.

4.1.4 Cleaning of glassware

In the analysis of samples containing components in the parts per billion range, the preparation of scrupulously clean glassware is necessary. Failure to do so can lead to a myriad of problems in the interpretation of the final chromatograms due to the presence of extraneous peaks resulting from contamination. Particular care must be taken with glassware such as Soxhlet extractors, Kuderna-Danish evaporative concentrators, sampling-train components, or any other glassware coming in contact with an extract that will be evaporated to a smaller volume. The process of concentrating the compounds of interest in this operation may similarly concentrate the contaminating substance(s), which distort the results.

The basic cleaning steps are:

1. Removal of surface residuals immediately after use;

2. Hot soak to loosen and float most particulate material;

3. Hot water rinse to flush away floated particulates;

4. Soak with an oxidizing agent to destroy traces of organic compounds;

5. Hot water rinse to flush away materials loosened by the deep penetrant soak;

6. Distilled water rinse to remove metallic deposits from the tap water;

7. Alcohol, e.g., isopropanol or methanol, rinse to flush off any final traces of organic materials and remove the water; and

8. Flushing the item immediately before use with some of the same solvent that will be used in the analysis.

Comments regarding each of the eight fundamental steps are discussed here in the order in which they appeared above:

Step 1: As soon as possible after glassware (i.e., beakers, pipets, flasks, or bottles) has come in contact with sample or standards, the glassware should be flushed with alcohol before it is placed in the hot detergent soak. If this is not done, the soak bath may serve to contaminate all other glassware placed therein.

Step 2: The hot soak consists of a bath of a suitable detergent in water of 50 °C or higher. The detergent, powder or liquid, should be entirely synthetic and not a fatty acid base. There are very few areas of the country where the water hardness is sufficiently low to avoid the formation of some hard-water scum resulting from the reaction between calcium and magnesium salts with a fatty acid soap. This hard-water scum or curd would have an affinity particularly for many chlorinated compounds and, being almost wholly water-insoluble, would deposit on all glassware in the bath in a thin film.

There are many suitable detergents on the wholesale and retail market. Most of the common liquid dishwashing detergents sold at retail are satisfactory but are more expensive than other comparable products sold industrially. Alconox, in powder or tablet form, is manufactured by Alconox, Inc., New York, and is marketed by a number of laboratory supply firms. Sparkleen, another powdered product, is distributed by Fisher Scientific Company.

Step 3: No comments required.

Step 4: **Chromic acid should not be used to clean glassware.** Commercial, non-chromate products (e.g., Nochromix) may be used in place of chromic acid, if adequate cleaning is documented by an analytical quality control program. Chromic acid should also not be used with plastic bottles.

The potential hazards of using chromic-sulfuric acid mixture are great and have been well publicized. There are now commercially available substitutes that possess the advantage of safety in handling. These are biodegradable concentrates with a claimed cleaning strength equal to the chromic acid solution. They are alkaline, equivalent to ca. 0.1 N NaOH upon dilution, and are claimed to remove dried blood, silicone greases, distillation residues, insoluble organic residues, etc. They are further claimed to remove radioactive traces and will not attack glass or exert a corrosive effect on skin or clothing. One such product is "Chem Solv 2157," manufactured by Mallinckrodt and available through laboratory supply firms. Another comparable product is "Detex," a product of Borer-Chemie, Solothurn, Switzerland. Other similarly effective products are Nochromix (Godax Laboratories) and Contrad 70 (Decon Labs).

Steps 5, 6, and 7: No comments required.

Step 8: There is always a possibility that between the time of washing and the next use, the glassware could pick up some contamination from either the air or direct contact. To prevent this, it is good practice to flush the item immediately before use with some of the same solvent that will be used in the analysis.

The drying and storage of the cleaned glassware is of critical importance to prevent the beneficial effects of the scrupulous cleaning from being nullified. Pegboard drying is not recommended. It is recommended that laboratory glassware and equipment be dried at 100 °C. Under no circumstances should such small items be left in the open without protective covering. The dust cloud raised by the daily sweeping of the laboratory floor can most effectively recontaminate the clean glassware.

As an alternate to solvent rinsing, the glassware can be heated to a minimum of 300 °C to vaporize any organics. Do not use this high temperature treatment on volumetric glassware, glassware with ground glass joints, or sintered glassware.

4.1.5 High concentration samples

Cross contamination of trace concentration samples may occur when prepared in the same laboratory with high concentration samples. Ideally, if both type samples are being handled, a laboratory and glassware dedicated solely to the preparation of high concentration samples would be available for this purpose. If this is not feasible, as a minimum when preparing high concentration samples, disposable glassware should be used or, at least, glassware dedicated entirely to the high concentration samples. Avoid cleaning glassware used for both trace and high concentration samples in the same area.

TABLE 4-1
RECOMMENDED SAMPLE CONTAINERS, PRESERVATION TECHNIQUES, AND HOLDING TIMES[a]
(Note: Footnotes are located on the last page of the table.)

VOLATILE ORGANICS

Sample Matrix	Container	Preservative[1]	Holding Time[1]
Concentrated waste samples	Method 5035: See the method. Method 5021: See the method. Methods 5031 and 5032: See the methods. Use PTFE-lined lids for all procedures.	Cool to ≤6 °C.	14 days
Aqueous samples with no residual chlorine present	Methods 5030, 5031, and 5032: 2 x 40-mL vials with PTFE-lined septum caps	Cool to ≤6 °C and adjust pH to less than 2 with H_2SO_4, HCl, or solid $NaHSO_4$	14 days
		If carbonaceous materials are present, or if MTBE and other fuel oxygenate ethers are present and a high temperature sample preparative method is to be used, do not acid preserve the samples.	*7 days*
		If vinyl chloride, styrene, or 2-chloroethyl vinyl ether are analytes of interest, collect a second set of samples without acid preservatives and analyze as soon as possible.	*7 days*

VOLATILE ORGANICS (continued)			
Sample Matrix	Container	Preservative[1]	Holding Time[1]
Aqueous samples WITH residual chlorine present	Methods 5030, 5031, and 5032: 2 x 40-mL vials with PTFE-lined septum caps	Collect sample in a 125-mL container which has been pre-preserved with 4 drops of 10% sodium thiosulfate solution. Gently swirl to mix sample and transfer to a 40-mL VOA vial. Cool to ≤6 °C and adjust pH to less than 2 with H_2SO_4, HCl, or solid $NaHSO_4$.	14 days
		If carbonaceous materials are present, or if MTBE and other fuel oxygenate ethers are present and a high temperature sample preparative method is to be used, do not acid preserve the samples.	*7 days*
		If vinyl chloride, styrene, or 2-chloroethyl vinyl ether are analytes of interest, collect a second set of samples without acid preservatives and analyze as soon as possible.	*7 days*
Acrolein and acrylonitrile in aqueous samples	Methods 5030, 5031, and 5032: 2 x 40-mL vials with PTFE-lined septum caps	Adjust to pH 4-5. Cool to ≤6 °C. *These compounds are highly reactive and should be analyzed as soon as possible.*	7days
Solid samples (e.g. soils, sediments, sludges, ash)	Method 5035: See the method. Method 5021: See the method. Methods 5031 and 5032: See the methods.	See the individual methods.	14 days
		If vinyl chloride, styrene, or 2-chloroethyl vinyl ether are analytes of interest, collect a second set of samples without acid preservatives and analyze as soon as possible.	7 days

TABLE 4-1 (Continued)

SEMIVOLATILE ORGANICS/ORGANOCHLORINE PESTICIDES AND HERBICIDES

Sample Matrix	Container	Preservative[1]	Holding Time[1]
Concentrated waste samples	125-mL wide-mouth glass with PTFE-lined lid	None	Samples extracted within 14 days and extracts analyzed within 40 days following extraction.
Aqueous samples with no residual chlorine present	4 x 1-L amber glass container with PTFE-lined lid, or other size, as appropriate, to allow use of entire sample for analysis.	Cool to $\leq$6 °C.	Samples extracted within 7 days and extracts analyzed within 40 days following extraction.

TABLE 4-1 (Continued)

SEMIVOLATILE ORGANICS/ORGANOCHLORINE PESTICIDES AND HERBICIDES (continued)			
Sample Matrix	Container	Preservative[1]	Holding Time[2]
Aqueous samples WITH residual chlorine present	4 x 1-L amber glass container with PTFE-lined lid, or other size, as appropriate, to allow use of entire sample for analysis.	Add 3-mL 10% sodium thiosulfate solution per gallon (or 0.008%). Addition of sodium thiosulfate solution to sample container may be performed in the laboratory prior to field use. Cool to ≤6 °C.	Samples extracted within 7 days and extracts analyzed within 40 days following extraction.
Solid samples (e.g. soils, sediments, sludges, ash)	250-mL wide-mouth glass container with PTFE-lined lid	Cool to ≤6 °C.	Samples extracted within 14 days and extracts analyzed within 40 days following extraction.

POLYCHLORINATED BIPHENYLS, POLYCHLORINATED DIBENZO-*p*-DIOXINS, AND POLYCHLORINATED DIBENZOFURANS			
Sample Matrix	Container	Preservative[1]	Holding Time[2]
Concentrated waste samples	125-mL wide-mouth glass with PTFE-lined lid	None	None
Aqueous samples with no residual chlorine present	4 x 1-L amber glass container with PTFE-lined lid, or other size, as appropriate, to allow use of entire sample for analysis.	Cool to ≤6 °C.	None

TABLE 4-1 (Continued)

POLYCHLORINATED BIPHENYLS, POLYCHLORINATED DIBENZO-*p*-DIOXINS, AND POLYCHLORINATED DIBENZOFURANS (continued)			
Sample Matrix	Container	Preservative[1]	Holding Time[2]
Aqueous samples WITH residual chlorine present	4 x 1-L amber glass container with PTFE-lined lid, or other size, as appropriate, to allow use of entire sample for analysis.	Add 3-mL 10% sodium thiosulfate solution per gallon (or 0.008%). Addition of sodium thiosulfate solution to sample container may be performed in the laboratory prior to field use. Cool to ≤6 °C	None
Solid samples (e.g. soils, sediments, sludges, ash)	250-mL wide-mouth glass container with PTFE-lined lid.	Cool to ≤6 °C.	None

[a] The information presented in this table does not represent EPA requirements, but rather it is intended solely as guidance. Selection of containers, preservation techniques and applicable holding times should be based on the stated project-specific data quality objectives.

[1] The exact sample, extract, and standard storage temperature should be based on project-specific requirements and/or manufacturer's recommendations for commercially available standards. Furthermore, alternative storage temperatures may be appropriate based on demonstrated analyte stability in a given matrix, provided the stated data quality objectives for a project-specific application are still attainable.

[2] A longer holding time may be appropriate if it can be demonstrated that the reported analyte concentrations are not adversely affected from preservation, storage and analyses performed outside the recommended holding times.

4.2 SAMPLE PREPARATION METHODS

Prior to employing the methods in this chapter, analysts are advised to consult the disclaimer statement at the front of this manual and the information in Chapter Two for guidance on the allowed flexibility in the choice of apparatus, reagents, and supplies. In addition, unless specified in a regulation, the use of SW-846 methods is not mandatory in response to Federal testing requirements. The information contained in each procedure is provided by EPA as guidance to be used by the analyst and the regulated community in making judgements necessary to meet the data quality objectives or needs for the intended use of the data.

4.2.1 Extractions and preparations

The following methods are included in this section:

Method 3500C:	Organic Extraction and Sample Preparation
Method 3510C:	Separatory Funnel Liquid-Liquid Extraction
Method 3520C:	Continuous Liquid-Liquid Extraction
Method 3535A:	Solid-Phase Extraction (SPE)
Method 3540C:	Soxhlet Extraction
Method 3541:	Automated Soxhlet Extraction
Method 3542:	Extraction of Semivolatile Analytes Collected Using Method 0010 (Modified Method 5 Sampling Train)
Method 3545A:	Pressurized Fluid Extraction (PFE)
Method 3546:	Microwave Extraction
Method 3550C:	Ultrasonic Extraction
Method 3560:	Supercritical Fluid Extraction of Total Recoverable Petroleum Hydrocarbons
Method 3561:	Supercritical Fluid Extraction of Polynuclear Aromatic Hydrocarbons
Method 3562:	Supercritical Fluid Extraction of Polychlorinated Biphenyls (PCBs) and Organochlorine Pesticides
Method 3580A:	Waste Dilution
Method 3585:	Waste Dilution for Volatile Organics
Method 5000:	Sample Preparation for Volatile Organic Compounds
Method 5021:	Volatile Organic Compounds in Soils and Other Solid Matrices Using Equilibrium Headspace Analysis
Method 5030B:	Purge-and-Trap for Aqueous Samples
Method 5031:	Volatile, Nonpurgeable, Water-Soluble Compounds by Azeotropic Distillation
Method 5032:	Volatile Organic Compounds by Vacuum Distillation
Method 5035:	Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples
Method 5041A:	Analysis for Desorption of Sorbent Cartridges from Volatile Organic Sampling Train (VOST)

4.2 Sample preparation methods

Prior to employing the methods in this chapter, analysts are advised to consult the disclaimer statement at the front of this manual and the information in Chapter Two for guidance on the allowed flexibility in the choice of apparatus, reagents, and supplies. In addition, unless specified in a regulation, the use of SW-846 methods is not mandatory in response to Federal testing requirements. The information contained in each procedure is provided by EPA as guidance to be used by the analyst and the regulated community in making judgements necessary to meet the data quality objectives or needs for the intended use of the data.

4.2.2 Cleanup

The following methods are included in this section:

Method 3600C: Cleanup
Method 3610B: Alumina Cleanup
Method 3611B: Alumina Column Cleanup and Separation of Petroleum Wastes
Method 3620C: Florisil Cleanup
Method 3630C: Silica Gel Cleanup
Method 3640A: Gel-Permeation Cleanup
Method 3650B: Acid-Base Partition Cleanup
Method 3660B: Sulfur Cleanup
Method 3665A: Sulfuric Acid/Permanganate Cleanup

4.3 DETERMINATION OF ORGANIC ANALYTES

Prior to employing the methods in this chapter, analysts are advised to consult the disclaimer statement at the front of this manual and the information in Chapter Two for guidance on the allowed flexibility in the choice of apparatus, reagents, and supplies. In addition, unless specified in a regulation, the use of SW-846 methods is not mandatory in response to Federal testing requirements. The information contained in each procedure is provided by EPA as guidance to be used by the analyst and the regulated community in making judgements necessary to meet the data quality objectives or needs for the intended use of the data.

4.3.1 Gas chromatographic methods

The following methods are included in this section:

Method 8000B:	Determinative Chromatographic Separations
Method 8011:	1,2-Dibromoethane and 1,2-Dibromo-3-chloropropane by Microextraction and Gas Chromatography
Method 8015C:	Nonhalogenated Organics by Gas Chromatography
Method 8021B:	Aromatic and Halogenated Volatiles by Gas Chromatography Using Photoionization and/or Electrolytic Conductivity Detectors
Method 8031:	Acrylonitrile by Gas Chromatography
Method 8032A:	Acrylamide by Gas Chromatography
Method 8033:	Acetonitrile by Gas Chromatography with Nitrogen-Phosphorus Detection
Method 8041A:	Phenols by Gas Chromatography
Method 8061A:	Phthalate Esters by Gas Chromatography with Electron Capture Detection (GC/ECD)
Method 8070A:	Nitrosamines by Gas Chromatography
Method 8081B:	Organochlorine Pesticides by Gas Chromatography
Method 8082A:	Polychlorinated Biphenyls (PCBs) by Gas Chromatography
Method 8085:	Compound-independent Elemental Quantitation of Pesticides by Gas Chromatography with Atomic Emission Detection (GC/AED)
Method 8091:	Nitroaromatics and Cyclic Ketones by Gas Chromatography
Method 8095:	Explosives by Gas Chromatography
Method 8100:	Polynuclear Aromatic Hydrocarbons
Method 8111:	Haloethers by Gas Chromatography
Method 8121:	Chlorinated Hydrocarbons by Gas Chromatography: Capillary Column Technique
Method 8131:	Aniline and Selected Derivatives by Gas Chromatography
Method 8141B:	Organophosphorus Compounds by Gas Chromatography
Method 8151A:	Chlorinated Herbicides by GC Using Methylation or Pentafluorobenzylation Derivatization

4.3.2 Gas chromatographic/mass spectrometric methods

Prior to employing the methods in this chapter, analysts are advised to consult the disclaimer statement at the front of this manual and the information in Chapter Two for guidance on the allowed flexibility in the choice of apparatus, reagents, and supplies. In addition, unless specified in a regulation, the use of SW-846 methods is not mandatory in response to Federal testing requirements. The information contained in each procedure is provided by EPA as guidance to be used by the analyst and the regulated community in making judgements necessary to meet the data quality objectives or needs for the intended use of the data.

The following methods are included in this section:

Method 8260B: Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)

Method 8261: Volatile Organic Compounds by Vacuum Distillation in Combination with Gas Chromatography/Mass Spectrometry (VD/GC/MS)

Method 8270D: Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)

Method 8275A: Semivolatile Organic Compounds (PAHs and PCBs) in Soils/Sludges and Solid Wastes Using Thermal Extraction/Gas Chromatography/Mass Spectrometry (TE/GC/MS)

Method 8280B: Polychlorinated Dibenzo-*p*-Dioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) by High-Resolution Gas Chromatography/Low Resolution Mass Spectrometry (HRGC/LRMS)

Method 8290A: Polychlorinated Dibenzo-*p*-dioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) by High-Resolution Gas Chromatography/High-Resolution Mass Spectrometry (HRGC/HRMS)

Appendix A: Procedures for the Collection, Handling, Analysis, and Reporting of Wipe Tests Performed within the Laboratory

4.3.3 High performance liquid chromatographic methods

Prior to employing the methods in this chapter, analysts are advised to consult the disclaimer statement at the front of this manual and the information in Chapter Two for guidance on the allowed flexibility in the choice of apparatus, reagents, and supplies. In addition, unless specified in a regulation, the use of SW-846 methods is not mandatory in response to Federal testing requirements. The information contained in each procedure is provided by EPA as guidance to be used by the analyst and the regulated community in making judgements necessary to meet the data quality objectives or needs for the intended use of the data.

The following methods are included in this section:

Method 8310:	Polynuclear Aromatic Hydrocarbons
Method 8315A:	Determination of Carbonyl Compounds by High Performance Liquid Chromatography (HPLC) **Appendix A:** Recrystallization of 2,4-Dinitrophenylhydrazine (DNPH)
Method 8316:	Acrylamide, Acrylonitrile and Acrolein by High Performance Liquid Chromatography (HPLC)
Method 8318A:	*N*-Methylcarbamates by High Performance Liquid Chromatography (HPLC)
Method 8321B:	Solvent-Extractable Nonvolatile Compounds by High-Performance Liquid Chromatography/Thermospray/Mass Spectrometry (HPLC/TS/MS) or Ultraviolet (UV) Detection
Method 8325:	Solvent Extractable Nonvolatile Compounds by High Performance Liquid Chromatography/Particle Beam/Mass Spectrometry (HPLC/PB/MS)
Method 8330A:	Nitroaromatics and Nitramines by High Performance Liquid Chromatography (HPLC)
Method 8331:	Tetrazene by Reverse Phase High Performance Liquid Chromatography (HPLC)
Method 8332:	Nitroglycerine by High Performance Liquid Chromatography

4.3.4 Infrared methods

Prior to employing the methods in this chapter, analysts are advised to consult the disclaimer statement at the front of this manual and the information in Chapter Two for guidance on the allowed flexibility in the choice of apparatus, reagents, and supplies. In addition, unless specified in a regulation, the use of SW-846 methods is not mandatory in response to Federal testing requirements. The information contained in each procedure is provided by EPA as guidance to be used by the analyst and the regulated community in making judgements necessary to meet the data quality objectives or needs for the intended use of the data.

The following methods are included in this section:

Method 8410: Gas Chromatography/Fourier Transform Infrared (GC/FT-IR) Spectrometry for Semivolatile Organics: Capillary Column

Method 8430: Analysis of Bis(2-chloroethyl) Ether and Hydrolysis Products by Direct Aqueous Injection GC/FT-IR

Method 8440: Total Recoverable Petroleum Hydrocarbons by Infrared Spectrophotometry

4.3.5 Miscellaneous spectrometric methods

Prior to employing the methods in this chapter, analysts are advised to consult the disclaimer statement at the front of this manual and the information in Chapter Two for guidance on the allowed flexibility in the choice of apparatus, reagents, and supplies. In addition, unless specified in a regulation, the use of SW-846 methods is not mandatory in response to Federal testing requirements. The information contained in each procedure is provided by EPA as guidance to be used by the analyst and the regulated community in making judgements necessary to meet the data quality objectives or needs for the intended use of the data.

The following method is included in this section:

Method 8520: Continuous Measurement of Formaldehyde in Ambient Air

4.4 IMMUNOASSAY METHODS

Prior to employing the methods in this chapter, analysts are advised to consult the disclaimer statement at the front of this manual and the information in Chapter Two for guidance on the allowed flexibility in the choice of apparatus, reagents, and supplies. In addition, unless specified in a regulation, the use of SW-846 methods is not mandatory in response to Federal testing requirements. The information contained in each procedure is provided by EPA as guidance to be used by the analyst and the regulated community in making judgements necessary to meet the data quality objectives or needs for the intended use of the data.

The following methods are included in this section:

Method 4000:	Immunoassay
Method 4010A:	Screening for Pentachlorophenol by Immunoassay
Method 4015:	Screening for 2,4-Dichlorophenoxyacetic Acid by Immunoassay
Method 4020:	Screening for Polychlorinated Biphenyls by Immunoassay
Method 4030:	Soil Screening for Petroleum Hydrocarbons by Immunoassay
Method 4035:	Soil Screening for Polynuclear Aromatic Hydrocarbons by Immunoassay
Method 4040:	Soil Screening for Toxaphene by Immunoassay
Method 4041:	Soil Screening for Chlordane by Immunoassay
Method 4042:	Soil Screening for DDT by Immunoassay
Method 4050:	TNT Explosives in Soil by Immunoassay
Method 4051:	Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) in Soil by Immunoassay
Method 4425:	Screening Extracts of Environmental Samples for Planar Organic Compounds (PAHs, PCBs, PCDDs/PCDFs) by a Reporter Gene on a Human Cell Line
Method 4670:	Triazine Herbicides as Atrazine in Water by Quantitative Immunoassay

4.5 MISCELLANEOUS SCREENING METHODS

Prior to employing the methods in this chapter, analysts are advised to consult the disclaimer statement at the front of this manual and the information in Chapter Two for guidance on the allowed flexibility in the choice of apparatus, reagents, and supplies. In addition, unless specified in a regulation, the use of SW-846 methods is not mandatory in response to Federal testing requirements. The information contained in each procedure is provided by EPA as guidance to be used by the analyst and the regulated community in making judgements necessary to meet the data quality objectives or needs for the intended use of the data.

The following methods are included in this section:

Method 3815:	Screening Solid Samples for Volatile Organics
Method 3820:	Hexadecane Extraction and Screening of Purgeable Organics
Method 8510:	Colorimetric Screening Procedure for RDX and HMX in Soil
Method 8515:	Colorimetric Screening Method for Trinitrotoluene (TNT) in Soil
Method 8535:	Screening Procedure for Total Volatile Organic Halides in Water
Method 8540:	Pentachlorophenol by UV-Induced Colorimetry
Method 9074:	Turbidimetric Screening Method for Total Recoverable Petroleum Hydrocarbons in Soil
Method 9078:	Screening Test Method for Polychlorinated Biphenyls in Soil
Method 9079:	Screening Test Method for Polychlorinated Biphenyls in Transformer Oil

CHAPTER FIVE

MISCELLANEOUS TEST METHODS

Prior to employing the methods in this chapter, analysts are advised to consult the disclaimer statement at the front of this manual and the information in Chapter Two for guidance on the allowed flexibility in the choice of apparatus, reagents, and supplies. In addition, unless specified in a regulation, the use of SW-846 methods is not mandatory in response to Federal testing requirements. The information contained in each procedure is provided by EPA as guidance to be used by the analyst and the regulated community in making judgements necessary to meet the data quality objectives or needs for the intended use of the data.

The following methods are found in Chapter Five:

Method 5050:	Bomb Preparation Method for Solid Waste
Method 9000:	Determination of Water in Waste Materials by Karl Fischer Titration
Method 9001:	Determination of Water in Waste Materials by Quantitative Calcium Hydride Reaction
Method 9010B:	Total and Amenable Cyanide: Distillation
Method 9012A:	Total and Amenable Cyanide (Automated Colorimetric, with Off-line Distillation)
Method 9013:	Cyanide Extraction Procedure for Solids and Oils
Method 9014:	Titrimetric and Manual Spectrophotometric Determinative Methods for Cyanide
Method 9020B:	Total Organic Halides (TOX)
Method 9021:	Purgeable Organic Halides (POX)
Method 9022:	Total Organic Halides (TOX) by Neutron Activation Analysis
Method 9023:	Extractable Organic Halides (EOX) in Solids
Method 9030B:	Acid-Soluble and Acid-Insoluble Sulfides: Distillation
Method 9031:	Extractable Sulfides
Method 9034:	Titrimetric Procedure for Acid-Soluble and Acid-Insoluble Sulfides
Method 9035:	Sulfate (Colorimetric, Automated, Chloranilate)
Method 9036:	Sulfate (Colorimetric, Automated, Methylthymol Blue, AA II)
Method 9038:	Sulfate (Turbidimetric)
Method 9056A:	Determination of Inorganic Anions by Ion Chromatography
Method 9057:	Determination of Chloride from HCl/Cl_2 Emission Sampling Train (Methods 0050 and 0051) by Anion Chromatography
Method 9060A:	Total Organic Carbon
Method 9065:	Phenolics (Spectrophotometric, Manual 4-AAP with Distillation)
Method 9066:	Phenolics (Colorimetric, Automated 4-AAP with Distillation)
Method 9067:	Phenolics (Spectrophotometric, MBTH with Distillation)
Method 9070A:	*n*-Hexane Extractable Material (HEM) for Aqueous Samples

Method 9071B: *n*-Hexane Extractable Material (HEM) for Sludge, Sediment, and Solid Samples

Method 9075: Test Method for Total Chlorine in New and Used Petroleum Products by X-Ray Fluorescence Spectrometry (XRF)

Method 9076: Test Method for Total Chlorine in New and Used Petroleum Products by Oxidative Combustion and Microcoulometry

Method 9077: Test Methods for Total Chlorine in New and Used Petroleum Products (Field Test Kit Methods)

- **Method A:** Fixed End Point Test Kit Method
- **Method B:** Reverse Titration Quantitative End Point Test Kit Method
- **Method C:** Direct Titration Quantitative End Point Test Kit Method

Method 9131: Total Coliform: Multiple Tube Fermentation Technique

Method 9132: Total Coliform: Membrane-Filter Technique

Method 9210A: Potentiometric Determination of Nitrate in Aqueous Samples with an Ion-Selective Electrode

Method 9211: Potentiometric Determination of Bromide in Aqueous Samples with Ion-Selective Electrode

Method 9212: Potentiometric Determination of Chloride in Aqueous Samples with Ion-Selective Electrode

Method 9213: Potentiometric Determination of Cyanide in Aqueous Samples and Distillates with Ion-Selective Electrode

Method 9214: Potentiometric Determination of Fluoride in Aqueous Samples with Ion-Selective Electrode

Method 9215: Potentiometric Determination of Sulfide in Aqueous Samples and Distillates with Ion-Selective Electrode

Method 9216: Potentiometric Determination of Nitrate in Aqueous Samples with Ion-Selective Electrode

Method 9250: Chloride (Colorimetric, Automated Ferricyanide AAI)

Method 9251: Chloride (Colorimetric, Automated Ferricyanide AAII)

Method 9253: Chloride (Titrimetric, Silver Nitrate)

Method 9320: Radium-228

CHAPTER SIX

PROPERTIES

This chapter addresses procedures for "method-defined parameters," where the analytical result is wholly dependant on the process used to make the measurement. Changes to the specific methods may change the end result and incorrectly identify a waste as nonhazardous. Therefore, when the measurement of such method-defined parameters is required by regulation, those methods are **not** subject to the flexibility afforded in other SW-846 methods (such as described in the Disclaimer and Chapter Two of this manual).

The following methods are found in Chapter Six:

Method 1030:	Ignitability of Solids
Method 1040:	Test Method for Oxidizing Solids
Method 1050:	Test Methods to Determine Substances Likely to Spontaneously Combust
Method 1120:	Dermal Corrosion
Method 1312:	Synthetic Precipitation Leaching Procedure
Method 1320:	Multiple Extraction Procedure
Method 1330A:	Extraction Procedure for Oily Wastes
Method 9041A:	pH Paper Method
Method 9045D:	Soil and Waste pH
Method 9050A:	Specific Conductance
Method 9080:	Cation-Exchange Capacity of Soils (Ammonium Acetate)
Method 9081:	Cation-Exchange Capacity of Soils (Sodium Acetate)
Method 9090A:	Compatibility Test for Wastes and Membrane Liners
Method 9095B:	Paint Filter Liquids Test
Method 9096:	Liquid Release Test (LRT) Procedure
	Appendix A: Liquid Release Test Pre-Test
Method 9100:	Saturated Hydraulic Conductivity, Saturated Leachate Conductivity, and Intrinsic Permeability
Method 9310:	Gross Alpha and Gross Beta
Method 9315:	Alpha-Emitting Radium Isotopes

CHAPTER SEVEN

CHARACTERISTICS INTRODUCTION AND REGULATORY DEFINITIONS

This chapter addresses procedures for required "method-defined parameters," where the analytical result is wholly dependant on the process used to make the measurement. Examples include the use of the toxicity characteristic leaching procedure (TCLP) to prepare a leachate, and the flash point, pH, paint filter liquids, and corrosivity tests. In these instances, changes to the specific methods may change the end result and incorrectly identify a waste as nonhazardous. Therefore, when the measurement of such method-defined parameters is required by regulation, those methods are not subject to the flexibility afforded in other SW-846 methods (such as described in the Disclaimer and Chapter Two of this manual).

7.1 IGNITABILITY

7.1.1 Introduction

The objective of the ignitability characteristic is to identify wastes that either present fire hazards under routine storage, disposal, and transportation or are capable of severely exacerbating a fire once started.

7.1.2 Regulatory Definition

See 40 CFR 261.21 for the regulatory definition of the hazardous waste characteristic of ignitability. Methods 1010 and 1020 of Chapter Eight refer the reader to the ASTM standards required by the RCRA regulations for the flash point of liquids at 40 CFR 261.21(1).

7.2 CORROSIVITY

7.2.1 Introduction

The corrosivity characteristic, as defined in 40 CFR 261.22, is designed to identify wastes that might pose a hazard to human health or the environment due to their ability to:

1. Mobilize toxic metals if discharged into a landfill environment;

2. Corrode handling, storage, transportation, and management equipment; or

3. Destroy human or animal tissue in the event of inadvertent contact.

In order to identify such potentially hazardous materials, EPA has selected two properties upon which to base the definition of a corrosive waste. These properties are pH and corrosivity toward Type SAE 1020 steel.

The procedures for measuring pH of aqueous wastes are detailed in Method 9040, Chapter Six. Method 1110, Chapter Eight, describes how to determine whether a waste is corrosive to steel. Use Method 9095, Paint Filter Liquids Test, Chapter Six, to determine free liquid.

7.2.2 Regulatory Definition

See 40 CFR 261.22 for the regulatory definition of the hazardous waste characteristic of corrosivity.

7.3 REACTIVITY

7.3.1 Introduction

The regulation in 40 CFR 261.23 defines reactive wastes to include wastes that have any of the following properties: (1) readily undergo violent chemical change; (2) react violently or form potentially explosive mixtures with water; (3) generate toxic fumes when mixed with water or, in the case of cyanide- or sulfide-bearing wastes, when exposed to mild acidic or basic conditions; (4) explode when subjected to a strong initiating force; (5) explode at normal temperatures and pressures; or (6) fit within the Department of Transportation's forbidden explosives, Class A explosives, or Class B explosives classifications.

This definition is intended to identify wastes that, because of their extreme instability and tendency to react violently or explode, pose a problem at all stages of the waste management process. The Agency relies entirely on a descriptive, prose definition of reactivity because available tests for measuring the variegated class of effects embraced by the reactivity definition suffer from a number of deficiencies.

7.3.2 Regulatory Definition

See 40 CFR 261.24 for the regulatory definition of the hazardous waste characteristic of reactivity.

7.4 TOXICITY CHARACTERISTIC LEACHING PROCEDURE

7.4.1 Introduction

The Toxicity Characteristic Leaching Procedure (TCLP) is designed to simulate the leaching a waste will undergo if disposed of in a sanitary landfill. This test is designed to simulate leaching that takes place in a sanitary landfill only. The extraction fluid employed is a function of the alkalinity of the solid phase of the waste. A subsample of a waste is extracted with the appropriate buffered acetic acid solution for 18 $\pm$ 2 hours. The extract obtained from the TCLP (the "TCLP extract") is then analyzed to determine if any of the thresholds established for the 40 Toxicity Characteristic (TC) constituents (listed in Table 7-1) have been exceeded or if the treatment standards established for the constituents listed in 40 CFR 268.40 have been met under the Land Disposal Restrictions (LDR) regulations. If the TCLP extract contains any one of the TC constituents in an amount equal to or exceeding the concentrations specified in 40 CFR 261.24, the waste possesses the characteristic of toxicity and is a hazardous waste. If the TCLP extract contains constituents in an amount exceeding the concentrations specified in 40 CFR 268.40, the treatment standard for that waste has not been met, and further treatment is necessary prior to land disposal.

7.4.2 Summary of Procedure

Figure 3 summarizes the procedures in the TCLP. The five basic steps of the TCLP are summarized below.

1. Separation Procedure

For liquid wastes (i.e., those containing less than 0.5% dry solid material), the waste, after filtration through a 0.6 to 0.8 µm glass fiber filter, is defined as the TCLP extract.

For wastes containing greater than or equal to 0.5% solids, the liquid, if any, is separated from the solid phase and stored for later analysis.

2. Particle Size Reduction

Prior to extraction, the solid material must pass through a 9.5-mm (0.375-in.) standard sieve, have a surface area per gram of material equal to or greater than 3.1 cm^2, or, be smaller than 1 cm in its narrowest dimension. If the surface area is smaller or the particle size larger than described above, the solid portion of the waste is prepared for extraction by crushing, cutting, or grinding the waste to the surface area or particle size described above. (Special precautions must be taken if the solids are prepared for organic volatiles extraction.)

3. Extraction of Solid Material

The solid material from Step 2 is extracted for 18 $\pm$ 2 hours with an amount of extraction fluid equal to 20 times the weight of the solid phase. The extraction fluid employed is a function of the alkalinity of the solid phase of the waste. A special extractor vessel is used when testing for volatile analytes.

4. Final Separation of the Extraction from the Remaining Solid

Following extraction, the liquid extract is separated from the solid phase by filtration through a 0.6 to 0.8 µm glass fiber filter. If compatible, the initial liquid phase of the waste is added to the liquid extract, and these are analyzed together. If incompatible, the liquids are analyzed separately and the results are mathematically combined to yield a volume-weighted average concentration.

5. Testing (Analysis) of TCLP Extract

Inorganic and organic species are identified and quantified using appropriate methods in the 6000, 7000, and 8000 series of methods in this manual or by other appropriate methods**.**

7.4.3 Regulatory Definition

Under the Toxicity Characteristic, a solid waste exhibits the characteristic of toxicity if the TCLP extract from a subsample of the waste contains any of the contaminants listed in Table 7-1 at a concentration greater than or equal to the respective value given in that table. If a waste contains <0.5% filterable solids, the waste itself, after filtering, is considered to be the extract for the purposes of analysis.

Under the Land Disposal Restrictions regulations (40 CFR, Part 268), a restricted waste identified in 40 CFR 268.40 cannot be land disposed if a TCLP extract of the waste or a TCLP extract of the treatment residue of the waste exceeds the values shown in the table of 40 CFR 268.40 for any hazardous constituent listed in the table for that waste. If a waste contains

<0.5% filterable solids, the waste itself, after filtering, is considered to be the extract for the purposes of analysis.

TABLE 7-1.
MAXIMUM CONCENTRATION OF CONTAMINANTS FOR TOXICITY CHARACTERISTIC

Contaminant	Regulatory Level (mg/L)
Arsenic	5.0
Barium	100.0
Benzene	0.5
Cadmium	1.0
Carbon tetrachloride	0.5
Chlordane	0.03
Chlorobenzene	100.0
Chloroform	6.0
Chromium	5.0
o-Cresol	200.0[1]
m-Cresol	200.0[1]
p-Cresol	200.0[1]
Cresol	200.0[1]
2,4-D	10.0
1,4-Dichlorobenzene	7.5
1,2-Dichloroethane	0.5
1,1-Dichloroethylene	0.7
2,4-Dinitrotoluene	0.13[2]
Endrin	0.02
Heptachlor (and its hydroxide)	0.008
Hexachlorobenzene	0.13[2]
Hexachloro-1,3-butadiene	0.5
Hexachloroethane	3.0
Lead	5.0
Lindane	0.4
Mercury	0.2
Methoxychlor	10.0
Methyl ethyl ketone	200.0
Nitrobenzene	2.0
Pentachlorophenol	100.0
Pyridine	5.0[2]
Selenium	1.0
Silver	5.0
Tetrachloroethylene	0.7
Toxaphene	0.5
Trichloroethylene	0.5
2,4,5-Trichlorophenol	400.0
2,4,6-Trichlorophenol	2.0
2,4,5-TP (Silvex)	1.0
Vinyl chloride	0.2

[1]If o-, m-, and p-cresol concentrations cannot be differentiated, the total cresol (D026) concentration is used. The regulatory level of total cresol is 200 mg/L.
[2]Quantitation limit is greater than the calculated regulatory level. The quantitation limit therefore becomes the regulatory level.

FIGURE 3.

TOXICITY CHARACTERISTIC LEACHING PROCEDURE FLOWCHART

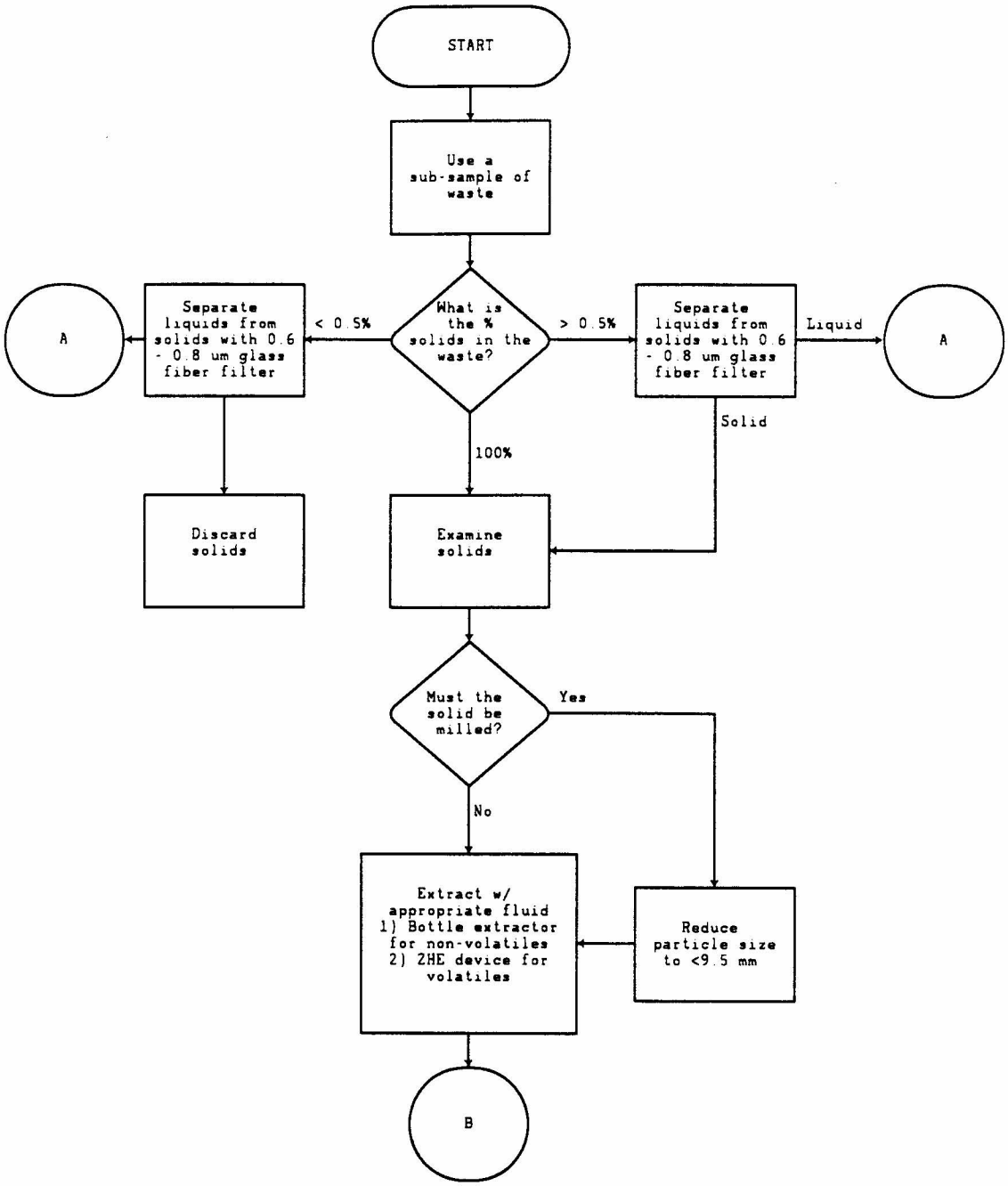
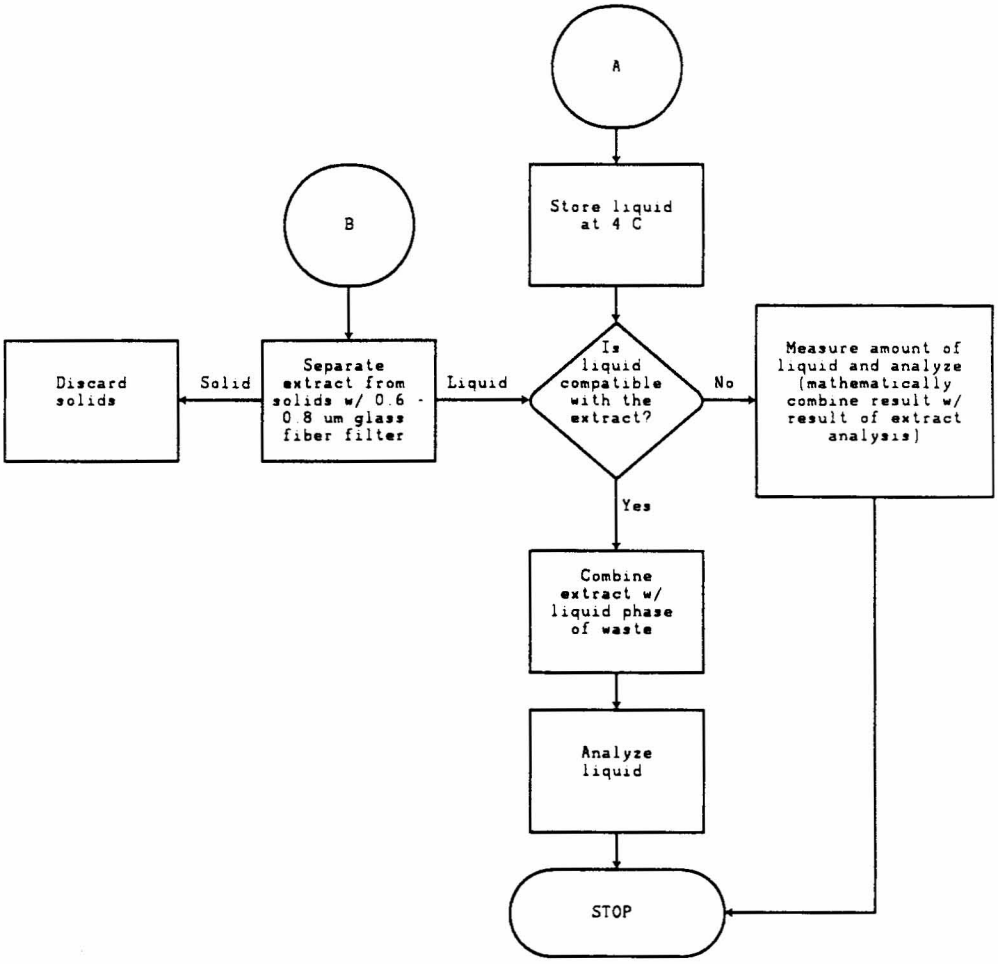


FIGURE 3 (continued)



CHAPTER EIGHT

METHODS FOR DETERMINING CHARACTERISTICS

This chapter addresses procedures for required method-defined parameters, where the analytical result is wholly dependant on the process used to make the measurement. Examples include the use of the toxicity characteristic leaching procedure (TCLP) to prepare a leachate, and the flash point, pH, paint filter liquids, and corrosivity tests. In these instances, changes to the specific methods may change the end result and incorrectly identify a waste as nonhazardous. Therefore, when the measurement of such method-defined parameters is required by regulation, those methods are not subject to the flexibility afforded in other SW-846 methods (such as described in the Disclaimer and Chapter Two of this manual).

Methods for determining the characteristics of ignitability for liquids, corrosivity for liquids, and toxicity are included. The text of the methods identified for the characteristic of ignitability refer the reader to the appropriate required ASTM methods. There are no required SW-846 methods for the analysis of the characteristic of reactivity.

8.1 Ignitability

This chapter addresses procedures for required method-defined parameters, where the analytical result is wholly dependant on the process used to make the measurement. Examples include the use of the toxicity characteristic leaching procedure (TCLP) to prepare a leachate, and the flash point, pH, paint filter liquids, and corrosivity tests. In these instances, changes to the specific methods may change the end result and incorrectly identify a waste as nonhazardous. Therefore, when the measurement of such method-defined parameters is required by regulation, those methods are not subject to the flexibility afforded in other SW-846 methods (such as described in the Disclaimer and Chapter Two of this manual).

The text of the methods identified for the characteristic of ignitability refer the reader to the appropriate required ASTM methods. The following methods are found in Sec. 8.1 of this chapter:

Method 1010A: Test Methods for Flash Point by Pensky-Martens Closed Cup Tester

Method 1020B : Standard Test Methods for Flash Point by Setaflash (Small Scale) Closed-cup Apparatus

8.2 Corrosivity

This chapter addresses procedures for required method-defined parameters, where the analytical result is wholly dependant on the process used to make the measurement. Examples include the use of the toxicity characteristic leaching procedure (TCLP) to prepare a leachate, and the flash point, pH, paint filter liquids, and corrosivity tests. In these instances, changes to the specific methods may change the end result and incorrectly identify a waste as nonhazardous. Therefore, when the measurement of such method-defined parameters is required by regulation, those methods are not subject to the flexibility afforded in other SW-846 methods (such as described in the Disclaimer and Chapter Two of this manual).

The following methods are found in Sec. 8.2 of this chapter:

Method 9040C: pH Electrometric Measurement
Method 1110A: Corrosivity Toward Steel

8.3 Toxicity

This chapter addresses procedures for required method-defined parameters, where the analytical result is wholly dependant on the process used to make the measurement. Examples include the use of the toxicity characteristic leaching procedure (TCLP) to prepare a leachate, and the flash point, pH, paint filter liquids, and corrosivity tests. In these instances, changes to the specific methods may change the end result and incorrectly identify a waste as nonhazardous. Therefore, when the measurement of such method-defined parameters is required by regulation, those methods are not subject to the flexibility afforded in other SW-846 methods (such as described in the Disclaimer and Chapter Two of this manual).

The following methods are found in Sec. 8.3 of this chapter:

Method 1310B:	Extraction Procedure (EP) Toxicity Test Method and Structural Integrity Test
Method 1311:	Toxicity Characteristic Leaching Procedure

CHAPTER NINE

SAMPLING PLAN

9.1 DESIGN AND DEVELOPMENT

The initial -- and perhaps most critical -- element in a program designed to evaluate the physical and chemical properties of a solid waste is the plan for sampling the waste. It is understandable that analytical studies, with their sophisticated instrumentation and high cost, are often perceived as the dominant element in a waste characterization program. Yet, despite that sophistication and high cost, analytical data generated by a scientifically defective sampling plan have limited utility, particularly in the case of regulatory proceedings.

This section of the manual addresses the development and implementation of a scientifically credible sampling plan for a solid waste and the documentation of the chain of custody for such a plan. The information presented in this section is relevant to the sampling of any solid waste, which has been defined by the EPA in its regulations for the identification and listing of hazardous wastes to include solid, semisolid, liquid, and contained gaseous materials. However, the physical and chemical diversity of those materials, as well as the dissimilarity of storage facilities (lagoons, open piles, tanks, drums, etc.) and sampling equipment associated with them, preclude a detailed consideration of any specific sampling plan. Consequently, because the burden of responsibility for developing a technically sound sampling plan rests with the waste producer, it is advisable that he/she seek competent advice before designing a plan. This is particularly true in the early developmental stages of a sampling plan, at which time at least a basic understanding of applied statistics is required. Applied statistics is the science of employing techniques that allow the uncertainty of inductive inferences (general conclusions based on partial knowledge) to be evaluated.

9.1.1 Development of Appropriate Sampling Plans

An appropriate sampling plan for a solid waste must be responsive to both regulatory and scientific objectives. Once those objectives have been clearly identified, a suitable sampling strategy, predicated upon fundamental statistical concepts, can be developed. The statistical terminology associated with those concepts is reviewed in Table 9-1; Student's "t" values for use in the statistics of Table 9-1 appear in Table 9-2.

9.1.1.1 Regulatory and Scientific Objectives

The EPA, in its hazardous waste management system, has required that certain solid wastes be analyzed for physical and chemical properties. It is mostly chemical properties that are of concern, and, in the case of a number of chemical contaminants, the EPA has promulgated levels (regulatory thresholds) that cannot be equaled or exceeded. The regulations pertaining to the management of hazardous wastes contain three references regarding the

TABLE 9-1. BASIC STATISTICAL TERMINOLOGY APPLICABLE TO SAMPLING PLANS FOR SOLID WASTES

Terminology	Symbol	Mathematical Equation	(Equation)
• Variable (e.g., barium or endrin)	x		
• Individual measurement of variable	x_i		
• Mean of possible measurements of variable (population mean)	μ	$\mu = \frac{\sum_{i=1}^{N} x_i}{N}$, with N = number of possible measurements	(1)
• Mean of measurements generated by sample (sample mean)	$\bar{x}$	Simple random sampling and systematic random sampling: $\bar{x} = \frac{\sum_{i=1}^{n} x_i}{n}$, with n = number of sample measurements	(2a)
		Stratified random sampling: $\bar{x} = \sum_{k=1}^{r} W_k \bar{x_k}$, with $\bar{x}_k$ = stratum mean and W_k = fraction of population represented by Stratum k (number of strata [k] range from 1 to r)	(2b)
• Variance of sample	s^2	Simple random sampling and systemaic random sampling: $s^2 = \frac{\sum_{i=1}^{n} x_i^2 - (\sum_{i=1}^{n} x_i)^2/n}{n-1}$	(3a)
		Stratified random sampling: $s^2 = \sum_{k-1}^{r} W_k s_k^2$, with s^2_k = stratum variance and W_k = fraction of population represent by Stratum k (number of strata [k] ranges from 1 to r)	(3b)

TABLE 9-1. (continued)

Terminology	Symbol	Mathematical Equation	(Equation)
• Standard deviation of sample	s	$s = \sqrt{s^2}$	(4)
• Standard error (also standard error of mean and standard deviation of mean) of sample	$s_{\bar{x}}$	$s_{\bar{x}} = \frac{s}{\sqrt{n}}$	(5)
• Confidence interval for μ[a]	CI	$CI = \bar{x} \pm t_{.20}\, s_{\bar{x}}$, with $t_{.20}$ obtained from Table 2 for appropriate degrees of freedom	(6)
• Regulatory threshold[a]	RT	Defined by EPA (e.g., 100 ppm for barium in elutriate of EP toxicity)	(7)
• Appropriate number of samples to collect from a solid waste (financial constraints not considered)	n	$n = \frac{t_{.20}^2\, s^2}{\Delta^2}$, with $\Delta = RT - \bar{x}$	(8)
• Degrees of freedom	df	df = n - 1	(9)
• Square root transformation	---	$X_i + ½$	(10)
• Arcsin transformation	---	Arcsin p; if necessary, refer to any text on basic statistics; measurements must be converted to percentages (p)	(11)

[a] The upper limit of the CI for μ is compared with the applicable regulatory threshold (RT) to determine if a solid waste contains the variable (chemical contaminant) of concern at a hazardous level. The contaminant of concern is not considered to be present in the waste at a hazardous level if the upper limit of the CI is less than the applicable RT. Otherwise, the opposite conclusion is reached.

TABLE 9-2. TABULATED VALUES OF STUDENT'S "t" FOR EVALUATING SOLID WASTES

Degrees of freedom (n-1)[a]	Tabulated "t" Value[b]
1	3.078
2	1.886
3	1.638
4	1.533
5	1.476
6	1.440
7	1.415
8	1.397
9	1.393
10	1.372
11	1.363
12	1.356
13	1.350
14	1.345
15	1.341
16	1.337
17	1.333
18	1.330
19	1.328
20	1.325
21	1.323
22	1.321
23	1.319
24	1.318
25	1.316
26	1.315
27	1.314
28	1.313
29	1.311
30	1.310
40	1.303
60	1.296
120	1.289
	1.282

[a] Degrees of freedom (df) are equal to the number of samples (n) collected from a solid waste less one.

[b] Tabulated "t" values are for a two-tailed confidence interval and a probability of 0.20 (the same values are applicable to a one-tailed confidence interval and a probability of 0.10).

sampling of solid wastes for analytical properties. The first reference, which occurs throughout the regulations, requires that representative samples of waste be collected and defines representative samples as exhibiting average properties of the whole waste. The second reference, which pertains just to petitions to exclude wastes from being listed as hazardous wastes, specifies that enough samples (but in no case less than four samples) be collected over a period of time sufficient to represent the variability of the wastes. The third reference, which applies only to ground water monitoring systems, mandates that four replicates (subsamples) be taken from each ground water sample intended for chemical analysis and that the mean concentration and variance for each chemical constituent be calculated from those four subsamples and compared with background levels for ground water. Even the statistical test to be employed in that comparison is specified (Student's t-test).

The first of the above-described references addresses the issue of sampling accuracy, and the second and third references focus on sampling variability or, conversely, sampling precision (actually the third reference relates to analytical variability, which, in many statistical tests, is indistinguishable from true sampling variability). Sampling accuracy (the closeness of a sample value to its true value) and sampling precision (the closeness of repeated sample values) are also the issues of overriding importance in any scientific assessment of sampling practices. Thus, from both regulatory and scientific perspectives, the primary objectives of a sampling plan for a solid waste are twofold: namely, to collect samples that will allow measurements of the chemical properties of the waste that are both accurate and precise. If the chemical measurements are sufficiently accurate and precise, they will be considered reliable estimates of the chemical properties of the waste.

It is now apparent that a judgment must be made as to the degree of sampling accuracy and precision that is required to estimate reliably the chemical characteristics of a solid waste for the purpose of comparing those characteristics with applicable regulatory thresholds. Generally, high accuracy and high precision are required if one or more chemical contaminants of a solid waste are present at a concentration that is close to the applicable regulatory threshold. Alternatively, relatively low accuracy and low precision can be tolerated if the contaminants of concern occur at levels far below or far above their applicable thresholds. However, a word of caution is in order. Low sampling precision is often associated with considerable savings in analytical, as well as sampling, costs and is clearly recognizable even in the simplest of statistical tests. On the other hand, low sampling accuracy may not entail cost savings and is always obscured in statistical tests (i.e., it cannot be evaluated). Therefore, although it is desirable to design sampling plans for solid wastes to achieve only the minimally required precision (at least two samples of a material are required for any estimate of precision), it is prudent to design the plans to attain the greatest possible accuracy.

The roles that inaccurate and imprecise sampling can play in causing a solid waste to be inappropriately judged hazardous are illustrated in Figure 9-1. When evaluating Figure 9-1, several points are worthy of consideration. Although a sampling plan for a solid waste generates a mean concentration ($\bar{x}$) and standard deviation (s, a measure of the extent to which individual sample concentrations are dispersed around $\bar{x}$) for each chemical contaminant of concern, it is not the variation of individual sample concentrations that is of ultimate concern, but rather the variation that characterizes $\bar{x}$ itself. That measure of dispersion is termed the standard deviation of the mean (also, the standard error of the mean or standard error) and is designated as $s_{\bar{x}}$. Those two sample values, $\bar{x}$ and $S_{\bar{x}}$, are used to estimate the interval (range) within which the true mean (μ) of the chemical concentration probably occurs, under the assumption that the individual concentrations exhibit a normal (bell-shaped) distribution. For the purposes of evaluating solid wastes, the probability level (confidence interval) of 80% has been selected. That is, for each chemical contaminant of concern, a confidence interval (CI) is described within which μ occurs if the sample is representative, which is expected of about 80 out of 100 samples. The upper limit of the 80% CI is then compared with the appropriate regulatory threshold. If the upper limit is less than the threshold, the chemical contaminant is not considered to be present in the waste at a hazardous level; otherwise, the opposite conclusion is drawn. One last point merits explanation. Even if the upper limit of an estimated 80% CI is only slightly less than the regulatory threshold (the worst case of chemical contamination that would be judged acceptable), there is only a 10% (not 20%) chance that the threshold is equaled or exceeded. That is because values of a normally distributed contaminant that are outside the limits of an 80% CI are equally distributed between the left (lower) and right (upper) tails of the normal curve. Consequently, the CI employed to evaluate solid wastes is, for all practical purposes, a 90% interval.

9.1.1.2 Fundamental Statistical Concepts

The concepts of sampling accuracy and precision have already been introduced, along with some measurements of central tendency ($\bar{x}$) and dispersion (standard deviation [s] and $s_{\bar{x}}$) for concentrations of a chemical contaminant of a solid waste. The utility of $\bar{x}$ and $s_{\bar{x}}$ in estimating a confidence interval that probably contains the true mean (μ) concentration of a contaminant has also been described. However, it was noted that the validity of that estimate is predicated upon the assumption that individual concentrations of the contaminant exhibit a normal distribution.

Statistical techniques for obtaining accurate and precise samples are relatively simple and easy to implement. Sampling accuracy is usually achieved by some form of random sampling. In random sampling, every unit in the population (e.g., every location in a lagoon used to store a solid waste) has a theoretically equal chance of being sampled and measured. Consequently, statistics generated by the sample (e.g., $\bar{x}$ and, to a lesser degree, $S_{\bar{x}}$) are unbiased (accurate) estimators of true population parameters (e.g., the CI for μ). In other words, the sample is representative of the population. One of the commonest methods of selecting a random sample is to divide the

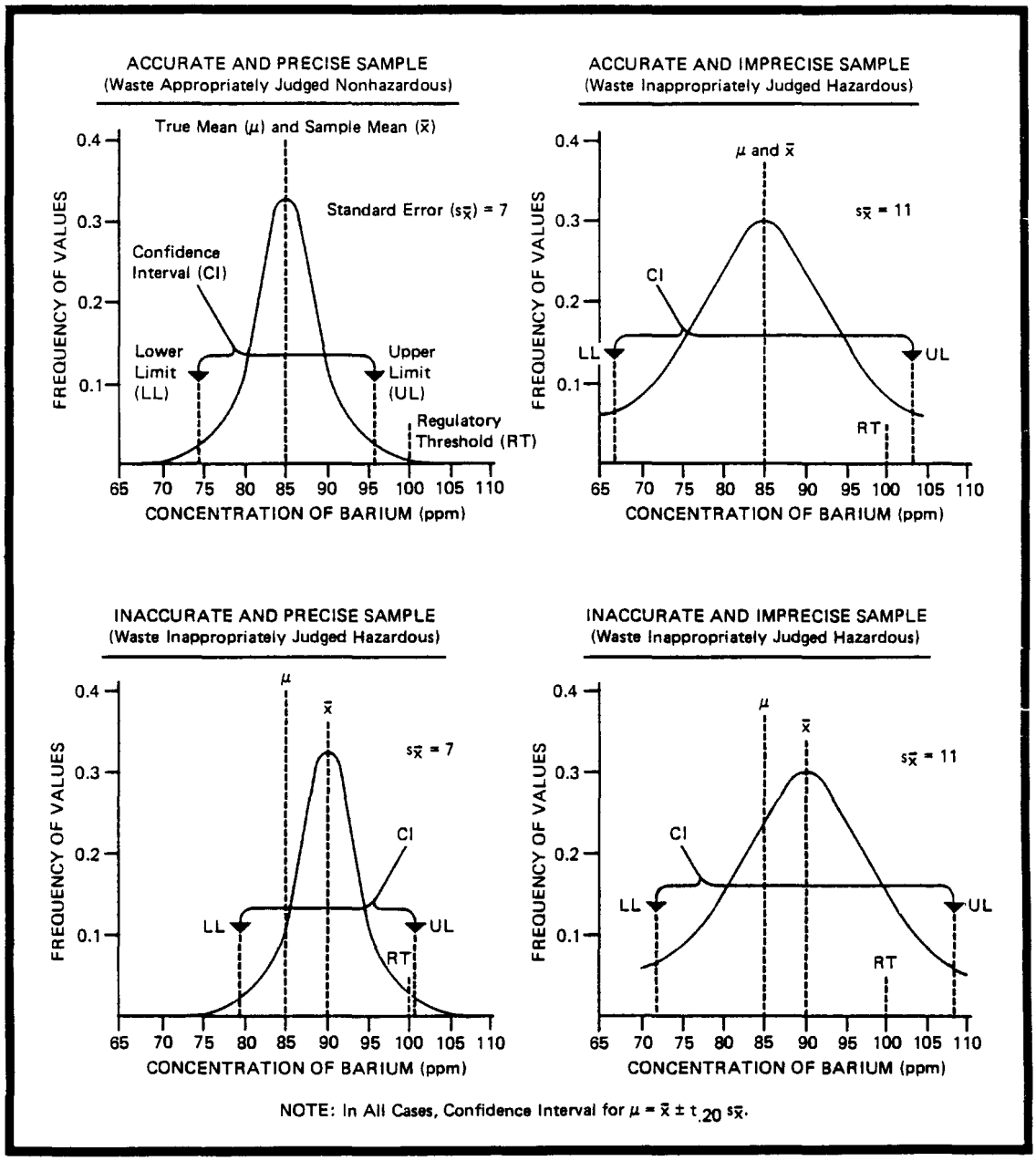


Figure 9-1. - Important theoretical relationships between sampling accuracy and precision and regulatory objectives for a chemical contaminant of a solid waste that occurs at a concentration marginally less than its regulatory threshold. In this example, barium is the chemical contaminant. The true mean concentration of barium in the elutriate of the EP toxicity test is 85 ppm, as compared to a regulatory threshold of 100 ppm. The upper limit of the confidence interval for the true mean concentration, which is estimated from the sample mean and standard error, must be less than the regulatory threshold if barium is judged to be present in the waste at a nonhazardous level.

population by an imaginary grid, assign a series of consecutive numbers to the units of the grid, and select the numbers (units) to be sampled through the use of a random-numbers table (such a table can be found in any text on basic statistics). It is important to emphasize that a haphazardly selected sample) is not a suitable substitute for a randomly selected sample. That is because there is no assurance that a person performing undisciplined sampling will not consciously or subconsciously favor the selection of certain units of the population, thus causing the sample to be unrepresentative of the population.

Sampling precision is most commonly achieved by taking an appropriate number of samples from the population. As can be observed from the equation for calculating $S_{\bar{x}}$, precision increases ($S_{\bar{x}}$ and the CI for μ decrease) as the number of samples (n) increases, although not in a 1:1 ratio. For example, a 100% increase in the number of samples from two to four causes the CI to decrease by approximately 62% (about 31% of that decrease is associated with the critical upper tail of the normal curve). However, another 100% increase in sampling effort from four to eight samples results in only an additional 39% decrease in the CI. Another technique for increasing sampling precision is to maximize the physical size (weight or volume) of the samples that are collected. That has the effect of minimizing between-sample variation and, consequently, decreasing $s_{\bar{x}}$. Increasing the number or size of samples taken from a population, in addition to increasing sampling precision, has the secondary effect of increasing sampling accuracy.

In summary, reliable information concerning the chemical properties of a solid waste is needed for the purpose of comparing those properties with applicable regulatory thresholds. If chemical information is to be considered reliable, it must be accurate and sufficiently precise. Accuracy is usually achieved by incorporating some form of randomness into the selection process for the samples that generate the chemical information. Sufficient precision is most often obtained by selecting an appropriate number of samples.

There are a few ramifications of the above-described concepts that merit elaboration. If, for example, as in the case of semiconductor etching solutions, each batch of a waste is completely homogeneous with regard to the chemical properties of concern and that chemical homogeneity is constant (uniform) over time (from batch to batch), a single sample collected from the waste at an arbitrary location and time would theoretically generate an accurate and precise estimate of the chemical properties. However, most wastes are heterogeneous in terms of their chemical properties. If a batch of waste is randomly heterogeneous with regard to its chemical characteristics and that random chemical heterogeneity remains constant from batch to batch, accuracy and appropriate precision can usually be achieved by simple random sampling. In that type of sampling, all units in the population (essentially all locations or points in all batches of waste from which a sample could be collected) are identified, and a suitable number of samples is randomly selected from the population. More complex stratified random sampling is appropriate if a batch of waste is known to be nonrandomly heterogeneous in terms of its chemical properties and/or nonrandom chemical heterogeneity is known to exist from batch to batch. In such cases, the population is stratified to isolate the known sources of nonrandom chemical heterogeneity.

After stratification, which may occur over space (locations or points in a batch of waste) and/or time (each batch of waste), the units in each stratum are numerically identified, and a simple random sample is taken from each stratum. As previously intimated, both simple and stratified random sampling generate accurate estimates of the chemical properties of a solid waste. The advantage of stratified random sampling over simple random sampling is that, for a given number of samples and a given sample size, the former technique often results in a more precise estimate of chemical properties of a waste (a lower value of $s_{\bar{x}}$) than the latter technique. However, greater precision is likely to be realized only if a waste exhibits substantial nonrandom chemical heterogeneity and stratification efficiently "divides" the waste into strata that exhibit maximum between-strata variability and minimum within-strata variability. If that does not occur, stratified random sampling can produce results that are less precise than in the case of simple random sampling. Therefore, it is reasonable to select stratified random sampling over simple random sampling only if the distribution of chemical contaminants in a waste is sufficiently known to allow an intelligent identification of strata and at least two or three samples can be collected in each stratum. If a strategy employing stratified random sampling is selected, a decision must be made regarding the allocation of sampling effort among strata. When chemical variation within each stratum can be estimated with a great degree of detail, samples should be optimally allocated among strata, i.e., the number of samples collected from each stratum should be directly proportional to the chemical variation encountered in the stratum. When detailed information concerning chemical variability within strata is not available, samples should be proportionally allocated among strata, i.e., sampling effort in each stratum should be directly proportional to the size of the stratum.

Simple random sampling and stratified random sampling are types of probability sampling. Which, because of a reliance upon mathematical and statistical theories, allows an evaluation of the effectiveness of sampling procedures. Another type of probability sampling is systematic random sampling, in which the first unit to be collected from a population is randomly selected, but all subsequent units are taken at fixed space or time intervals. An example of systematic random sampling is the sampling of a waste lagoon along a transect in which the first sampling point on the transect is 1 m from a randomly selected location on the shore and subsequent sampling points are located at 2-m intervals along the transect. The advantages of systematic random sampling over simple random sampling and stratified random sampling are the ease with which samples are identified and collected (the selection of the first sampling unit determines the remainder of the units) and, sometimes, an increase in precision. In certain cases, for example, systematic random sampling might be expected to be a little more precise than stratified random sampling with one unit per stratum because samples are distributed more evenly over the population. As will be demonstrated shortly, disadvantages of systematic random sampling are the poor accuracy and precision that can occur when unrecognized trends or cycles occur in the population. For those reasons, systematic random sampling is recommended only when a population is essentially random or contains at most a modest stratification. In such cases, systematic random sampling would be employed for the sake of convenience, with little expectation of an increase in precision over other random sampling techniques.

Probability sampling is contrasted with authoritative sampling, in which an individual who is well acquainted with the solid waste to be sampled selects a sample without regard to randomization. The validity of data gathered in that manner is totally dependent on the knowledge of the sampler and although valid data can sometimes be obtained, authoritative sampling is not recommended for the chemical characterization of most wastes.

It may now be useful to offer a generalization regarding the four sampling strategies that have been identified for solid wastes. If little or no information is available concerning the distribution of chemical contaminants of a waste, simple random sampling is the most appropriate sampling strategy. As more information is accumulated for the contaminants of concern, greater consideration can be given (in order of the additional information required) to stratified random sampling, systematic random sampling, and, perhaps, authoritative sampling.

The validity of a CI for the true mean (μ) concentration of a chemical contaminant of a solid waste is, as previously noted, based on the assumption that individual concentrations of the contaminant exhibit a normal distribution. This is true regardless of the strategy that is employed to sample the waste. Although there are computational procedures for evaluating the correctness of the assumption of normality, those procedures are meaningful only if a large number of samples are collected from a waste. Because sampling plans for most solid wastes entail just a few samples, one can do little more than superficially examine resulting data for obvious departures from normality (this can be done by simple graphical methods), keeping in mind that even if individual measurements of a chemical contaminant of a waste exhibit a considerably abnormal distribution, such abnormality is not likely to be the case for sample means, which are our primary concern. One can also compare the mean of the sample ($\bar{x}$) with the variance of the sample (s^2). In a normally distributed population, $\bar{x}$ would be expected to be greater than s^2 (assuming that the number of samples [n] is reasonably large). If that is not the case, the chemical contaminant of concern may be characterized by a Poison distribution ($\bar{x}$ is approximately equal to s^2) or a negative binomial distribution ($\bar{x}$ is less than s^2). In the former circumstance, normality can often be achieved by transforming data according to the square root transformation. In the latter circumstance, normality may be realized through use of the arcsine transformation. If either transformation is required, all subsequent statistical evaluations must be performed on the transformed scale.

Finally, it is necessary to address the appropriate number of samples to be employed in the chemical characterization of a solid waste. As has already been emphasized, the appropriate number of samples is the least number of samples required to generate a sufficiently precise estimate of the true mean (μ) concentration of a chemical contaminant of a waste. From the perspective of most waste producers, that means the minimal number of samples needed to demonstrate that the upper limit of the CI for μ is less than the applicable regulatory threshold (RT). The formula for estimating appropriate sampling effort (Table 9-1, Equation 8) indicates that increased sampling effort is generally justified as s^2 or the "$t_{.20}$" value (probable error rate) increases

and as $\Delta(RT - \bar{x})$ decreases. In a well-designed sampling plan for a solid waste, an effort is made to estimate the values of $\bar{x}$ and s^2 before sampling is initiated. Such preliminary estimates, which may be derived from information pertaining to similar wastes, process engineering data, or limited analytical studies, are used to identify the approximate number of samples that must be collected from the waste. It is always prudent to collect a somewhat greater number of samples than indicated by preliminary estimates of $\bar{x}$ and s^2 since poor preliminary estimates of those statistics can result in an underestimate of the appropriate number of samples to collect. It is usually possible to process and store the extra samples appropriately until analysis of the initially identified samples is completed and it can be determined if analysis of the additional samples is warranted.

9.1.1.3 Basic Sampling Strategies

It is now appropriate to present general procedures for implementing the three previously introduced sampling strategies (simple random sampling, stratified random sampling, and systematic random sampling) and a hypothetical example of each sampling strategy. The hypothetical examples illustrate the statistical calculations that must be performed in most situations likely to be encountered by a waste producer and, also, provide some insight into the efficiency of the three sampling strategies in meeting regulatory objectives.

The following hypothetical conditions are assumed to exist for all three sampling strategies. First, barium, which has an RT of 100 ppm as measured in the EP elutriate test, is the only chemical contaminant of concern. Second, barium is discharged in particulate form to a waste lagoon and accumulates in the lagoon in the form of a sludge, which has built up to approximately the same thickness throughout the lagoon. Third, concentrations of barium are relatively homogeneous along the vertical gradient (from the water-sludge interface to the sludge-lagoon interface), suggesting a highly controlled manufacturing process (little between-batch variation in barium concentrations). Fourth, the physical size of sludge samples collected from the lagoon is as large as practical, and barium concentrations derived from those samples are normally distributed (note that we do not refer to barium levels in the samples of sludge because barium measurements are actually made on the elutriate from EP toxicity tests performed with the samples). Last, a preliminary study of barium levels in the elutriate of four EP toxicity tests conducted with sludge collected from the lagoon several years ago identified values of 86 and 90 ppm for material collected near the outfall (in the upper third) of the lagoon and values of 98 and 104 ppm for material obtained from the far end (the lower two-thirds) of the lagoon.

For all sampling strategies, it is important to remember that barium will be determined to be present in the sludge at a hazardous level if the upper limit of the CI for μ is equal to or greater than the RT of 100 ppm (Table 9-1, Equations 6 and 7).

9.1.1.3.1 Simple Random Sampling

Simple random sampling (Box 1) is performed by general procedures in which preliminary estimates of $\bar{x}$ and s^2, as well as a knowledge of the RT, for each chemical contaminant of a solid waste that is of concern are employed to estimate the appropriate number of samples (n) to be collected from the waste. That number of samples is subsequently analyzed for each chemical contaminant of concern. The resulting analytical data are then used to conclude definitively that each contaminant is or is not present in the waste at a hazardous concentration or, alternatively, to suggest a reiterative process, involving increased sampling effort, through which the presence or absence of hazard can be definitively determined.

In the hypothetical example for simple random sampling (Box 1), preliminary estimates of $\bar{x}$ and s^2 indicated a sampling effort consisting of six samples. That number of samples was collected and initially analyzed generating analytical data somewhat different from the preliminary data (s^2 was substantially greater than was preliminarily estimated). Consequently, the upper limit of the CI was unexpectedly greater than the applicable RT, resulting in a tentative conclusion of hazard. However, a reestimation of appropriate sampling effort, based on statistics derived from the six samples, suggested that such a conclusion might be reversed through the collection and analysis of just one more sample. Fortunately, a resampling effort was not required because of the foresight of the waste producer in obtaining three extra samples during the initial sampling effort, which, because of their influence in decreasing the final values of $\bar{x}$, $S_{\bar{x}}$, $t_{.20}$, and, consequently, the upper limit of the CI -- values obtained from all nine samples -- resulted in a definitive conclusion of nonhazard.

9.1.1.3.2 Stratified Random Sampling

Stratified random sampling (Box 2) is conducted by general procedures that are similar to the procedures described for simple random sampling. The only difference is that, in stratified random sampling, values of $\bar{x}$ and s^2 are calculated for each stratum in the population and then integrated into overall estimates of those statistics, the standard deviation (s), $s_{\bar{x}}$, and the appropriate number of samples (n) for all strata.

The hypothetical example for stratified random sampling (Box 2) is based on the same nine sludge samples previously identified in the example of simple random sampling (Box 1) so that the relative efficiencies of the two sampling strategies can be fully compared. The efficiency generated through the process of stratification is first evident in the preliminary estimate of n (Step 2 in Boxes 1 and 2), which is six for simple random sampling and four for stratified random sampling. (The lesser value for stratified sampling is the consequence of a dramatic decrease in s^2 which more than compensated for a modest increase in Δ.) The most relevant indication of sampling efficiency is the value of $S_{\bar{x}}$, which is directly employed to calculate the CI. In the case of simple random sampling, $S_{\bar{x}}$ is calculated as 2.58 (Step 9 in Box 1), and, for stratified random sampling, $S_{\bar{x}}$ is determined to be 2.35 (Steps 5 and 7 in Box 2). Consequently, the gain in efficiency attributable to stratification is approximately 9% (0.23/2.58).

BOX 1. STRATEGY FOR DETERMINING IF CHEMICAL CONTAMINANTS OF SOLID WASTES ARE PRESENT AT HAZARDOUS LEVELS - SIMPLE RANDOM SAMPLING

Step	General Procedures

1. Obtain preliminary estimates of $\bar{x}$ and s^2 for each chemical contaminant of a solid waste that is of concern. The two above-identified statistics are calculated by, respectively, Equations 2a and 3a (Table 9-1).

2. Estimate the appropriate number of samples (n_1) to be collected from the waste through use of Equation 8 (Table 9-1) and Table 9-2. Derive individual values of n_1 for each chemical contaminant of concern. The appropriate number of samples to be taken from the waste is the greatest of the individual n_1 values.

3. Randomly collect at least n_1 (or $n_2 - n_1$, $n_3 - n_2$, etc., as will be indicated later in this box) samples from the waste (collection of a few extra samples will provide protection against poor preliminary estimates of $\bar{x}$ and s^2). Maximize the physical size (weight or volume) of all samples that are collected.

4. Analyze the n_1 (or $n_2 - n_1$, $n_3 - n_2$ etc.) samples for each chemical contaminant of concern. Superficially (graphically) examine each set of analytical data for obvious departures from normality.

5. Calculate $\bar{x}$, s^2, the standard deviation (s), and $s_{\bar{x}}$ for each set of analytical data by, respectively, Equations 2a, 3a, 4, and 5 (Table 9-1).

6. If $\bar{x}$ for a chemical contaminant is equal to or greater than the applicable RT (Equation 7, Table 9-1) and is believed to be an accurate estimator of μ, the contaminant is considered to be present in the waste at a hazardous concentration, and the study is completed. Otherwise, continue the study. In the case of a set of analytical data that does not exhibit obvious abnormality and for which $\bar{x}$ is greater than s^2, perform the following calculations with nontransformed data. Otherwise, consider transforming the data by the square root transformation (if $\bar{x}$ is about equal to s^2) or the arcsine transformation (if $\bar{x}$ is less than s^2) and performing all subsequent calculations with transformed data. Square root and arcsine transformations are defined by, respectively, Equations 10 and 11 (Table 9-1).

7. Determine the CI for each chemical contaminant of concern by Equation 6 (Table 9-1) and Table 9-2. If the upper limit of the CI is less than the applicable RT (Equations 6 and 7, Table 9-1), the chemical contaminant is not considered to be present in the waste at a hazardous concentration and the study is completed. Otherwise, the opposite conclusion is tentatively reached.

8. If a tentative conclusion of hazard is reached, reestimate the total number of samples (n_2) to be collected from the waste by use of Equation 8 (Table 9-1) and Table 9-2. When deriving n_2, employ the newly calculated (not preliminary) values of x and s^2. If additional $n_2 - n_1$ samples of waste cannot reasonably be collected, the study is completed, and a definitive conclusion of hazard is reached. Otherwise, collect extra $n_2 - n_1$ samples of waste.

9. Repeat the basic operations described in Steps 3 through 8 until the waste is judged to be nonhazardous or, if the opposite conclusion continues to be reached, until increased sampling effort is impractical.

Hypothetical Example

Step

1. The preliminary study of barium levels in the elutriate of four EP toxicity tests, conducted with sludge collected from the lagoon several years ago, generated values of 86 and 90 ppm for sludge obtained from the upper third of the lagoon and values of 98 and 104 ppm for sludge from the lower two-thirds of the lagoon. Those two sets of values are not judged to be indicative of nonrandom chemical heterogeneity (stratification) within the lagoon. Therefore, preliminary estimates of $\bar{x}$ and s^2 are calculated as:

$$\bar{x} = \frac{\sum_{i=1}^{n} x_i}{n} = \frac{86 + 90 + 98 + 104}{4} = 94.50 \text{ , and} \qquad \text{(Equation 2a)}$$

$$s^2 = \frac{\sum_{i=1}^{n} x_i^2 - (\sum_{i=1}^{n} x_i)^2/n}{n - 1} \qquad \text{(Equation 3a)}$$

$$= \frac{35{,}916.00 - 35{,}721.00}{3} = 65.00.$$

2. Based on the preliminary estimates of $\bar{x}$ and s^2 as well as the knowledge that the RT for barium is 100 ppm,

$$n_1 = \frac{t_{.20}^2 \, s^2}{\Delta^2} = \frac{(1.638^2)\,(65.00)}{5.50^2} = 5.77. \qquad \text{(Equation 8)}$$

3. As indicated above, the appropriate number of sludge samples (n_1) to be collected from the lagoon is six. That number of samples (plus three extra samples for protection against poor preliminary estimates of $\bar{x}$ and s^2) is collected from the lagoon by a single randomization process (Figure 9-2). All samples consist of the greatest volume of sludge that can be

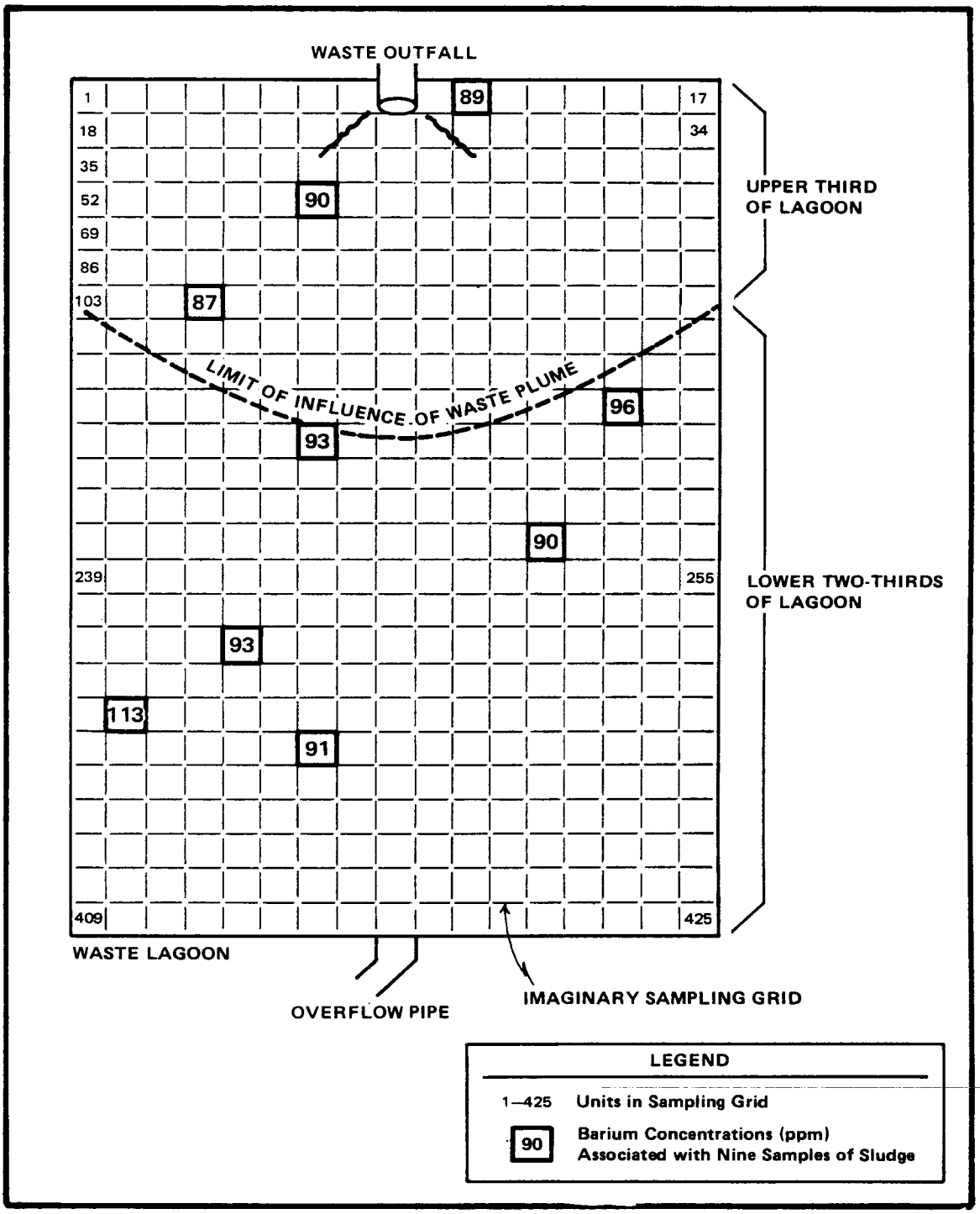


Figure 9-2. Hypothetical sampling conditions in waste lagoon containing sludge contaminated with barium. Barium concentrations associated with samples of sludge refer to levels measured in the elutriate of EP toxicity tests conducted with the samples.

practically collected. The three extra samples are suitably processed and stored for possible later analysis.

4. The six samples of sludge (n_1) designated for immediate analysis generate the following concentrations of barium in the EP toxicity test: 89, 90, 87, 96, 93, and 113 ppm. Although the value of 113 ppm appears unusual as compared with the other data, there is no obvious indication that the data are not normally distributed.

5. New values for $\bar{x}$ and s^2 and associated values for the standard deviation (s) and $s_{\bar{x}}$ are calculated as:

$$\bar{x} = \frac{\sum_{i=1}^{n} x_i}{n} = \frac{89 + 90 + 87 + 96 + 93 + 113}{6} = 94.67\ , \qquad \text{(Equation 2a)}$$

$$s^2 = \frac{\sum_{i=1}^{n} x_i^2 - (\sum_{i=1}^{n} x_i)^2/n}{n - 1} \qquad \text{(Equation 3a)}$$

$$= \frac{54{,}224.00 - 53{,}770.67}{5} = 90.67,$$

$$s = \sqrt{s^2} = 9.52, \text{ and} \qquad \text{(Equation 4)}$$

$$s_{\bar{x}} = s/\sqrt{n} = 9.52/\sqrt{6} = 3.89. \qquad \text{(Equation 5)}$$

6. The new value for $\bar{x}$ (94.67) is less than the RT (100). In addition, $\bar{x}$ is greater (only slightly) than s^2 (90.67), and, as previously indicated, the raw data are not characterized by obvious abnormality. Consequently, the study is continued, with the following calculations performed with nontransformed data.

7. $$CI = \bar{x} \pm t_{.20}\, s_{\bar{x}} = 94.67 \pm (1.476)(3.89) \qquad \text{(Equation 6)}$$

$$= 94.67 \pm 5.74.$$

Because the upper limit of the CI (100.41) is greater than the applicable RT (100), it is tentatively concluded that barium is present in the sludge at a hazardous concentration.

8. n is now reestimated as:

$$n_2 = \frac{t^2_{.20}\, s^2}{\Delta^2} \quad \frac{(1.476^2)\,(90.67)}{5.33^2} = 6.95. \qquad \text{(Equation 8)}$$

The value for n_2 (approximately 7) indicates that an additional (n_2 - n_1 = 1) sludge sample should be collected from the lagoon.

9. The additional sampling effort is not necessary because of the three extra samples that were initially collected from the lagoon. All extra samples are analyzed, generating the following levels of barium for the EP toxicity test: 93, 90, and 91 ppm. Consequently, $\bar{x}$, s^2 the standard deviation (s), and $s_{\bar{x}}$ are recalculated as:

$$\bar{X} = \frac{\sum_{i=1}^{n} X_i}{n} = \frac{86 + 90 + \ldots + 91}{9} = 93.56\,, \qquad \text{(Equation 2a)}$$

$$s^2 = \frac{\sum_{i=1}^{n} X_i^2 - \left(\sum_{i=1}^{n} x_i\right)^2 / n}{n - 1} \qquad \text{(Equation 3a)}$$

$$= \frac{79{,}254.00 - 78{,}773.78}{8} = 60.03\,,$$

$$s = \sqrt{s^2} = 7.75, \textit{ and} \qquad \text{(Equation 4)}$$

$$s_{\bar{x}} = s/\sqrt{n} = 7.75/\sqrt{9} = 2.58. \qquad \text{(Equation 5)}$$

The value for $\bar{x}$ (93.56) is again less than the RT (100), and there is no indication that the nine data points, considered collectively, are abnormally distributed (in particular, $\bar{x}$ is now substantially greater than s^2). Consequently, CI, calculated with nontransformed data, is determined to be:

$$CI = \bar{X} \pm t_{.20}\, s_{\bar{x}} = 93.56 \pm (1.397)(2.58) \qquad \text{(Equation 6)}$$

$$= 93.56 \pm 3.60.$$

The upper limit of the CI (97.16) is now less than the RT of 100. Consequently, it is definitively concluded that barium is not present in the sludge at a hazardous level.

BOX 2. STRATEGY FOR DETERMINING IF CHEMICAL CONTAMINANTS OF SOLID WASTES ARE PRESENT AT HAZARDOUS LEVELS - STRATIFIED RANDOM SAMPLING

Step	General Procedures

1. Obtain preliminary estimates of $\bar{x}$ and s^2 for each chemical contaminant of a solid waste that is of concern. The two above-identified statistics are calculated by, respectively, Equations 2b and 3b (Table 9-1).

2. Estimate the appropriate number of samples (n_1) to be collected from the waste through use of Equation 8 (Table 9-1) and Table 9-2. Derive individual values of n_1 for each chemical contaminant of concern. The appropriate number of samples to be taken from the waste is the greatest of the individual n_1 values.

3. Randomly collect at least n_1 (or $n_2 - n_1$, $n_3 - n_2$, etc., as will be indicated later in this box) samples from the waste (collection of a few extra samples will provide protection against poor preliminary estimates of $\bar{x}$ and s^2). If s_k for each stratum (see Equation 3b) is believed to be an accurate estimate, optimally allocate samples among strata (i.e., allocate samples among strata so that the number of samples collected from each stratum is directly proportional to s_k for that stratum). Otherwise, proportionally allocate samples among strata according to size of the strata. Maximize the physical size (weight or volume) of all samples that are collected from the strata.

4. Analyze the n_1 (or $n_2 - n_1$, $n_3 - n_2$ etc.) samples for each chemical contaminant of concern. Superficially (graphically) examine each set of analytical data from each stratum for obvious departures from normality.

5. Calculate $\bar{x}$, s_2, the standard deviation (s), and $_{\bar{x}}s$ for each set of analytical data by, respectively, Equations 2b, 3b, 4, and 5 (Table 9-1).

6. If $\bar{x}$ for a chemical contaminant is equal to or greater than the applicable RT (Equation 7, Table 9-1) and is believed to be an accurate estimator of μ, the contaminant is considered to be present in the waste at a hazardous concentration, and the study is completed. Otherwise, continue the study. In the case of a set of analytical data that does not exhibit obvious abnormality and for which $\bar{x}$ is greater than s^2, perform the following calculations with nontransformed data. Otherwise, consider transforming the data by the square root transformation (if $\bar{x}$ is about equal to s^2) or the arcsine transformation (if $\bar{x}$ is less than s^2) and performing all subsequent calculations with transformed data. Square root and arcsine transformations are defined by, respectively, Equations 10 and 11 (Table 9-1).

7. Determine the CI for each chemical contaminant of concern by Equation 6 (Table 9-1) and Table 9-2. If the upper limit of the CI is less than the applicable RT (Equations 6 and 7, Table 9-1), the chemical contaminant is not considered to be present in the waste at a hazardous concentration, and the study is completed. Otherwise, the opposite conclusion is tentatively reached.

8. If a tentative conclusion of hazard is reached, reestimate the total number of samples (n_2) to be collected from the waste by use of Equation 8 (Table 9-1) and Table 9-2. When deriving n_2, employ the newly calculated (not preliminary) values of $\bar{x}$ and s^2. If additional $n_2 - n_1$ samples of waste cannot reasonably be collected, the study is completed, and a definitive conclusion of hazard is reached. Otherwise, collect extra $n_2 - n_1$ samples of waste.

9. Repeat the basic operations described in steps 3 through 8 until the waste is judged to be nonhazardous or, if the opposite conclusion continues to be reached, until increased sampling effort is impractical.

Hypothetical Example

Step

1. The preliminary study of barium levels in the elutriate of four EP toxicity tests, conducted with sludge collected from the lagoon several years ago, generated values of 86 and 90 ppm for sludge obtained from the upper third of the lagoon and values of 98 and 104 ppm for sludge from the lower two-thirds of the lagoon. Those two sets of values are not judged to be indicative of nonrandom chemical heterogeneity (stratification) within the lagoon. Therefore, preliminary estimates of $\bar{x}$ and s^2 are calculated as:

$$\bar{x} = \sum_{k=1}^{r} W_k \bar{x}_k = \frac{(1)(88.00)}{3} + \frac{(2)(101.00)}{3} = 96.67 \text{ , and} \qquad \text{(Equation 2b)}$$

$$s^2 = \sum_{k=1}^{r} W_k s_k^2 = \frac{(1)(8.00)}{3} + \frac{(2)(18.00)}{3} = 14.67 . \qquad \text{(Equation 3b)}$$

2. Based on the preliminary estimates of $\bar{x}$ and s^2 as well as the knowledge that the RT for barium is 100 ppm,

$$n_1 = \frac{t_{.20}^2 \, s^2}{\Delta^2} = \frac{(1.368^2)\,(14.67)}{3.33^2} = 3.55. \qquad \text{(Equation 8)}$$

3. As indicated above, the appropriate number of sludge samples (n_1) to be collected from the lagoon is four. However, for purposes of comparison with simple random sampling (Box 1), six samples (plus three extra samples for protection against poor preliminary estimates of $\bar{x}$ and s^2) are collected from the lagoon by a two-stage randomization process (Figure 2). Because s_k for the upper (2.12 ppm) and lower (5.66 ppm) strata are not believed to be very accurate estimates, the nine samples to be collected from the lagoon are not optimally allocated between the two strata (optimum allocation would require two and seven samples to be

collected from the upper and lower strata, respectively). Alternatively, proportional allocation is employed: three samples are collected from the upper stratum (which represents one-third of the lagoon), and six samples are taken from the lower stratum (two-thirds of the lagoon). All samples consist of the greatest volume of sludge that can be practically collected.

4. The nine samples of sludge generate the following concentrations of barium in the EP toxicity test: upper stratum -- 89, 90, and 87 ppm; lower stratum -- 96, 93, 113, 93, 90, and 91 ppm. Although the value of 113 ppm appears unusual as compared with the other data for the lower stratum, there is no obvious indication that the data are not normally distributed.

5. New values for $\bar{x}$ and s^2 and associated values for the standard deviation (s) and $s_{\bar{x}}$ are calculated as:

$$\bar{x} = \sum_{k=1}^{r} W_k \bar{x}_k = \frac{(1)(88.67)}{3} + \frac{(2)(96.00)}{3} = 93.56 , \qquad \text{(Equation 2b)}$$

$$s^2 = \sum_{k=1}^{r} W_k s_k^2 = \frac{(1)(2.33)}{3} + \frac{(2)(73.60)}{3} = 49.84 , \qquad \text{(Equation 3b)}$$

$$s = \sqrt{s^2} = 7.06, \textit{ and} \qquad \text{(Equation 4)}$$

$$s_{\bar{x}} = s/\sqrt{n} = 7.06/\sqrt{9} = 2.35. \qquad \text{(Equation 5)}$$

6. The new value for $\bar{x}$ (93.56) is less than the RT (100). In addition, $\bar{x}$ is greater than s^2 (49.84), and, as previously indicated, the raw data are not characterized by obvious abnormality. Consequently, the study is continued, with the following calculations performed with nontransformed data.

7. $CI = \bar{x} \pm t_{.20}\, s_{\bar{x}} = 93.56 \pm (1.397)(2.35)$ (Equation 6)

$= 93.56 \pm 3.28.$

The upper limit of the CI (96.84) is less than the applicable RT (100). Therefore, it is concluded that barium is not present in the sludge at a hazardous concentration.

9.1.1.3.3 Systematic Random Sampling

Systematic random sampling (Box 3) is implemented by general procedures that are identical to the procedures identified for simple random sampling. The hypothetical example for systematic random sampling (Box 3) demonstrates the bias and imprecision that are associated with that type of sampling when unrecognized trends or cycles exist in the population.

9.1.1.4 Special Considerations

The preceding discussion has addressed the major issues that are critical to the development of a reliable sampling strategy for a solid waste. The remaining discussion focuses on several "secondary" issues that should be considered when designing an appropriate sampling strategy. These secondary issues are applicable to all three of the basic sampling strategies that have been identified.

9.1.1.4.1 Composite Sampling

In composite sampling, a number of random samples are initially collected from a waste and combined into a single sample, which is then analyzed for the chemical contaminants of concern. The major disadvantage of composite sampling, as compared with noncomposite sampling, is that information concerning the chemical contaminants is lost, i.e., each initial set of samples generates only a single estimate of the concentration of each contaminant. Consequently, because the number of analytical measurements (n) is small, $s_{\bar{x}}$ and $t_{.20}$ are large, thus decreasing the likelihood that a contaminant will be judged to occur in the waste at a nonhazardous level (refer to appropriate equations in Table 9-1 and to Table 9-2). A remedy to that situation is to collect and analyze a relatively large number of composite samples, thereby offsetting the savings in analytical costs that are often associated with composite sampling, but achieving better representation of the waste than would occur with noncomposite sampling.

The appropriate number of composite samples to be collected from a solid waste is estimated by use of Equation 8 (Table 9-1), as previously described for the three basic sampling strategies. In comparison with noncomposite sampling, composite sampling may have the effect of minimizing between-sample variation (the same phenomenon that occurs when the physical size of a sample is maximized), thereby reducing somewhat the number of samples that must be collected from the waste.

9.1.1.4.2 Subsampling

The variance (s^2) associated with a chemical contaminant of a waste consists of two components in that:

$$s^2 = s_s^2 + \frac{s_a^2}{m}, \qquad \text{(Equation 12)}$$

BOX 3. STRATEGY FOR DETERMINING IF CHEMICAL CONTAMINANTS OF SOLID WASTES ARE PRESENT AT HAZARDOUS LEVELS - SYSTEMATIC RANDOM SAMPLING

Step	General Procedures
1.	Follow general procedures presented for simple random sampling of solid wastes (Box 1).

Step	Hypothetical Example
1.	The example presented in Box 1 is applicable to systematic random sampling, with the understanding that the nine sludge samples obtained from the lagoon would be collected at equal intervals along a transect running from a randomly selected location on one bank of the lagoon to the opposite bank. If that randomly selected transect were established between Units 1 and 409 of the sampling grid (Figure 9-2) and sampling were performed at Unit 1 and thereafter at three-unit intervals along the transect (i.e., Unit 1, Unit 52, Unit 103, ... , and Unit 409), it is apparent that only two samples would be collected in the upper third of the lagoon, whereas seven samples would be obtained from the lower two-thirds of the lagoon. If, as suggested by the barium concentrations illustrated in Figure 9-2, the lower part of the lagoon is characterized by greater and more variable barium contamination than the upper part of the lagoon, systematic random sampling along the above-identified transect, by placing undue (disproportionate) emphasis on the lower part of the lagoon, might be expected to result in an inaccurate (overestimated) and imprecise characterization of barium levels in the whole lagoon, as compared with either simple random sampling or stratified random sampling. Such inaccuracy and imprecision, which are typical of systematic random sampling when unrecognized trends or cycles occur in the population, would be magnified if, for example, the randomly selected transect were established solely in the lower part of the lagoon, e.g., between Units 239 and 255 of the sampling grid.

where s_s^2 = a component attributable to sampling (sample) variation, s_a^2 = a component attributable to analytical (subsample) variation, and m = number of subsamples. In general, s_a^2 should not be allowed to exceed one-ninth of s_s^2. If a preliminary study indicates that s_a^2 exceeds that threshold, a sampling strategy involving subsampling should be considered. In such a strategy, a number of replicate measurements are randomly made on a relatively limited number of randomly collected samples. Consequently, analytical effort is allocated as a function of analytical variability. The efficiency of that general strategy in meeting regulatory objectives has already been demonstrated in the previous discussions of sampling effort.

The appropriate number of samples (n) to be collected from a solid waste for which subsampling will be employed is again estimated by Equation 8 (Table 9-1). In the case of simple random sampling or systematic random sampling with an equal number of subsamples analyzed per sample:

$$\overline{x} = \sum_{i=1}^{n} x_i / n, \qquad \text{(Equation 13)}$$

where $\bar{x}_i$ = sample mean (calculated from values for subsamples) and n = number of samples. Also,

$$s^2 = \frac{\sum_{i=1}^{n} \overline{x_i}^2 - (\sum_{i=1}^{n} \overline{x_i})^2 / n}{n - 1} \qquad \text{(Equation 14)}$$

The optimum number of subsamples to be taken from each sample ($m_{opt.}$) is estimated as:

$$m_{(opt.)} = \frac{s_a}{s_s} \qquad \text{(Equation 15)}$$

when cost factors are not considered. The value for s_a is calculated from available data as:

$$s_a = \sqrt{\frac{\sum_{i=1}^{n} \sum_{j=1}^{m} x_{ij}^2 - (\sum x_{ij})^2 / m}{n\,(m - 1)}}, \qquad \text{(Equation 16)}$$

and s_s, which can have a negative characteristic, is defined as:

$$S_s = \sqrt{s^2 - \frac{s_a^2}{m}}, \qquad \text{(Equation 17)}$$

with s_2 calculated as indicated in Equation 14.

In the case of stratified random sampling with subsampling, critical formulas for estimating sample size (n) by Equation 8 (Table 9-1) include:

$$\overline{x} = \sum_{k=1}^{r} W_k \overline{x_k} \ , \qquad \text{(Equation 2b)}$$

where $\bar{x}_k$ = stratum mean and W_k = fraction of population represented by Stratum K (number of strata, k, ranges from 1 to r). In Equation 2b, $\bar{x}_k$ for each stratum is calculated as the average of all sample means in the stratum (sample means are calculated from values for subsamples). In addition, s^2 is calculated by:

$$s^2 = \sum_{k=1}^{r} W_k s_k^2 \ , \qquad \text{(Equation 3b)}$$

with s_k^2 for each stratum calculated from all sample means in the stratum. The optimum subsampling effort when cost factors are not considered and all replication is symmetrical is again estimated as:

$$m_{(opt.)} = \frac{s_a}{s_s} \ , \ with \qquad \text{(Equation 15)}$$

$$s_a = \sqrt{\frac{\sum_{k=1}^{r} \sum_{i=1}^{n} \sum_{j=1}^{m} X_{kij}^2 - (\Sigma X_{kij})^2/m}{rn\,(m-1)}} \ , \ and \qquad \text{(Equation 18)}$$

$$s_s = \sqrt{s^2 - \frac{s_a^2}{m}} \ , \qquad \text{(Equation 17)}$$

with s^2 derived as shown in Equation 3b.

9.1.1.5 Cost and Loss Functions

The cost of chemically characterizing a waste is dependent on the specific strategy that is employed to sample the waste. For example, in the case of simple random sampling without subsampling, a reasonable cost function might be:

$$C_{(n)} = C_0 + C_1 n, \qquad \text{(Equation 19)}$$

where $C_{(n)}$ = cost of employing a sample size of n, C_0 = an overhead cost (which is independent of the number of samples that are collected and analyzed), and C_1 = a sample-dependent cost. A consideration of $C_{(n)}$ mandates an evaluation of $L_{(n)}$, which is the sample-size-dependent expected financial loss related to the erroneous conclusion that a waste is hazardous. A simple loss function is:

$$L_{(n)} = \frac{\alpha s^2}{n}, \qquad \text{(Equation 20)}$$

with α = a constant related to the cost of a waste management program if the waste is judged to be hazardous, s^2 = sample variance, and n = number of samples. A primary objective of any sampling strategy is to minimize $C_{(n)} + L_{(n)}$. Differentiation of Equations 19 and 20 indicates that the number of samples (n) that minimize $C_{(n)} + L_{(n)}$ is:

$$n = \sqrt{\frac{\alpha s^2}{C_1}}\ . \qquad \text{(Equation 21)}$$

As is evident from Equation 21, a comparatively large number of samples (n) is justified if the value of α or s^2 is large, whereas a relatively small number of samples is appropriate if the value of C_1 is large. These general conclusions are valid for any sampling strategy for a solid waste.

9.2 IMPLEMENTATION

This section discusses the implementation of a sampling plan for the collection of a "solid waste," as defined by Section 261.2 of the Resource Conservation and Recovery Act (RCRA) regulations. Due to the uniqueness of each sampling effort, the following discussion is in the general form of guidance which, when applied to each sampling effort, should improve and document the quality of the sampling and the representativeness of samples.

The following subsections address elements of a sampling effort in a logical order, from defining objectives through compositing samples prior to analysis.

9.2.1 Definition Of Objectives

After verifying the need for sampling, those personnel directing the sampling effort should define the program's objectives. The need for a sampling effort should not be confused with the objective. When management, a regulation, or a regulatory agency requires sampling, the need for sampling is established but the objectives must be defined.

The primary objective of any waste sampling effort is to obtain information that can be used to evaluate a waste. It is essential that the specific information needed and its uses are defined in detail at this stage. The information needed is usually more complex than just a concentration of a specified parameter; it may be further qualified (e.g., by sampling location or sampling time.) The manner in which the information is to be used can also have a substantial impact on the design of a sampling plan. (Are the data to be used in a qualitative or quantitative manner? If quantitative, what are the accuracy and precision requirements?)

All pertinent information should be gathered. For example, if the primary objective has been roughly defined as "collecting samples of waste which will be analyzed to comply with environmental regulations," then ask the following questions:

1. The sampling is being done to comply with which environmental regulation? Certain regulations detail specific or minimum protocols (e.g., exclusion petitions as defined in §260.22 of the RCRA regulations); the sampling effort must comply with these regulatory requirements.

2. The collected samples are to be analyzed for which parameters? Why those and not others? Should the samples be analyzed for more or fewer parameters?

3. What waste is to be sampled: the waste as generated? The waste prior to or after mixing with other wastes or stabilizing agents? The waste after aging or drying or just prior to disposal? Should waste disposed of 10 years ago be sampled to acquire historical data?

4. What is the end-use of the generated data base? What are the required degrees of accuracy and precision?

By asking such questions, both the primary objective and specific sampling, analytical, and data objectives can be established.

Two sampling efforts could have identical primary objectives but different specific objectives. For example, consider two situations in which the primary objective is to determine if the concentration of barium is less than the regulatory threshold of 100 ppm. The specific objectives will vary and have a substantial effect on sampling. (This situation is presented graphically in Figures 9-3 and 9-4.) In Figure 9-3, under the assumption that the true distribution of barium concentrations throughout the waste of interest is as shown, limited information has indicated that the average concentration is approximately 50 ppm. In Figure 9-4, assume that historical data indicated an average concentration of 90 ppm and the true distribution of barium concentrations is as shown. Therefore, the specific data objective for the latter case is to generate a data base that can discriminate between 90 and 100 ppm, whereas in the former case the data objective is to discriminate between 50 and 100 ppm. Greater accuracy and precision are required to discriminate between 90 and 100 ppm; this fact will affect the number, size, and degree of compositing of samples collected and analyzed.

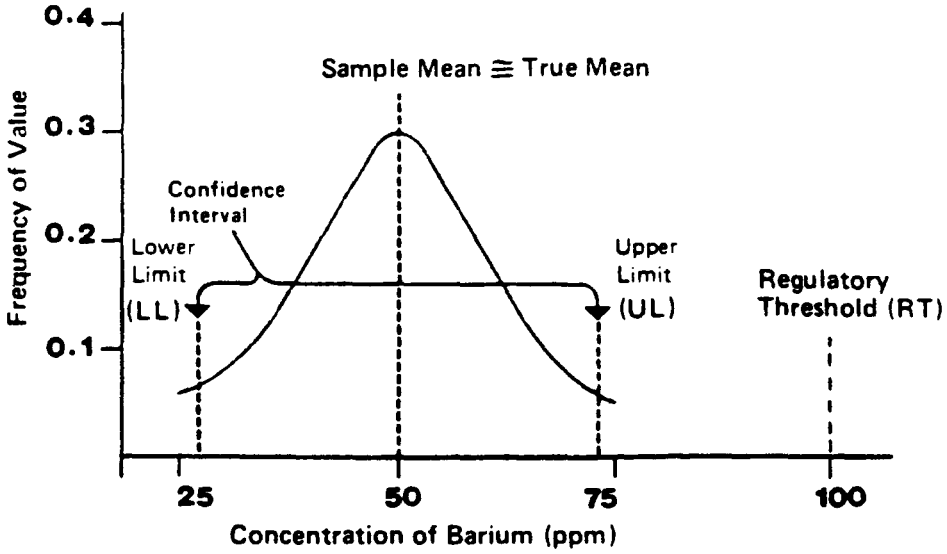


Figure 9-3. Distribution of barium concentration removed from a regulatory threshold.

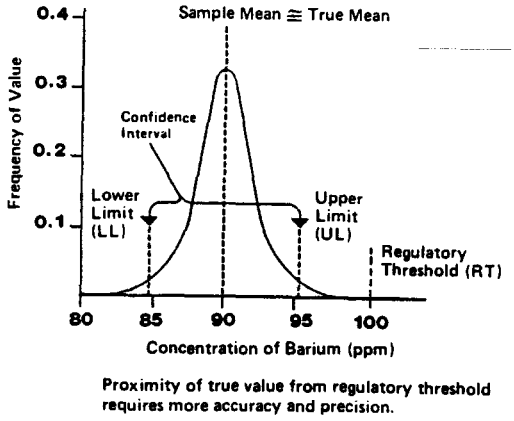


Figure 9-4. Distribution of barium concentration near a regulatory threshold.

The form in Figure 9-5 can be used to document primary and specific objectives prior to development of a sampling plan. Once the objectives of a sampling effort are developed, it is important to adhere to them to ensure that the program maintains its direction.

9.2.2 Sampling Plan Considerations

The sampling plan is usually a written document that describes the objectives and details the individual tasks of a sampling effort and how they will be performed. (Under unusual circumstances, time may not allow for the sampling plan to be documented in writing, e.g., sampling during an emergency spill. When operating under these conditions, it is essential that the person directing the sampling effort be aware of the various elements of a sampling plan.) The more detailed the sampling plan, the less the opportunity for oversight or misunderstanding during sampling, analysis, and data treatment.

To ensure that the sampling plan is designed properly, it is wise to have all aspects of the effort represented. Those designing the sampling plan should include the following personnel:

1. An end-user of the data, who will be using the data to attain program objectives and thus would be best prepared to ensure that the data objectives are understood and incorporated into the sampling plan.

2. An experienced member of the field team who will actually collect samples, who can offer hands-on insight into potential problems and solutions, and who, having acquired a comprehensive understanding of the entire sampling effort during the design phase, will be better prepared to implement the sampling plan.

3. An analytical chemist, because the analytical requirements for sampling, preservation, and holding times will be factors around which the sampling plan will be written. A sampling effort cannot succeed if an improperly collected or preserved sample or an inadequate volume of sample is submitted to the laboratory for chemical, physical, or biological testing. The appropriate analytical chemist should be consulted on these matters.

4. An engineer should be involved if a complex manufacturing process is being sampled. Representation of the appropriate engineering discipline will allow for the optimization of sampling locations and safety during sampling and should ensure that all waste-stream variations are accounted for.

5. A statistician, who will review the sampling approach and verify that the resulting data will be suitable for any required statistical calculations or decisions.

6. A quality assurance representative, who will review the applicability of standard operating procedures and determine the number of blanks, duplicates, spike samples, and other steps required to document the accuracy and precision of the resulting data base.

Sampling Site: _____

_____

_____

Address: _____

_____

_____

Description of Waste to be Sampled: _____

_____

_____

Primary Objective: _____

_____

_____

Specific Sampling Objectives: _____

_____

_____

Specific Analysis Objectives: _____

_____

_____

Specific Data Objectives: _____

_____

_____

Figure 9-5. Form for Documenting Primary and Specific Objectives

At least one person should be familiar with the site to be sampled. If not, then a presampling site visit should be arranged to acquire site-specific information. If no one is familiar with the site and a presampling site visit cannot be arranged, then the sampling plan must be written so that it can address contingencies that may occur.

Even in those cases in which a detailed sampling plan is authored and a comprehensive knowledge of the site exists, it is unusual for a sampling plan to be implemented exactly as written. Waste-stream changes, inappropriate weather, sampling equipment failure, and problems in gaining access to the waste are some reasons why a sampling plan must be altered. Thus it is always necessary to have at least one experienced sampler as a member of a sampling team.

The sampling plan should address the considerations discussed below.

9.2.2.1 Statistics

A discussion of waste sampling often leads to a discussion of statistics. The goals of waste sampling and statistics are identical, i.e., to make inferences about a parent population based upon the information contained in a sample.

Thus it is not surprising that waste sampling relies heavily upon the highly developed science of statistics and that a sampling/analytical effort usually contains the same elements as does a statistical experiment. Analogously, the Harris pollster collects opinions from randomly chosen people, whereas environmental scientists collect waste at randomly chosen locations or times. The pollster analyzes the information into a useable data base; laboratories analyze waste samples and generate data. Then the unbiased data base is used to draw inferences about the entire population, which for the Harris pollster may be the voting population of a large city, whereas for the environmental scientist the population may mean the entire contents of a landfill.

During the implementation of a waste sampling plan or a statistical experiment, an effort is made to minimize the possibility of drawing incorrect inferences by obtaining samples that are representative of a population. In fact, the term "representative sample" is commonly used to denote a sample that (1) has the properties and chemical composition of the population from which it was collected, and (2) has them in the same average proportions as are found in the population.

In regard to waste sampling, the term "representative sample" can be misleading unless one is dealing with a homogeneous waste from which one sample can represent the whole population. In most cases, it would be best to consider a "representative data base" generated by the collection and analysis of more than one sample that defines the average properties or composition of the waste. A "representative data base" is a more realistic term because the evaluation of most wastes requires numerous samples to determine the average properties or concentrations of parameters in a waste. (The additional samples needed to generate a representative data base can also be used to determine the variability of these properties or concentrations throughout the waste population.)

Statisticians have developed a number of strategies to obtain samples that are unbiased and collectively representative of a population. A detailed discussion of these strategies is presented in Section 9.1 of this chapter. The following discussion of statistical considerations is a less technical summary of these strategies. It was written to complement Section 9.1 and will be most useful after Section 9.1 is read and studied.

Section 9.1 describes three basic sampling strategies: simple random, stratified random, and systematic random sampling. It should be noted that the word random has more than one meaning. When used in statistical discussions, it does not mean haphazard: it means that every part of a waste has a theoretically equal chance of being sampled. Random sampling, which entails detailed planning and painstaking implementation, is distinctly different from haphazard sampling, which may introduce bias into the collection of samples and the resulting data.

Systematic random sampling and authoritative sampling strategies require a substantial knowledge of the waste to ensure that: (1) a cycle or trend in waste composition does not coincide with the sampling locations: or (2) in the case of authoritative sampling, all or most of the assumptions regarding waste composition or generation are true. Because the variabilities of waste composition and the waste generation process are often unknown, systematic random and authoritative sampling strategies are usually not applicable to waste evaluation.

Therefore, for waste sampling, the usual options are simple or stratified random sampling. Of these two strategies, simple random sampling is the option of choice unless: (1) there are known distinct strata divisions) in the waste over time or in space: (2) one wants to prove or disprove that there are distinct time and/or space strata in the waste of interest; or (3) one is collecting a minimum number of samples and desires to minimize the size of a hot spot (area of high concentration) that could go unsampled. If any of these three conditions exists, it may be determined that stratified random sampling would be the optimum strategy. To explain how these strategies can be employed, a few examples follow:

Example 1: Simple Random Sampling of Tanks

A batch manufacturing process had been generating a liquid waste over a period of years and storing it in a large open-top tank. As this tank approached capacity, some of the waste was allowed to overflow to a smaller enclosed tank. This smaller tank allowed for limited access through an inspection port on its top.

Because the on-site tank storage was approaching capacity, it was determined that the waste would have to be disposed of off-site.

The operators of the facility had determined that the waste was a nonhazardous solid waste when the RCRA regulations were first promulgated. However, upon recent passage of more stringent state regulations and concerns of potential liability, the operators determined that they should perform a more comprehensive analysis of the waste.

Because the waste was generated in a batch mode over a period of years, the operators were concerned that the waste composition might have varied between batches and that stratification might have occurred in the tank at unknown and random depths. Based on their knowledge, the operators knew that a grab sample would not suffice and that a sampling program would have to be designed to address the heterogeneity of the waste.

Because the operators intended to dispose of the entire contents of the tank and lacked any specific information regarding stratification and variability of the waste, it was decided that a simple random strategy would be employed. (If the operators had treated portions of the waste differently or had been aware of distinct strata, then stratified random sampling might have been more appropriate.)

The large, unenclosed tank had a diameter of 50 ft, a height of 20 ft, and an approximate volume of 295,000 gal allowed. It was encircled and traversed by catwalks (refer to Figure 9-6), which allowed access to the entire waste surface. The smaller tank had a diameter of 10 ft, a height of 10 ft, and an approximate volume of 6,000 gal: an inspection port located on the top allowed limited access. It was determined that the different construction of the two tanks would require different simple random sampling approaches.

In the case of the large tank, it was decided that vertical composite samples would be collected because the operators were interested in the average composition and variability of the waste and not in determining if different vertical strata existed. It was decided to select points randomly along the circumference (157 ft) and along the radius (25 ft). These numbers, which would constitute the coordinates of the sampling locations, were chosen from a random-number table by indiscriminately choosing a page and then a column on that page. The circumference coordinates were then chosen by proceeding down the column and listing the first 15 numbers that are greater than or equal to 0, but less than or equal to 157. The radius coordinates were chosen by continuing down the column and listing the first 15 numbers that are greater than or equal to 0, but less than or equal to 25. These numbers were paired to form the coordinates that determined the location of the 15 randomly chosen sampling points. These coordinates were recorded in the field notebook (refer to Table 9-3). Because no precision data on waste composition existed prior to sampling, the number of samples (15) was chosen as a conservative figure to more than allow for a sound statistical decision.

The actual samples were collected by employing a sampling device, which was constructed on site from available materials, and a weighted bottle. This device, which was used to access more remote areas of the tank, consisted of a weighted bottle, a rope marked off at 1-ft increments, and a discarded spool that originally contained electrical wire (refer to Figure 9-7).

Samples were collected by a three-person team. The person controlling the weighted bottle walked to the first circumference coordinate (149 ft), while the two persons holding the ropes attached to the spool walked along opposing catwalks toward the center of the tank. The person controlling the

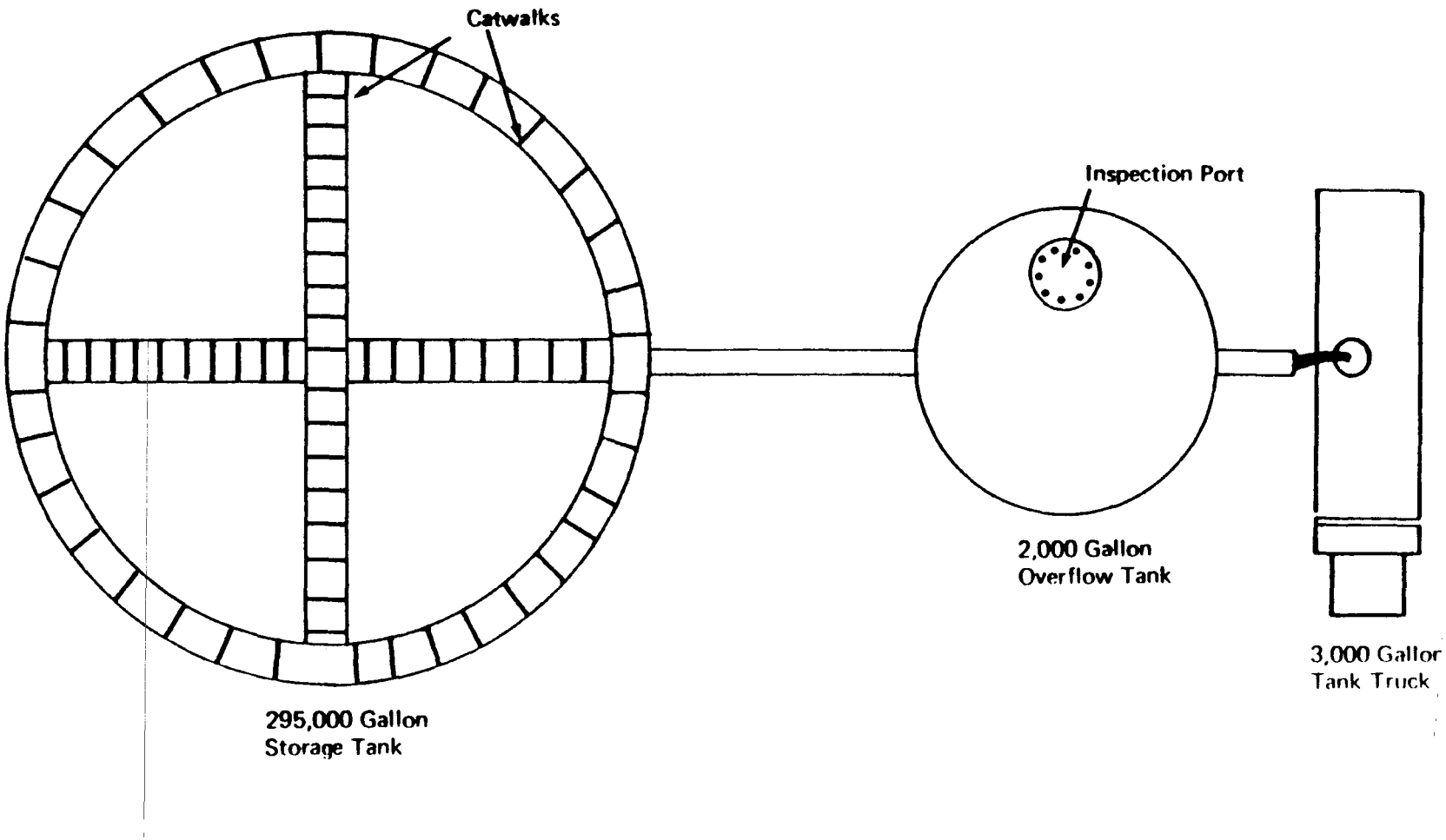


Figure 9-6. Bird's eye view of waste tank, overflow tank, tank truck and connecting plumbing.

TABLE 9-3. RANDOM COORDINATES FOR 295,000-GAL TANK

Sampling Point	Circumference	Radius
1	149	4
2	86	22
3	94	13
4	99	0
5	23	10
6	58	2
7	52	22
8	104	16
9	23	25
10	51	4
11	77	14
12	12	5
13	151	15
14	83	23
15	99	18

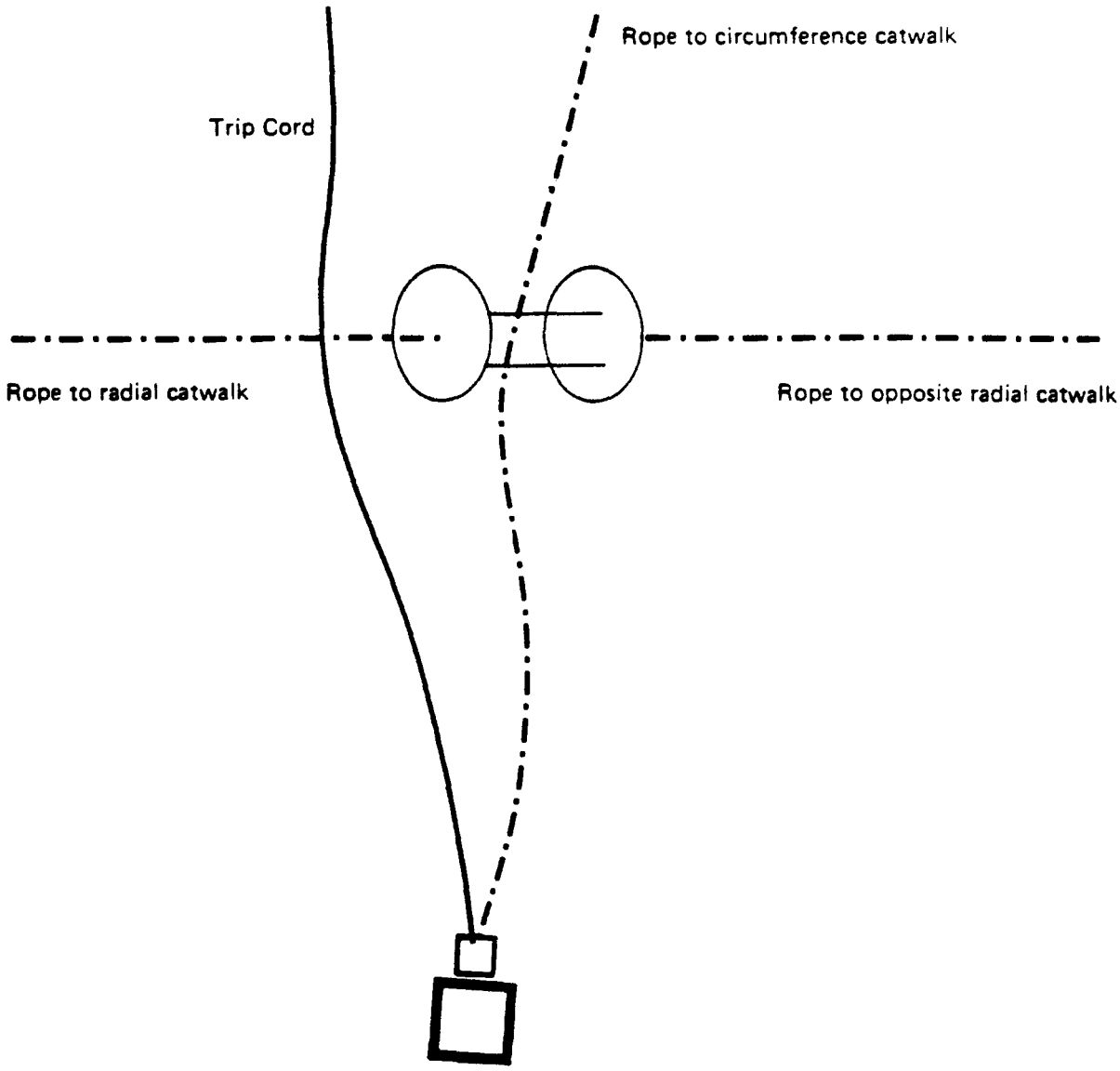


Figure 9-7. Device used to collect sample from the open tank.

weighted bottle measured off the radius coordinate (4 ft). The spool was then centered in the quadrant, the weighted bottle was lowered to the surface, and a sample was collected from the first 2 ft of waste. This sample was then transferred into a large, labeled sample container, which was used for compositing. This same process was repeated nine more times at the same location at different 2-ft depth intervals, resulting in the collection of a total of 10 component depth samples that were compiled in the field into one sample for that sampling point. This process was repeated at the remaining 14 sampling points, resulting in the collection of 15 vertical composite samples. These vertical composite samples were taken to address any vertical stratification that may have occurred.

The samples were properly preserved and stored, chain-of-custody procedures were completed, and the samples were submitted to the laboratory. A cost/benefit decision was made to composite aliquots of the samples into five composite samples that were submitted for analysis. (Following analysis, Equation 8 of Section 9.1 of this chapter was employed to determine if enough samples were analyzed to make a statistically sound decision. If the number of samples analyzed was not sufficient, then the samples would be recomposited to a lesser degree or analyzed individually.)

Because there was no information to prove that the waste in the smaller tank was the same as that in the larger tank, the operators decided that the smaller tank must also be sampled. The different construction of the smaller, enclosed tank mandated that a different sampling plan be designed. The only access to the tank was through a small inspection port on the top of the tank. This port would allow sampling only of a small portion of the tank contents; thus, to make a decision on the entire contents of the tank, one would have to assume that the waste in the vicinity of the inspection port was representative of the remainder of the tank contents. The operators were not willing to make this assumption because they determined that the liability of an incorrect decision overrode the convenience of facilitating the sampling effort.

To randomly sample the entire contents of the tank, a different plan was designed. This plan exploited the relatively small volume (approximately 6,000 gal) of the tank. A decision was made to rent two tank trucks and to sample the waste randomly over time as it drained from the tank into the tank trucks.

It was calculated that at a rate of 20 gal/min, it would take 300 min to drain the tank. From the random-number tables, 15 numbers that were greater than or equal to 0, but less than or equal to 300, were chosen in a manner similar to that employed for the larger tank. These numbers were recorded in the field notebook (refer to Table 9-4) at the time that they were encountered in the random-number table and were then assigned sampling point numbers according to their chronological order.

The 15 samples were collected at the previously chosen random times as the waste exited from a drainage hose into the tank trucks. These samples were collected in separate labeled containers, properly preserved and stored; chain-of-custody procedures were employed for transferral of the samples to the laboratory.

TABLE 9-4. RANDOM TIMES FOR 6,000-GAL TANK

Sampling point	Time (min)
11	153
10	122
8	85
6	55
5	46
15	294
12	195
1	5
13	213
9	99
2	29
4	41
7	74
3	31
14	219

The above example employed simple random sampling to determine the average composition and variance of the waste contained in the two tanks. The contents of the large tank were sampled randomly in space, whereas the contents of the smaller tank were sampled randomly over time.

The following example will involve the use of stratified random sampling, which is used when: (1) distinct strata are known to exist or (2) it is not known whether different strata exist, but an objective of the sampling effort is to discover the existence or nonexistence of strata.

A variation of this second reason for employing stratified random sampling is when cost considerations limit the number of samples that can be collected (e.g., when the budget allows for the collection of only six samples in a 40-acre lagoon). In this situation, where little is known about the composition of the waste, a concern exists that an area of the lagoon may be highly contaminated and yet may not be sampled. The smaller the number of samples, the greater the probability that an area of high contamination (a distinct stratum) could be missed, and the greater the probability that the sampling accuracy will suffer. Under such circumstances, a sampling plan may employ stratified random sampling to minimize the size of a highly contaminated area that could go unsampled.

For example, consider the situation where the budget allows only for the collection of six samples in a 40-acre lagoon. If simple random sampling is employed with such a small number of samples, there is a certain probability that large areas of the lagoon may go unsampled. One approach to minimizing the size of areas that may go unsampled is to divide the lagoon into three strata of equal size and randomly sample each stratum separately. This approach decreases the size of an area that can go unsampled to something less than one-third of the total lagoon area.

The following example details more traditional applications of stratified random sampling.

Example 2: Stratified Random Sampling of Effluents and Lagoons

A pigment manufacturing process has been generating wastes over a number of years. The pigment is generated in large batches that involve a 24-hr cycle. During the first 16 hr of the cycle, an aqueous sludge stream is discharged. This waste contains a high percentage of large-sized black particulate matter. The waste generated during the remaining 8 hr of the manufacturing cycle is an aqueous-based white sludge that consists of much smaller-sized particles than those found in the sludge generated in the first 16 hr of the batch process. This waste has been disposed of over the years into a 40-acre settling lagoon, allowing the particulate matter to settle out of solution while the water phase drains to an NPDES outfall at the opposite end of the lagoon. The smaller white pigment particles released in the last 8 hr of the batch process settle more slowly than the much larger black particles generated in the previous 16 hr. This settling pattern is quite apparent from the distinct colors of the wastes. The sludge in the quadrant closest to the waste influent pipe is black; the next quadrant is a light gray color, resulting from settling of both waste streams. The last two quadrants contain a pure white sludge, resulting from the settling of the small pigment particles.

Eventually, the facility operators decided that the settled particulate matter had to be removed to keep the settling lagoon functioning. In the past, this residual lagoon waste was found to be a hazardous waste due to its leachable barium content. Further studies determined that the source of the barium was a certain raw material that was released during the first 16 hr of batch process.

To minimize present disposal costs, the operators wanted to determine if the white sludge in the last two quadrants and the light gray waste were nonhazardous. Also, the operators had recently changed raw materials, with the intention of removing the source of barium in an attempt to minimize future disposal costs. Thus, the operators were interested in determining whether the currently generated waste was hazardous. If the altered waste stream was not hazardous, future lagoon sludge could be disposed of more economically as a solid waste. If the waste generated during the first 16 hr of the process remained hazardous but the waste generated during the following 8 hr was nonhazardous, the operators were willing to shift this latter waste to a second lagoon reserved for nonhazardous wastes. By sequestering the waste streams in this manner, the operators intended to decrease the amount of hazardous waste by precluding generation of additional amounts of hazardous waste under the "mixture rule."

To decide how the lagoon sludge should be handled, the operators arranged to have the lagoon sludge sampled. The objectives of sampling the lagoon sludge were to determine the average concentration and variance of leachable barium for the sludge in the entire lagoon and for each of the different sludges.

The dimensions of the 40-acre square lagoon were calculated to be 1,320 ft on a side, with the black and the gray sludge each covering a quadrant measuring 1,320 ft by 330 ft, and the white sludge covering the remaining area of the lagoon, which measured 1,320 ft by 660 ft (refer to Figure 9-8). The sludge had settled to a uniform thickness throughout the lagoon and was covered with 2 ft of water.

Because the leachable barium was assumed to be associated with the black sludge, which was concentrated in the first quadrant, a stratified random sampling approach was chosen. (Because of the obvious strata in the lagoon sludge, the stratified sampling strategy was expected to give a more precise estimate of the leachable barium, in addition to giving information specific to each stratum.)

When the actual sampling was being planned, it was decided that the hazards presented by the lagoon waste were minimal, and, that if proper precautions were employed, a stable and unsinkable boat could be used to collect samples. The samples were collected with a core sampler at random locations throughout each stratum. Because the cost of collecting samples was reasonable and no historical data were available to help determine the optimum number of samples, the operators decided to collect a total of 10 samples from each of the smaller strata and a total of 20 samples from the larger strata. They had confidence that this number of samples would allow them to detect a small significant difference between the mean concentration of leachable barium and the applicable regulatory threshold.

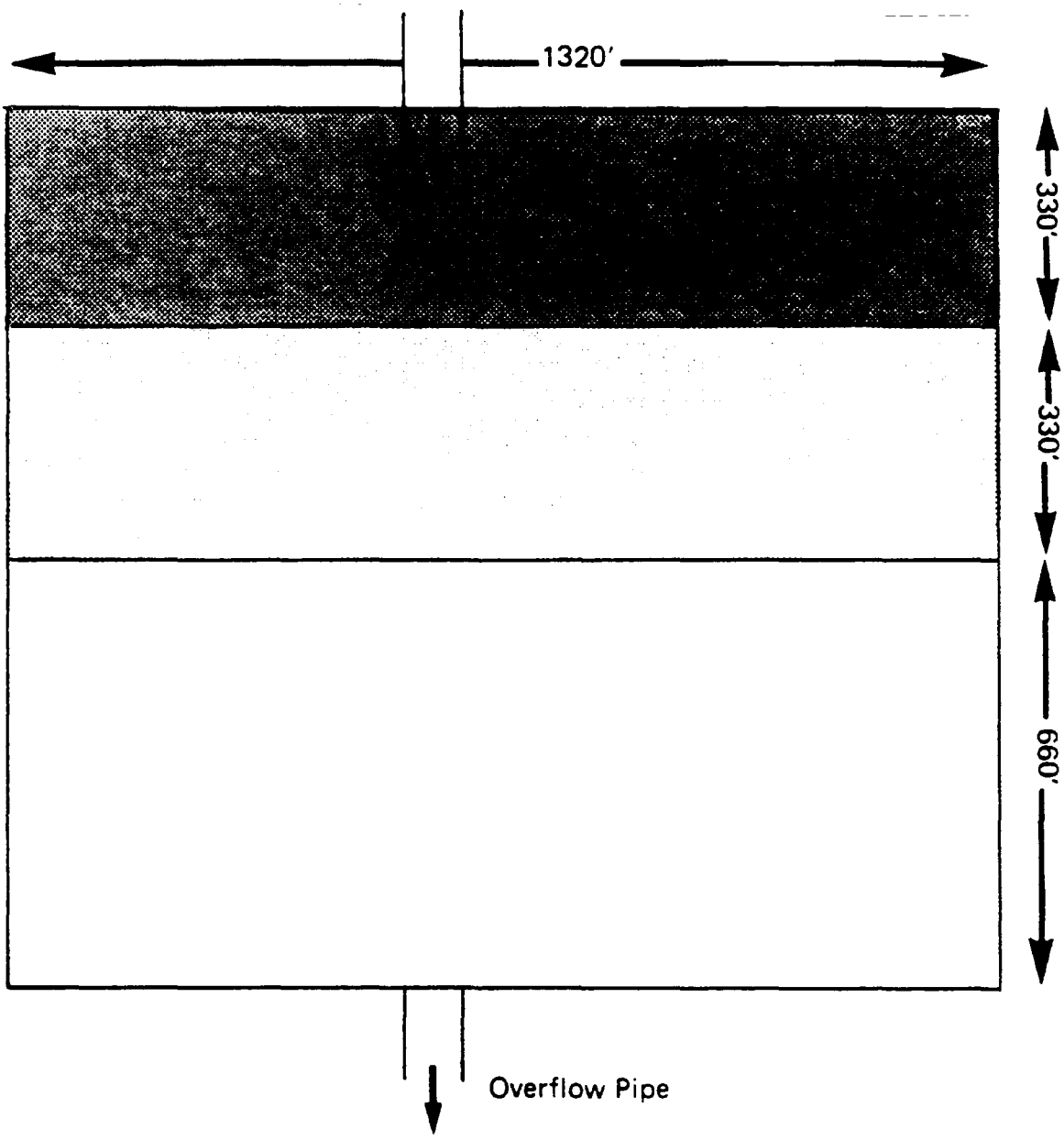


Figure 9-8. Schematic of the 40-acre settling lagoon displaying strata generated by a waste stream.

The locations of the random sampling points were determined by selecting length and width coordinates from a random-number table. This was done by indiscriminately choosing a page from the random-number tables and then a column on that page. The width coordinates of the two smaller quadrants were then chosen by proceeding down the column and listing the first 20 numbers that were greater than or equal to 0, but less than or equal to 330. The width coordinate for the third and largest stratum was chosen by proceeding down the column and selecting the first 20 numbers that were greater than or equal to 0, but less than or equal to 660. Because the lengths of the three quadrants were all 1,320 ft, the length coordinates were chosen by listing the first 40 numbers that were greater than or equal to 0 but less than or equal to 1,320. These coordinates were recorded in the field notebook (refer to nable 9-5).

The samples were collected by a four-person team. Two people remained onshore while two maneuvered the boat and collected the samples. The first sample in the first quadrant was collected by launching the boat at a distance of 41 ft from the corner, which was designated the origin, 0 ft. The boat proceeded out into the lagoon perpendicular to the long side of the quadrant. The person onshore released 134 ft of a measured rope, which allowed the boat to stop at the first sampling point (41, 134). The sample was then collected with a core sampler and transferred to a sample container. This process was repeated for all sampling points in the three strata. The samples were properly preserved and stored, and the chain-of-custody records documented the transfer of samples to the laboratory.

Aliquots of the samples were composited into five composite samples for each stratum. The mean and variance of each stratum were calculated by Equations 2(a) and 3(a), respectively. The mean and variance for the total lagoon were calculated by using Equations 2(b) and 3(b), respectively. Equation 6 was used to calculate a confidence interval for the leachable barium concentration, and the upper limit of this interval was compared with the regulatory threshold. (See Table 9-1, Section 9.1 of this chapter, for equations.)

As previously mentioned, the operators had recently changed their raw materials and were also interested in discovering if the currently generated waste was nonhazardous or if portions of this waste stream were nonhazardous. As described above, the waste effluent for the first 16 hr of the day was different from that discharged during the last 8 hr. However, because the same large plumbing system was used for both waste streams, there were two 2-hr periods during which the discharged waste was a mixture of the two different wastes.

With the above objectives in mind, the operators decided to employ stratified random sampling with four strata occurring over time, as opposed to the strata in space that were employed for sampling the lagoon. The four time strata were from 6:00 to 8:00 hr, from 8:00 to 20:00 hr, from 20:00 to 22:00 hr, and from 22:00 to 6:00 hr the following day. The two 2-hr strata were those time periods during which the waste was a mixture of the two different waste streams. The 12-hr stratum was the time period during which the large-sized particulate black waste was being discharged. The smaller particulate white waste was being discharged during the 8-hr stratum.

TABLE 9-5.RANDOM COORDINATES FOR EACH STRATUM
IN THE 40-ACRE SETTLING LAGOON

	Sampling Point	Length (ft)	Width (ft)
Stratum #1 (Black)	1	41	134
	2	271	51
	3	968	32
	4	129	228
	5	472	137
	6	1,198	56
	7	700	261
	8	286	8
	9	940	26
	10	151	121
Stratum #2 (Gray)	1	1,173	109
	2	277	2
	3	438	302
	4	780	5
	5	525	135
	6	50	37
	7	26	127
	8	1,207	149
	9	1,231	325
	10	840	32
Stratum #3 (White)	1	54	374
	2	909	434
	3	1,163	390
	4	1,251	449
	5	1	609
	6	1,126	140
	7	717	235
	8	1,155	148
	9	668	433
	10	66	642
	11	462	455
	12	213	305
	13	1,220	541
	14	1,038	644
	15	508	376
	16	1,293	270
	17	30	38
	18	114	52
	19	1,229	570
	20	392	613

The flow rate was constant throughout the 24-hr period, and there were no precision data available for the waste. Therefore, it was decided that the number of samples collected in the 8- and 12-hr strata would be proportional to time. Because the 2-hr periods were times during which the composition of the waste was changing, it was decided to collect more samples to get a more precise estimate of the average composition of the waste during these time strata. Thus a total of 28 samples was collected.

The samples were collected at randomly chosen times within each time stratum. The random sampling times were chosen by employing a random-number table. After indiscriminately selecting a starting point, the first four numbers greater than or equal to 0, but less than or equal to 120 were selected for the 120-min strata from 6:00 to 8:00 hr. These minutes were then added to the starting time to determine when the four samples would be collected. In similar fashion, the remaining 24 sampling times were chosen. The random-number data were recorded in a laboratory notebook (refer to Table 9-6).

The samples were collected from the waste influent pipe with a wide-mouth bottle at the randomly chosen sampling times. The samples were properly preserved and stored and shipped to the laboratory, along with chain-of-custody records. The samples were subjected to analysis, and the data were evaluated in a manner similar to that employed for the samples of sludge collected in the different strata of the lagoon.

9.2.2.2 Waste

The sampling plan must address a number of factors in addition to statistical considerations. Obviously, one of the most important factors is the waste itself and its properties. The following waste properties are examples of what must be considered when designing a sampling plan:

1. Physical state: The physical state of the waste will affect most aspects of a sampling effort. The sampling device will vary according to whether the sample is liquid, gas, solid, or multiphasic. It will also vary according to whether the liquid is viscous or free-flowing, or whether the solid is hard or soft, powdery, monolithic, or clay-like.

   Wide-mouth sample containers will be needed for most solid samples and for sludges or liquids with substantial amounts of suspended matter. Narrow-mouth containers can be used for other wastes, and bottles with air-tight closures will be needed for gas samples or gases adsorbed on solids or dissolved in liquids.

   The physical state will also affect how sampling devices are deployed. A different plan will be developed for sampling a soil-like waste that can easily support the weight of a sampling team and its equipment than for a lagoon filled with a viscous sludge or a liquid waste.

TABLE 9-6. RANDOM TIMES FOR THE WASTE EFFLUENT

	Sampling Point	Random Minute	Time
Stratum #1	1	28	6:28
(6:00 to 8:00	2	62	7:02
hours)	3	99	7:39
	4	112	7:52
Stratum #2	1	11	8:11
(8:00 to 20:00	2	107	9:47
hours)	3	156	10:36
	4	173	10:53
	5	296	12:56
	6	313	13:13
	7	398	14:38
	8	497	16:17
	9	555	17:15
	10	600	18:00
	11	637	18:37
	12	706	19:46
Stratum #3	1	13	20:13
(20:00 to 22:00	2	52	20:52
hours)	3	88	21:28
	4	108	21:48
Stratum #4	1	48	22:48
(22:00 to 6:00	2	113	23:53
hours)	3	153	24:33
	4	189	1:09
	5	227	1:47
	6	290	2:49
	7	314	3:14
	8	474	5:44

The sampling strategy will have to vary if the physical state of the waste allows for stratification (e.g., liquid wastes that vary in density or viscosity or have a suspended solid phase), homogenization or random heterogeneity.

2. Volume: The volume of the waste, which has to be represented by the samples collected, will have an effect upon the choice of sampling equipment and strategies. Sampling a 40-acre lagoon requires a different approach from sampling a 4-sq-ft container. Although a 3-ft depth can be sampled with a Coliwasa or a drum thief, a weighted bottle may be required to sample a 50-ft depth.

3. Hazardous properties: Safety and health precautions and methods of sampling and shipping will vary dramatically with the toxicity, ignitability, corrosivity, and reactivity of the waste.

4. Composition: The chosen sampling strategy will reflect the homogeneity, random heterogeneity, or stratification of the waste in time or over space.

9.2.2.3 Site

Site-specific factors must be considered when designing a sampling plan. A thorough examination of these factors will minimize oversights that can affect the success of sampling and prevent attainment of the program objectives. At least one person involved in the design and implementation of the sampling plan should be familiar with the site, or a presampling site visit should be arranged. If nobody is familiar with the site and a visit cannot be arranged, the sampling plan must be written to account for the possible contingencies. Examples of site-specific factors that should be considered follow:

1. Accessibility: The accessibility of waste can vary substantially. Some wastes are accessed by the simple turning of a valve; others may require that an entire tank be emptied or that heavy equipment be employed. The accessibility of a waste at the chosen sampling location must be determined prior to design of a sampling plan.

2. Waste generation and handling: The waste generation and handling process must be understood to ensure that collected samples are representative of the waste. Factors which must be known and accounted for in the sampling plan include: if the waste is generated in batches; if there is a change in the raw materials used in a manufacturing process; if waste composition can vary substantially as a function of process temperatures or pressures; and if storage time after generation may vary.

3. Transitory events: Start-up, shut-down, slow-down, and maintenance transients can result in the generation of a waste that is not representative of the normal waste stream. If a sample was unknowingly collected at one of these intervals, incorrect conclusions could be drawn.

4. Climate: The sampling plan should specify any clothing needed for personnel to accommodate any extreme heat or cold that may be encountered. Dehydration and extensive exposure to sun, insects, or poisonous snakes must be considered.

5. Hazards: Each site can have hazards -- both expected and unexpected. For example, a general understanding of a process may lead a sampling team to be prepared for dealing with toxic or reactive material, but not for dealing with an electrical hazard or the potential for suffocation in a confined space. A thorough sampling plan will include a health and safety plan that will counsel team members to be alert to potential hazards.

9.2.2.4 Equipment

The choice of sampling equipment and sample containers will depend upon the previously described waste and site considerations. For the following reasons, the analytical chemist will play an important role in the selection of sampling equipment:

1. The analytical chemist is aware of the potential interactions between sampling equipment or container material with analytes of interest. As a result, he/she can suggest a material that minimizes losses by adsorption, volatilization, or contamination caused by leaching from containers or sampling devices.

2. The analytical chemist can specify cleaning procedures for sampling devices and containers that minimize sample contamination and cross contamination between consecutive samples.

3. The analytical chemist's awareness of analyte-specific properties is useful in selecting the optimum equipment (e.g., choice of sampling devices that minimize agitation for those samples that will be subjected to analysis for volatile compounds).

The final choice of containers and sampling devices will be made jointly by the analytical chemist and the group designing the sampling plan. The factors that will be considered when choosing a sampling device are:

1. Negative contamination: The potential for the measured analyte concentration to be artificially low because of losses from volatilization or adsorption.

2. Positive contamination: The potential for the measured analyte to be artificially high because of leaching or the introduction of foreign matter into the sample by particle fallout or gaseous air contaminants.

3. Cross contamination: A type of positive contamination caused by the introduction of part of one sample into a second sample during sampling, shipping, or storage.

4. Required sample volume: For physical and/or chemical analysis.

5. "Ease of use" of the sampling device and containers under the conditions that will be encountered on-site. This includes the ease of shipping to and from the site, ease of deployment, and ease of cleaning.

6. The degree of hazard associated with the deployment of one sampling device versus another.

7. Cost of the sampling device and of the labor for its deployment.

This section describes examples of sampling equipment and suggests potential uses for this equipment. Some of these devices are commercially available, but others will have to be fabricated by the user. The information in this section is general in nature and therefore limited.

Because each sampling situation is unique, the cited equipment and applications may have to be modified to ensure that a representative sample is collected and its physical and chemical integrity are maintained. It is the responsibility of those persons conducting sampling programs to make the appropriate modifications.

Table 9-7 contains examples of sampling equipment and potential applications. It should be noted that these suggested sampling devices may not be applicable to a user's situation due to waste- or site-specific factors. For example, if a waste is highly viscous or if a solid is clay-like, these properties may preclude the use of certain sampling devices. The size and depth of a lagoon or tank, or difficulties associated with accessing the waste, may also preclude use of a given device or require modification of its deployment.

The most important factors to consider when choosing containers for hazardous waste samples are compatibility with the waste, cost, resistance to breakage, and volume. Containers must not distort, rupture, or leak as a result of chemical reactions with constituents of waste samples. Thus, it is important to have some idea of the properties and composition of the waste. The containers must have adequate wall thickness to withstand handling during sample collection and transport to the laboratory. Containers with wide mouths are often desirable to facilitate transfer of samples from samplers to containers. Also, the containers must be large enough to contain the optimum sample volume.

Containers for collecting and storing hazardous waste samples are usually made of plastic or glass. Plastics that are commonly used to make the containers include high-density or linear polyethylene (LPE), conventional polyethylene, polypropylene, polycarbonate, Teflon FEP (fluorinated ethylene propylene), polyvinyl chloride (PVC), or polymethylpentene. Teflon FEP is almost universally usable due to its chemical inertness and resistance to breakage. However, its high cost severely limits its use. LPE, on the other hand, usually offers the best combination of chemical resistance and low cost when samples are to be analyzed for inorganic parameters.

TABLE 9-7. EXAMPLES OF SAMPLING EQUIPMENT FOR PARTICULAR WASTE TYPES

Waste Type	Waste Location or Container								
	Drum	Sacks and Bags	Open-bed Truck	Closed-Bed Truck	Storage Tanks or Bins	Waste Piles	Ponds, Lagoons, & Pits	Convey-or Belt	Pipe
Free-flowing liquids and slurries	Coliwasa	N/A	N/A	Coliwasa	Weighted bottle	N/A	Dipper	N/A	Dipper
Sludges	Trier	N/A	Trier	Trier	Trier	a	a		
Moist powders or granules	Trier	Trier	Trier	Trier	Trier	Trier	Trier	Shovel	Dipper
Dry powders or granules	Thief	Thief	Thief	Thief	a	Thief	Thief	Shovel	Dipper
Sand or packed powders and granules	Auger	Auger	Auger	Auger	Thief	Thief	a	Dipper	Dipper
Large-grained solids	Large Trier	Large Trier	Large Trier	Large Trier	Large Trier	Large Trier	Large Trier	Trier	Dipper

[a] This type of sampling situation can present significant logistical sampling problems, and sampling equipment must be specifically selected or designed based on site and waste conditions. No general statement about appropriate sampling equipment can be made.

Glass containers are relatively inert to most chemicals and can be used to collect and store almost all hazardous waste samples, except those that contain strong alkali and hydrofluoric acid. Glass soda bottles are suggested due to their low cost and ready availability. Borosilicate glass containers, such as Pyrex and Corex, are more inert and more resistant to breakage than soda glass, but are expensive and not always readily available. Glass containers are generally more fragile and much heavier than plastic containers. Glass or FEP containers must be used for waste samples that will be analyzed for organic compounds.

The containers must have tight, screw-type lids. Plastic bottles are usually provided with screw caps made of the same material as the bottles. Buttress threads are recommended. Cap liners are not usually required for plastic containers. Teflon cap liners should be used with glass containers supplied with rigid plastic screw caps. (These caps are usually provided with waxed paper liners.) Teflon liners may be purchased from plastic specialty supply houses (e.g., Scientific Specialties Service, Inc., P.O. Box 352, Randallstown, Maryland 21133). Other liners that may be suitable are polyethylene, polypropylene, and neoprene plastics.

If the samples are to be submitted for analysis of volatile compounds, the samples must be sealed in air-tight containers.

Prior to sampling, a detailed equipment list should be compiled. This equipment list should be comprehensive and leave nothing to memory. The categories of materials that should be considered are:

1. Personnel equipment, which will include boots, rain gear, disposable coveralls, face masks and cartridges, gloves, etc.

2. Safety equipment, such as portable eyewash stations and a first-aid kit.

3. Field test equipment, such as pH meters and Draeger tube samplers.

4. An ample supply of containers to address the fact that once in the field, the sampling team may want to collect 50% more samples than originally planned or to collect a liquid sample, although the sampling plan had specified solids only.

5. Additional sampling equipment for use if a problem arises, e.g., a tool kit.

6. Shipping and office supplies, such as tape, labels, shipping forms, chain-of-custody forms and seals, field notebooks, random-number tables, scissors, pens, etc.

Composite Liquid Waste Sampler (Coliwasa)

The Coliwasa is a device employed to sample free-flowing liquids and slurries contained in drums, shallow tanks, pits, and similar containers. It is especially useful for sampling wastes that consist of several immiscible liquid phases.

The Coliwasa consists of a glass, plastic, or metal tube equipped with an end closure that can be opened and closed while the tube is submerged in the material to be sampled (refer to Figure 9-9).

Weighted Bottle

This sampler consists of a glass or plastic bottle, sinker, stopper, and a line that is used to lower, raise, and open the bottle. The weighted bottle samples liquids and free-flowing slurries. A weighted bottle with line is built to the specifications in ASTM Methods D270 and E300. Figure 9-10 shows the configuration of a weighted-bottle sampler.

Dipper

The dipper consists of a glass or plastic beaker clamped to the end of a two- or three-piece telescoping aluminum or fiberglass pole that serves as the handle. A dipper samples liquids and free-flowing slurries. Dippers are not available commercially and must be fabricated (Figure 9-11).

Thief

A thief consists of two slotted concentric tubes, usually made of stainless steel or brass. The outer tube has a conical pointed tip that permits the sampler to penetrate the material being sampled. The inner tube is rotated to open and close the sampler. A thief is used to sample dry granules or powdered wastes whose particle diameter is less than one-third the width of the slots. A thief (Figure 9-12) is available at laboratory supply stores.

Trier

A trier consists of a tube cut in half lengthwise with a sharpened tip that allows the sampler to cut into sticky solids and to loosen soil. A trier samples moist or sticky solids with a particle diameter less than one-half the diameter of the trier. Triers 61 to 100 cm long and 1.27 to 2.54 cm in diameter are available at laboratory supply stores. A large trier can be fabricated (see Figure 9-13).

Auger

An auger consists of sharpened spiral blades attached to a hard metal central shaft. An auger samples hard or packed solid wastes or soil. Augers are available at hardware and laboratory supply stores.

Scoops and Shovels

Scoops and shovels are used to sample granular or powdered material in bins, shallow containers, and conveyor belts. Scoops are available at laboratory supply houses. Flat-nosed shovels are available at hardware stores.

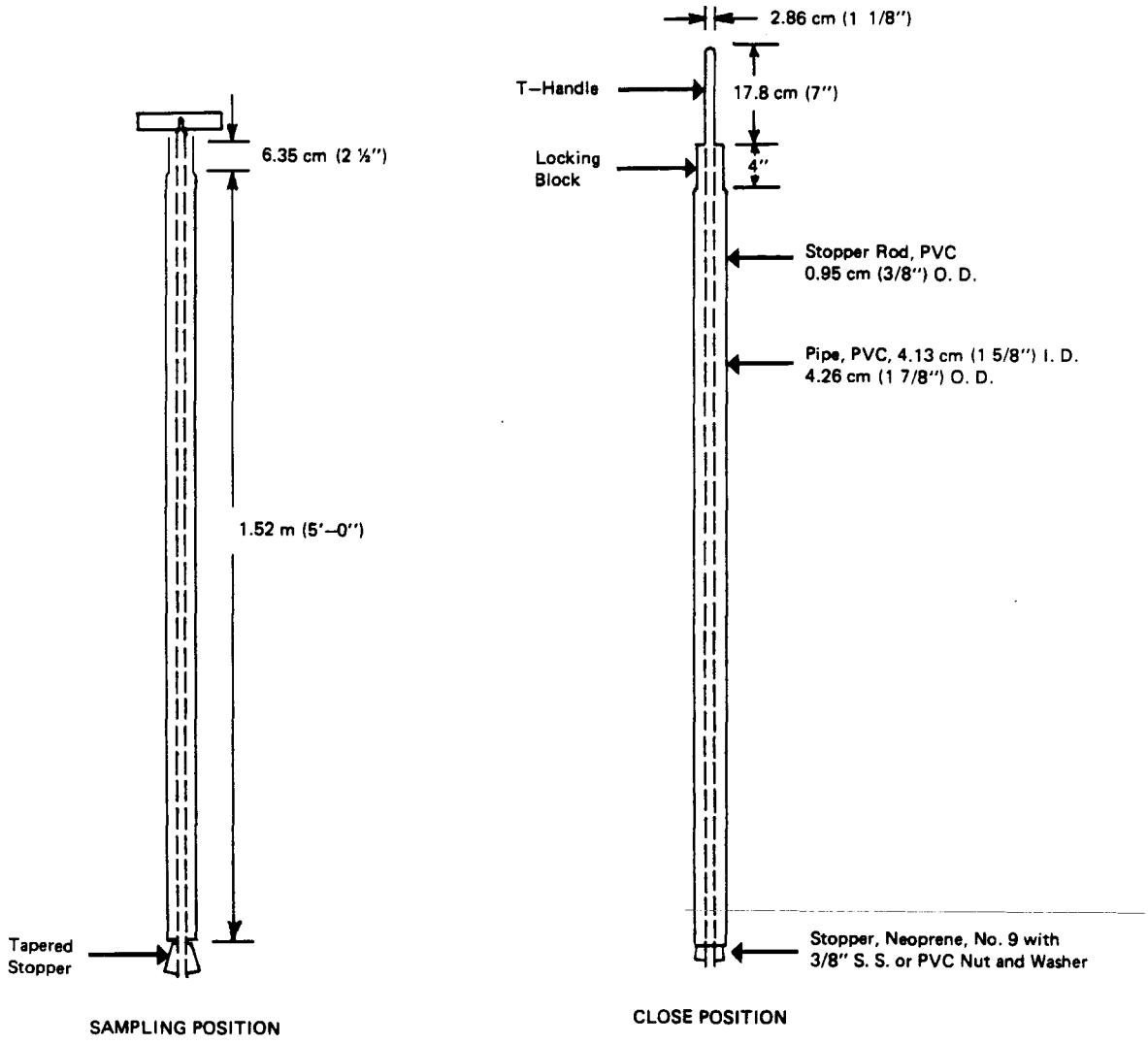


Figure 9-9. Composite liquid waste sampler (Coliwasa).

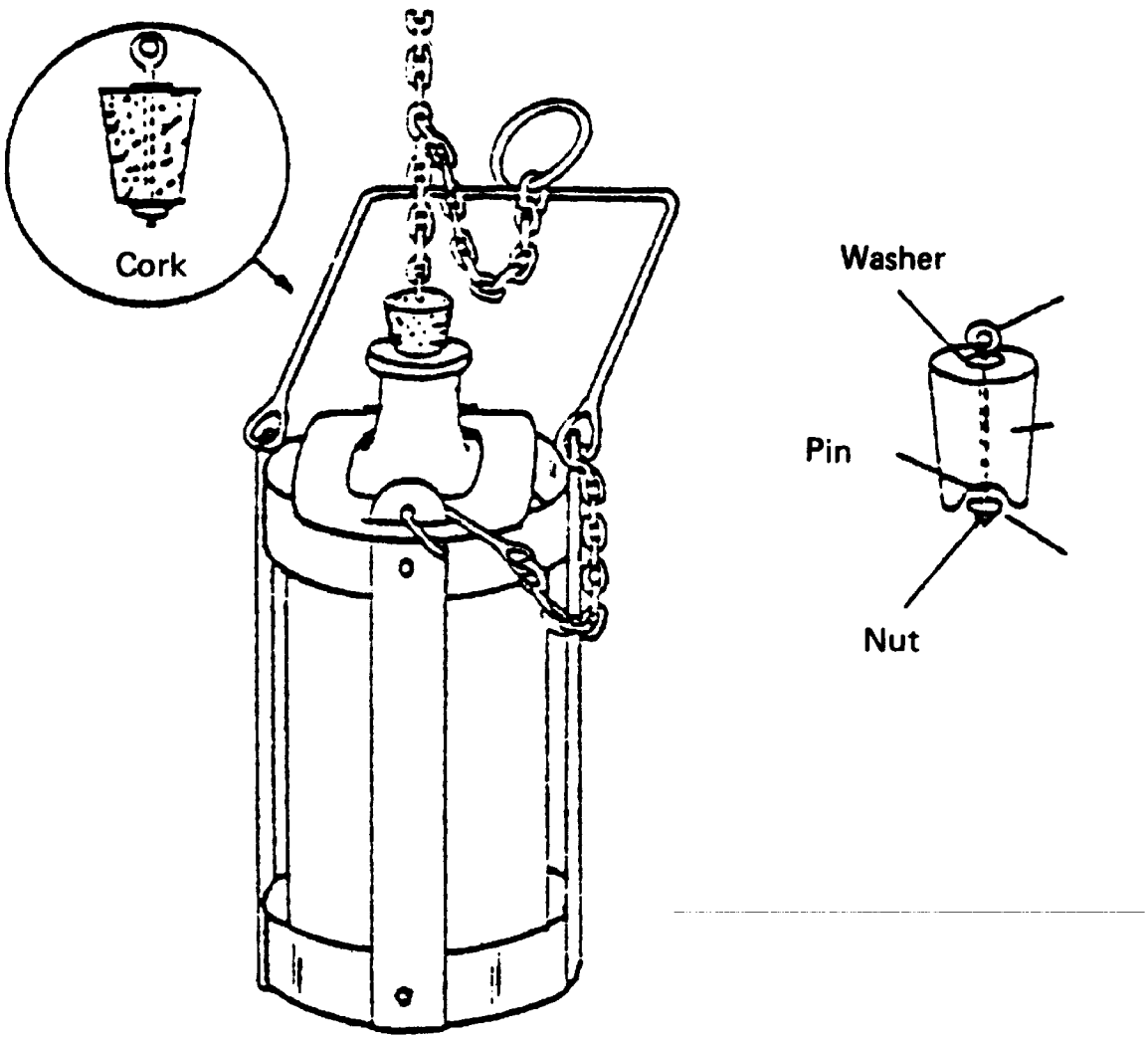


Figure 9-10. Weighted bottle sampler.

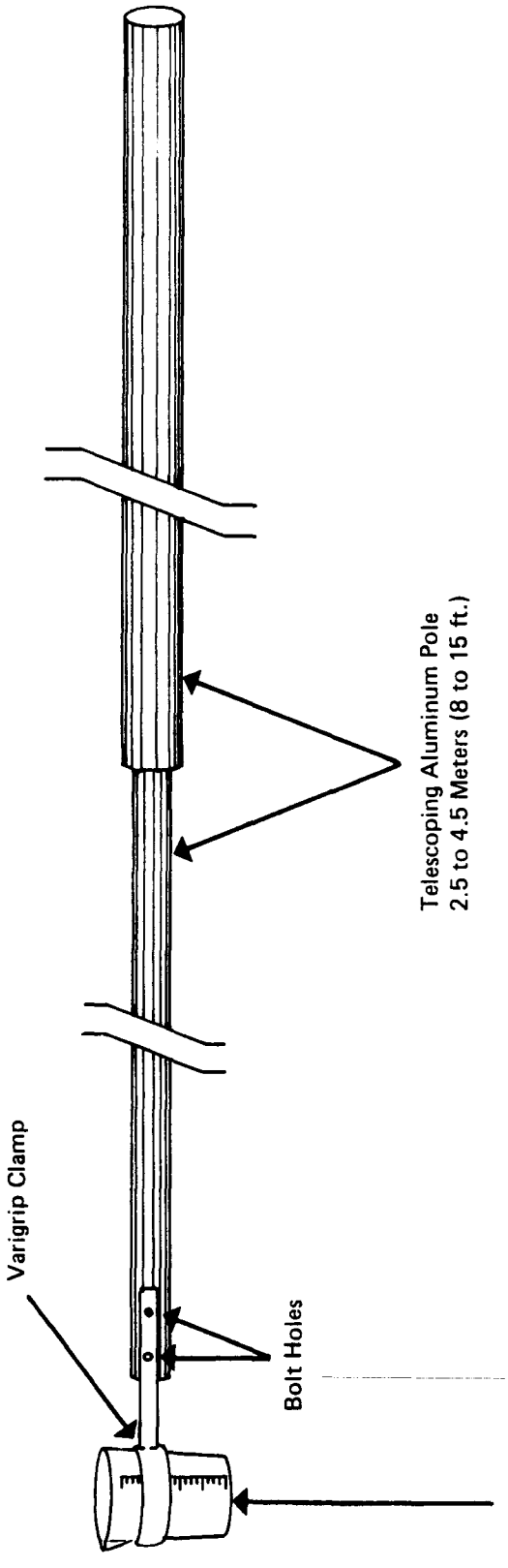


Figure 9-11. Dipper.

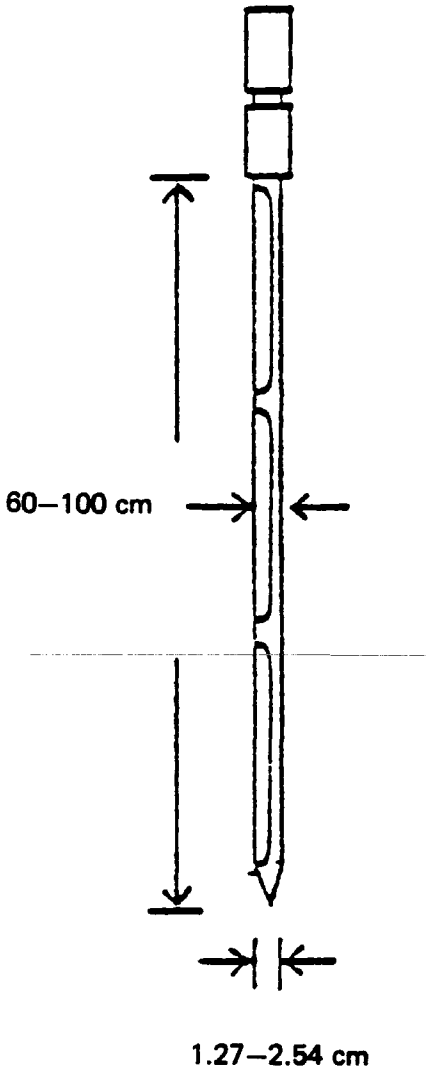


Figure 9-12. Thief sampler.

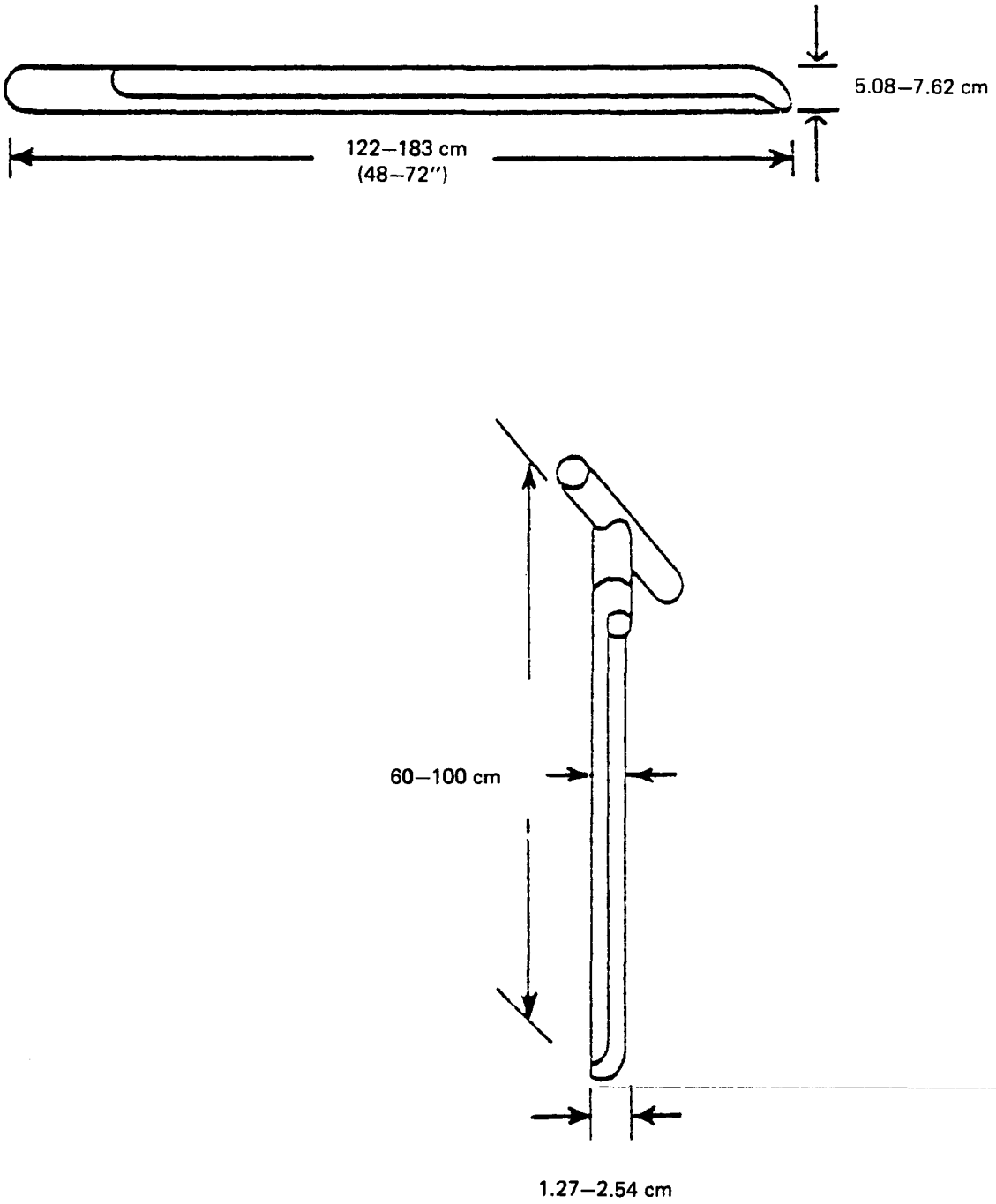


Figure 9-13. Sampling triers.

Bailer

The bailer is employed for sampling well water. It consists of a container attached to a cable that is lowered into the well to retrieve a sample. Bailers can be of various designs. The simplest is a weighted bottle or basally capped length of pipe that fills from the top as it is lowered into the well. Some bailers have a check valve, located at the base, which allows water to enter from the bottom as it is lowered into the well. When the bailer is lifted, the check valve closes, allowing water in the bailer to be brought to the surface. More sophisticated bailers are available that remain open at both ends while being lowered, but can be sealed at both top and bottom by activating a triggering mechanism from the surface. This allows more reliable sampling at discrete depths within a well. Perhaps the best known bailer of this latter design is the Kemmerer sampler.

Bailers generally provide an excellent means for collecting samples from monitoring wells. They can be constructed from a wide variety of materials compatible with the parameter of interest. Because they are relatively inexpensive, bailers can be easily dedicated to an individual well to minimize cross contamination during sampling. If not dedicated to a well, they can be easily cleaned to prevent cross contamination. Unfortunately, bailers are frequently not suited for well evacuation because of their small volume.

Suction Pumps

As the name implies, suction pumps operate by creating a partial vacuum in a sampling tube. This vacuum allows the pressure exerted by the atmosphere on the water in the well to force water up the tube to the surface. Accordingly, these pumps are located at the surface and require only that a transmission tube be lowered into the well. Unfortunately, their use is limited by their reliance on suction to depths of 20 to 25 ft, depending on the pump. In addition, their use may result in out-gassing of dissolved gases or volatile organics and is therefore limited in many sampling applications. In spite of this, suction methods may provide a suitable means for well evacuation because the water remaining in the well is left reasonably undisturbed.

A variety of pumps that operate on this principle are available, but the ones most commonly suggested for monitoring purposes are the centrifugal and peristaltic pumps. In the centrifugal pump, the fluid is displaced by the action of an impeller rotating inside the pump chamber. This discharges water by centrifugal force. The resulting pressure drop in the chamber creates a suction and causes water to enter the intake pipe in the well. These pumps can provide substantial yields and are readily available and inexpensive. The disadvantages are that they require an external power source and may be difficult to clean between sampling events. In addition, the materials with which these pumps are constructed may frequently be incompatible with certain sample constituents. However, their substantial pumping rates make them suitable for well evacuation.

Peristaltic pumps operate in a manner similar to centrifugal pumps but displace the fluid by mechanical peristalsis. A flexible transmission line is mounted around the perimeter of the pump chamber, and rotating rollers compress the tubing, forcing fluid movement ahead (the peristaltic effect) and inducing suction behind each roller. This design isolates the sample from the moving part of the pump and allows for easy cleaning by removal and replacement of the flexible tubing. Unfortunately, peristaltic pumps are generally capable of providing only relatively low yields. They are, therefore, not ideally suited to well evacuation.

Positive Displacement Pumps

A variety of positive displacement pumps are available for use in withdrawing water from wells. These methods utilize some pumping mechanism, placed in the well, that forces water from the bottom of the well to the surface by some means of positive displacement. This minimizes the potential for aerating or stripping volatile organics from the sample during removal from the well.

The submersible centrifugal pump is one common example of a positive displacement pump. It works in a manner similar to the centrifugal suction lift pump previously described, except that, in this case, both the pump and electric motor are lowered into the well. As the impeller rotates and fluid is brought into the pump, fluid is displaced up the transmission line and out of the well. These pumps are capable of providing a high yield. However, they require an external source of power and are frequently constructed with materials and contain lubricants incompatible with certain sample constituents, particularly organics. They also require considerable equipment and effort to move from well to well. Cleaning between sampling events is difficult as well, and, until recently, they have not been available for well diameters smaller than 3 in.

Piston-driven or reciprocating piston pumps are another example of common positive displacement pumps. These pumps consist of a piston in a submerged cylinder operated by a rod connected to the drive mechanism at the surface. A flap valve or ball-check valve is located immediately above or below the piston cylinder. As the piston is lowered in the cylinder, the check valve opens, and water fills the chamber. On the upstroke, the check valve closes, and water is forced out of the cylinder, up into the transmission line, and to the surface. The transmission line or piston contains a second check valve that closes on the downstroke, preventing water from re-entering the cylinder. These pumps are capable of providing high yields. However, moving these pumps from well to well is difficult, and their use in monitoring programs may require that a pump be dedicated to each well. Many of these pumps may not be constructed with materials compatible with monitoring certain constituents.

A special adaptation of this pump has recently become available for use in ground water monitoring. These piston pumps use compressed gas, rather than a rod connected to a driving mechanism at the surface, to drive the pistons. This provides a much more convenient and portable means for collecting samples from monitoring wells. Compressed-gas pumps provide good yields and can be constructed with materials compatible with many sampling programs.

Another positive displacement pump applicable for monitoring purposes is the gas-operated squeeze pump. This pump was originally developed by R. F. Middleburg of the U.S.G.S. and consequently is referred to as the Middleburg pump. It consists principally of a collapsible membrane inside a long, rigid housing, a compressed gas supply, and appropriate control valves. When the pump is submerged, water enters the collapsible membrane through the bottom check valve. After the membrane has filled, gas pressure is applied to the annular space between the rigid housing and membrane, forcing the water upward through a sampling tube. When the pressure is released, the top check valve prevents the sample from flowing back down the discharge line, and water from the well again enters the pump through the bottom check valve.

Gas-operated squeeze pumps offer a number of advantages for use in ground water monitoring programs. They can be constructed in diameters as small as 1 in. and from a wide variety of materials. They are also relatively portable and are capable of providing a fair range of pumping rates. Most important, the driving gas does not contact the water sample, so that possible contamination or gas stripping does not occur. However, they do require a gas source, and withdrawal of water from substantial depths may require large gas volumes and long pumping cycles.

Jet pumps, a common type of submersible pump used in small domestic water wells, may in some cases be suggested for use in monitoring wells. These pumps operate by injecting water through a pipe down into the well. A venturi device is located at the intake portion of the pump. As the water injected from the surface passes through the constricted portion of the venturi, the velocity increases and pressures decrease according to Bernoulli's principle. If the discharge velocity at the nozzle is great enough, the pressure at this point will be lowered sufficiently to draw water into the venturi assembly through the intake and to bring it to the surface with the original water injected into the well. This additional increment of water is then made available at the surface as the pump's output. Because jet pumps require priming with water and because the water taken from the well mixes with water circulating in the system, they are clearly not applicable to collecting samples for monitoring purposes. For similar reasons, their use is not recommended for well evacuation.

Pressure-Vacuum Lysimeters

The basic construction of pressure-vacuum lysimeters (Wood, 1973), shown in Figure 9-14, consists of a porous ceramic cup, with a bubbling pressure of 1 bar or greater, attached to a short piece of PVC pipe of suitable diameter. Two tubes extend down into the device, as illustrated. Data by Silkworth and Grigal (1981) indicate that, of the two commercially available sampler sizes (2.2 and 4.8 cm diameter), the larger ceramic cup sampler is more reliable, influences water quality less, and yields samples of suitable volume for analysis.

Detailed installation instructions for pressure-vacuum lysimeters are given by Parizek and Lane (1970). Significant modification may be necessary to adapt these instruments to field use when heavy equipment is used. To prevent channelling of contaminated surface water directly to the sampling device, the sampler may be installed in the side wall of an access trench. Because random placement procedures may locate a sampler in the middle of an

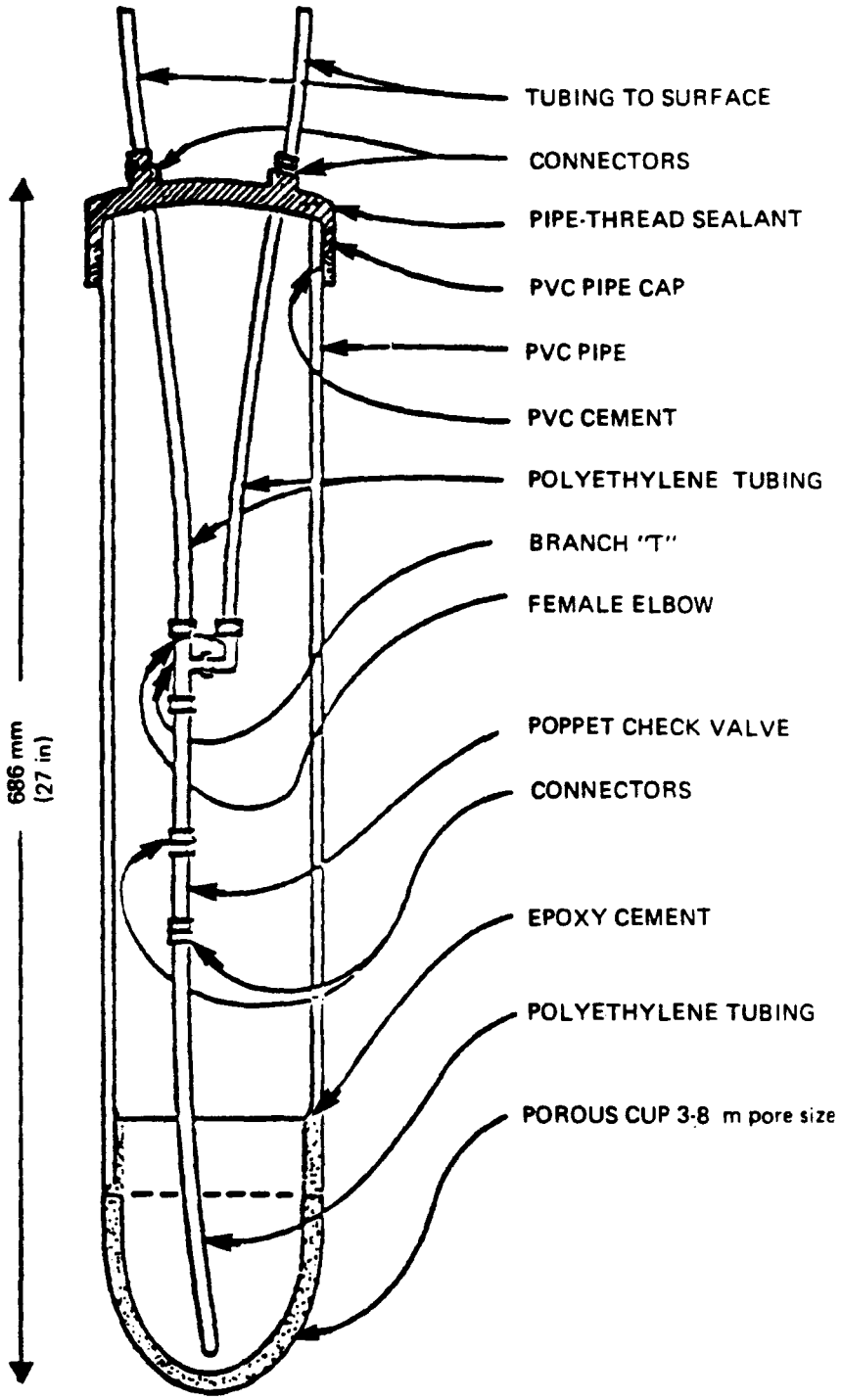


Figure 9-14. One example of a pressure-vacuum lysimeter (Wood, 1973). Reprinted by permission of the American Geophysical Union.

active area, the sample collection tube should be protected at the surface from heavy equipment by a manhole cover, brightly painted steel cage, or other structure. Another problem associated with such sampler placement is that its presence may alter waste management activities (i.e., waste applications, tilling, etc., will avoid the location): therefore, the sampler may not yield representative leachate samples. This problem may be avoided by running the collection tube horizontally underground about 10 m before surfacing.

For sampling after the unit is in place, a vacuum is placed on the system and the tubes are clamped off. Surrounding soil water is drawn into the ceramic cup and up the polyethylene tube. To collect the water sample, the vacuum is released, and one tube is placed in a sample container. Air pressure is applied to the other tube, forcing the liquid up the tube and into the sample container. Preliminary testing should ensure that waste products can pass into the ceramic cup. If sampling for organics, an inert tubing, such as one made of Teflon, should be substituted for the polyethylene pipe to prevent organic contamination.

The major advantages of these sampling devices are that they are easily available, relatively inexpensive to purchase and install, and quite reliable. The major disadvantage is the potential for water quality alterations due to the ceramic cup; this possible problem requires further testing. For a given installation, the device chosen should be specifically tested using solutions containing the soluble hazardous constituents of the waste to be land treated. This device is not recommended for volatiles unless a special trap device is used (Hazardous Waste Land Treatment, SW-874).

Vacuum Extractor

Vacuum extractors were developed by Duke and Haise (1973) to extract moisture from soils above the ground water table. The basic device consists of a stainless steel trough that contains ceramic tubes packed in soil. The unit is sized not to interfere with ambient soil water potentials (Corey, 1974); it is installed at a given depth in the soil with a slight slope toward the collection bottle, which is in the bottom of an adjacent access hole. The system is evacuated and moisture is moved from the adjacent soil into the ceramic tubes and into the collection bottle, from which it can be withdrawn as desired. The advantage of this system is that it yields a quantitative estimate of leachate flux as well as provides a water sample for analysis. The volume of collected leachate per unit area per unit time is an estimate of the downward movement of leachate water at that depth. The major disadvantages to this system are: it is delicate; it requires a trained operator; it estimates leachate quantity somewhat lower than actual field drainage; and it disturbs the soil above the sampler. Further details about the use of the vacuum extractor are given by Trout et al. (1975). Performance of this device when installed in clay soils is generally poor.

Trench Lysimeters

Trench lysimeters are named for the large access trench, or caisson, necessary for operation. Basic installation, as described by Parizek and Lane (1970), involves excavating a rather large trench and shoring up the side walls, taking care to leave open areas so that samplers can be placed in the side walls. Sample trays are imbedded in the side walls and connected by tubing to sample collection containers. The entire trench area is then covered to prevent flooding. One significant danger in using this system is the potential for accumulation of hazardous fumes in the trench, possibly endangering the health and safety of the person collecting the samples.

Trench lysimeters function by intercepting downward-moving water and diverting it into a collection device located at a lower elevation. The intercepting agent may be an open-ended pipe, sheet metal trough, pan, or other similar device. Pans 0.9 to 1.2 m in diameter have been successfully used in the field by Tyler and Thomas (1977). Because there is no vacuum applied to the system, only free water in excess of saturation is sampled. Consequently, samples are plentiful during rainy seasons but are nonexistent during the dry season.

Another variation of this system is to use a funnel filled with clean sand inserted into the sidewall of the trench. Free water will drain into a collection chamber, from which a sample is periodically removed by vacuum. A small sample collection device such as this may be preferable to the large trench because the necessary hole is smaller, so that installation is easier (Figure 9-15).

9.2.2.5 Quality Assurance and Quality Control

Quality assurance (QA) can briefly be defined as the process for ensuring that all data and the decisions based on these data are technically sound, statistically valid, and properly documented. Quality control (QC) procedures are the tools employed to measure the degree to which these quality assurance objectives are met.

A data base cannot be properly evaluated for accuracy and precision unless it is accompanied by quality assurance data. In the case of waste evaluation, these quality assurance data result from the implementation of quality control procedures during sampling and analysis. Quality control requirements for specific analytical methods are given in detail in each method in this manual: in this subsection, quality assurance and quality control procedures for sampling will be discussed.

Quality control procedures that are employed to document the accuracy and precision of sampling are:

1. Trip Blanks: Trip blanks should accompany sample containers to and from the field. These samples can be used to detect any contamination or cross-contamination during handling and transportation.

2. Field Blanks: Field blanks should be collected at specified frequencies, which will vary according to the probability of

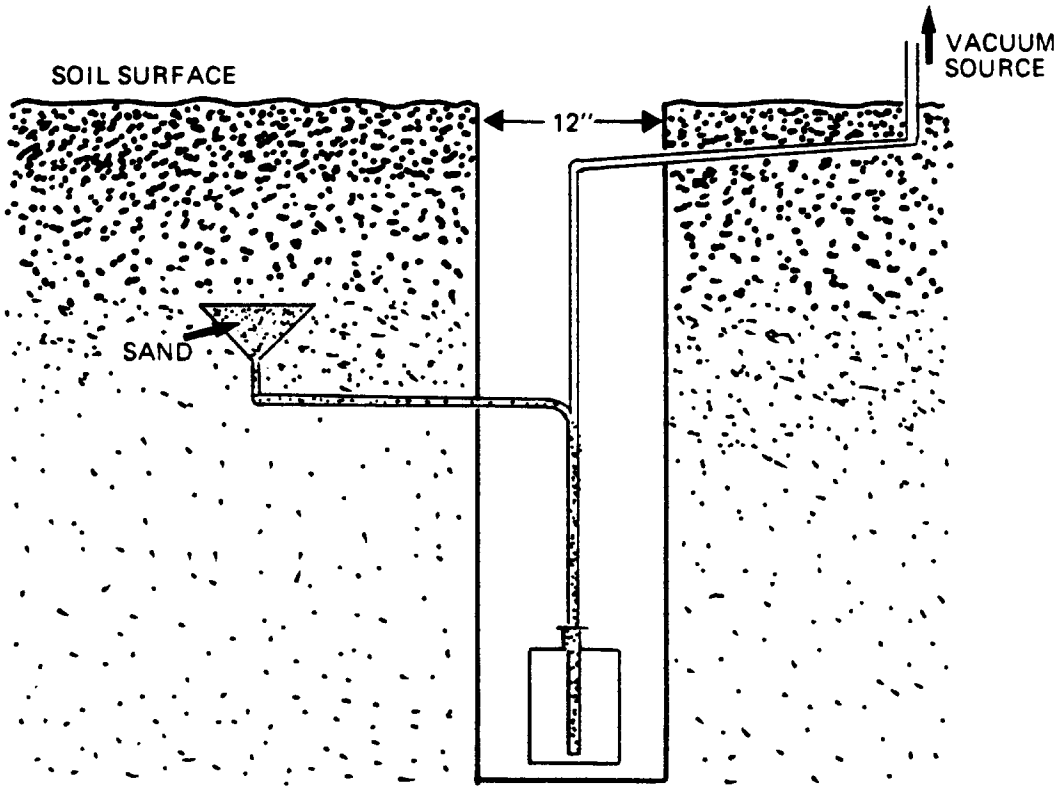


Figure 9-15. Schematic diagram of a sand filled funnel used to collect leachate from the unsaturated zone.

contamination or cross-contamination. Field blanks are often metal- and/or organic-free water aliquots that contact sampling equipment under field conditions and are analyzed to detect any contamination from sampling equipment, cross contamination from previously collected samples, or contamination from conditions during sampling (e.g., airborne contaminants that are not from the waste being sampled).

3. Field Duplicates: Field duplicates are collected at specified frequencies and are employed to document precision. The precision resulting from field duplicates is a function of the variance of waste composition, the variance of the sampling technique, and the variance of the analytical technique.

4. Field Spikes: Field spikes are infrequently used to determine the loss of parameters of interest during sampling and shipment to the laboratories. Because spiking is done in the field, the making of spiked samples or spiked blanks is susceptible to error. In addition, compounds can be lost during spiking, and equipment can be contaminated with spiking solutions. To eliminate these and other problems, some analysts spike blanks or matrices similar to the waste in the laboratory and ship them, along with sample containers, to the field. This approach also has its limitation because the matrix and the handling of the spike are different from those of the actual sample. In all cases, the meaning of a low field-spike recovery is difficult to interpret, and thus, field spikes are not commonly used.

In addition to the above quality control samples, a complete quality assurance program will ensure that standard operating procedures (SOPs) exist for all essential aspects of a sampling effort. SOPs should exist for the following steps in a sampling effort:

1. Definition of objectives (refer to Section 9.2.1).

2. Design of sampling plans (refer to Section 9.2.2).

3. Preparation of containers and equipment (refer to the specific analytical methods).

4. Maintenance, calibration, and cleaning of field equipment (refer to instrument manuals or consult a chemist for cleaning protocols).

5. Sample preservation, packaging, and shipping (refer to the analytical methods and to Section 9.2.2.7).

6. Health and safety protocols (refer to Section 9.2.2.6).

7. Chain-of-custody protocols (refer to Section 9.2.2.7).

In addition to the above protocols, numerous other QA/QC protocols must be employed to document the accuracy of the analytical portion of a waste evaluation program.

9.2.2.6 Health and Safety

Safety and health must also be considered when implementing a sampling plan. A comprehensive health and safety plan has three basic elements: (1) monitoring the health of field personnel; (2) routine safety procedures; and (3) emergency procedures.

Employees who perform field work, as well as those exposed to chemicals in the laboratory, should have a medical examination at the initiation of employment and routinely thereafter. This exam should preferably be performed and evaluated by medical doctors who specialize in industrial medicine. Some examples of parts of a medical examination that ought to be performed are: documentation of medical history; a standard physical exam; pulmonary functions screening; chest X-ray: EKG; urinalysis; and blood chemistry. These procedures are useful to: (1) document the quality of an employee's health at the time of matriculation: (2) ensure the maintenance of good health; and (3) detect early signs of bodily reactions to chemical exposures so they can be treated in a timely fashion. Unscheduled examinations should be performed in the event of an accident, illness, or exposure or suspected exposure to toxic materials.

Regarding safety procedures, personnel should be aware of the common routes of exposure to chemicals (i.e., inhalation, contact, and ingestion) and be instructed in the proper use of safety equipment, such as Draeger tube air samplers to detect air contamination, and in the proper use of protective clothing and respiratory equipment. Protocols should also be defined stating when safety equipment should be employed and designating safe areas where facilities are available for washing. drinking, and eating.

Even when the utmost care is taken, an emergency situation can occur as a result of an unanticipated explosion, electrical hazard, fall, or exposure to a hazardous substance. To minimize the impact of an emergency, field personnel should be aware of basic first aid and have immediate access to a first-aid kit. Phone numbers for both police and the nearest hospital should be obtained and kept by each team member before entering the site. Directions to the nearest hospital should also be obtained so that anyone suffering an injury can be transported quickly for treatment.

9.2.2.7 Chain of Custody

An essential part of any sampling/analytical scheme is ensuring the integrity of the sample from collection to data reporting. The possession and handling of samples should be traceable from the time of collection through analysis and final disposition. This documentation of the history of the sample is referred to as chain of custody.

Chain of custody is necessary if there is any possibility that the analytical data or conclusions based upon analytical data will be used in litigation. In cases where litigation is not involved, many of the chain-of-custody procedures are still useful for routine control of sample flow. The components of chain of custody -- sample seals, a field logbook, chain-of-custody record, and sample analysis request sheet -- and the procedures for their use are described in this section.

A sample is considered is considered to be under a person's custody if it is (1) in a person's physical possession, (2) in view of the person after taking possession, and (3) secured by that person so that no one can tamper with it, or secured by that person in an area that is restricted to authorized personnel. A person who has samples in custody must comply with the following procedures.

(The material presented here briefly summarizes the major aspects of chain of custody. The reader is referred to NEIC Policies and Procedures, EPA-330/9/78/001-R [as revised 1/82], or other manual, as appropriate, for more information.)

Sample labels (Figure 9-16) are necessary to prevent misidentification of samples. Gummed paper labels or tags are adequate and should include at least the following information:

Sample number.
Name of collector.
Date and time of collection.
Place of collection.

Labels should be affixed to sample containers prior to or at the time of sampling and should be filled out at the time of collection.

Sample seals are used to detect unauthorized tampering of samples following sample collection up to the time of analysis. Gummed paper seals may be used for this purpose. The paper seal should include, minimally, the following information:

Sample number. (This number must be identical with the number on the sample label.)
Name of collector.
Date and time of sampling.
Place of collection.

The seal must be attached in such a way that it is necessary to break it in order to open the sample container. (An example of an official sample seal is shown in Figure 9-17.) Seals must be affixed to containers before the samples leave the custody of sampling personnel.

All information pertinent to a field survey or sampling must be recorded in a logbook. This should be bound, preferably with consecutively numbered pages that are 21.6 by 27.9 cm (8-1/2 by 11 in.). At a minimum, entries in the logbook must include the following:

Location of sampling point.
Name and address of field contact.
Producer of waste and address, if different from location.
Type of process producing waste (if known).
Type of waste (e.g., sludge, wastewater).
Suspected waste composition, including concentrations.
Number and volume of sample taken.

Collector _____ Sample No. _____

Place of Collection _____

_____

Date Sampled _____ Time Sampled _____

Field Information _____

_____

Figure 9-16. Example of Sample Label

NAME AND ADDRESS OF ORGANIZATION COLLECTING SAMPLES

Person Collecting Sample _____ Sample No. _____
(signature)

Date Collected _____ Time Collected _____

Place Collected _____

Figure 9-17. Example of Official Sample Seal

Purpose of sampling (e.g., surveillance, contract number).
Description of sampling point and sampling methodology.
Date and time of collection.
Collector's sample identification number(s).
Sample distribution and how transported (e.g., name of laboratory, UPS, Federal Express).
References, such as maps or photographs of the sampling site.
Field observations.
Any field measurements made (e.g., pH, flammability, explosivity).
Signatures of personnel responsible for observations.

Sampling situations vary widely. No general rule can be given as to the extent of information that must be entered in the logbook. A good rule, however, is to record sufficient information so that anyone can reconstruct the sampling without reliance on the collector's memory. The logbook must be stored safely.

To establish the documentation necessary to trace sample possession from the time of collection, a chain-of-custody record should be filled out and should accompany every sample. This record becomes especially important if the sample is to be introduced as evidence in a court litigation. (A chain-of-custody record is illustrated in Figure 9-18.)

The record should contain, minimally, the following information:

Sample number.
Signature of collector.
Date and time of collection.
Place and address of collection.
Waste type.
Signature of persons involved in the chain of possession.
Inclusive dates of possession.

The sample analysis request sheet (Figure 9-19) is intended to accompany the sample on delivery to the laboratory. The field portion of this form is completed by the person collecting the sample and should include most of the pertinent information noted in the logbook. The laboratory portion of this form is intended to be completed by laboratory personnel and to include, minimally:

Name of person receiving the sample.
Laboratory sample number.
Date and time of sample receipt.
Sample allocation.
Analyses to be performed.

The sample should be delivered to the laboratory for analysis as soon as practicable -- usually within 1 or 2 days after sampling. The sample must be accompanied by the chain-of-custody record (Figure 9-18) and by a sample analysis request sheet (Figure 9-19). The sample must be delivered to the person in the laboratory authorized to receive samples (often referred to as the sample custodian).

CHAIN OF CUSTODY RECORD

Proj No.	Project Name												
Samplers *(Signature)*													
Sta. No.	Date	Time	Comp.	Grab	Station Location	No. of Containers							Remarks

Relinquished by: *(Signature)*	Date Time	Received by: *(Signature)*	Relinquished by: *(Signature)*	Date Time	Received by: *(Signature)*
Relinquished by: *(Signature)*	Date Time	Received by: *(Signature)*	Relinquished by: *(Signature)*	Date Time	Received by: *(Signature)*
Relinquished by: *(Signature)*	Date Time	Received for Laboratory by: *(Signature)*		Remarks	

Figure 9-18.

SAMPLING ANALYSIS REQUEST

Part I: Field Section

Collector _____ Date Sampled _____ Time _____ hours

Affiliation of Sampler _____

Address _____
number street city state zip

Telephone ( ) _____ Company Contact _____

LABORATORY SAMPLE NUMBER	COLLECTOR'S SAMPLE NO.	TYPE OF SAMPLE*	FIELD INFORMATION**

Analysis Requested _____

Special Handling and/or Storage _____

PART II: LABORATORY SECTION**

Received by _____ Title _____ Date _____

Analysis Required _____

* Indicate whether sample is soil, sludge, etc.
** Use back of page for additional information relative to sample location.

Figure 9-19. Example of hazardous waste sample analysis sheet.

Any material that is identified in the DOT Hazardous Material Table (49 CFR 172.101) must be transported as prescribed in the table. All other hazardous waste samples must be transported as follows:

1. Collect sample in a 16-oz or smaller glass or polyethylene container with nonmetallic Teflon-lined screw cap. For liquids, allow sufficient air space, approximately 10% by volume) so that the container is not full at 54°C (130 °F). If collecting a solid material, the container plus contents should not exceed 1 lb net weight. If sampling for volatile organic analysis, fill VOA container to septum but place the VOA container inside a 16-oz or smaller container so that the required air space may be provided. Large quantities, up to 3.785 liters (1 gal), may be collected if the sample's flash point if 23°C (75°F) or higher. In this case, the flash point must be marked on the outside container (e.g., carton or cooler), and shipping paper should state that "Flash point is 73°F or higher."

2. Seal sample and place in a 4-mil-thick polyethylene bag, one sample per bag.

3. Place sealed bag inside a metal can with noncombustible, absorbent cushioning material (e.g., vermiculite or earth) to prevent breakage, one bag per can. Pressure-close the can and use clips, tape, or other positive means to hold the lid securely.

4. Mark the can with:

   Name and address of originator.
   "Flammable Liquid, N.O.S. UN 1993."
   (or, "Flammable Solid, N.O.S. UN 1325".)

NOTE: UN numbers are now required in proper shipping names.

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5. Place one or more metal cans in a strong outside container such as a picnic cooler or fiberboard box. Preservatives are not used for hazardous waste site samples.

6. Prepare for shipping: The words "Flammable Liquid, N.O.S. UN 1993" or "Flammable Solid, N.O.S. UN 1325"; "Cargo Aircraft Only" (if more than 1 qt net per outside package); "Limited Quantity" or "Ltd. Qty."; "Laboratory Samples"; "Net Weight ___" or "Net Volume ____" (of hazardous contents) should be indicated on shipping papers and on the outside of the outside shipping container. The words "This Side Up" or "This End Up" should also be on container. Sign the shipper certification.

7. Stand by for possible carrier requests to open outside containers for inspection or to modify packaging. (It is wise to contact carrier before packing to ascertain local packaging requirements.) Remain in the departure area until the carrier vehicle (aircraft, truck, etc.) is on its way.

At the laboratory, a sample custodian should be assigned to receive the samples. Upon receipt of a sample, the custodian should inspect the condition of the sample and the sample seal, reconcile the information on the sample label and seal against that on the chain-of-custody record, assign a laboratory number, log in the sample in the laboratory logbook, and store it in a secured sample storage room or cabinet until it is assigned to an analyst for analysis.

The sample custodian should inspect the sample for any leakage from the container. A leaky container containing a multiphase sample should not be accepted for analysis. This sample will no longer be a representative sample. If the sample is contained in a plastic bottle and the container walls show that the sample is under pressure or releasing gases, the sample should be treated with caution because it may be explosive or release extremely poisonous gases. The custodian should examine whether the sample seal is intact or broken, because a broken seal may mean sample tampering and would make analysis results inadmissible as evidence in court. Any discrepancies between the information on the sample label and seal and the information that is on the chain-of-custody record and the sample analysis request sheet should be resolved before the sample is assigned for analysis. This effort might require communication with the sample collector. Results of the inspection should be noted on the sample analysis request sheet and on the laboratory sample logbook.

Incoming samples usually carry the inspector's or collector's identification numbers. To identify these samples further, the laboratory should assign its own identification numbers, which normally are given consecutively. Each sample should be marked with the assigned laboratory number. This number is correspondingly recorded on a laboratory sample log book along with the information describing the sample. The sample information is copied from the sample analysis request sheet and cross-checked against that on the sample label.

In most cases, the laboratory supervisor assigns the sample for analysis. The supervisor should review the information on the sample analysis request sheet, which now includes inspection notes recorded by the laboratory sample custodian. The technician assigned to analysis should record in the laboratory notebook the identifying information about the sample, the date of receipt, and other pertinent information. This record should also include the subsequent testing data and calculations. The sample may have to be split with other laboratories in order to obtain all the necessary analytical information. In this case, the same type of chain-of-custody procedures must be employed while the sample is being transported and at the other laboratory.

Once the sample has been received in the laboratory, the supervisor or his/her assignee is responsible for its care and custody. That person should be prepared to testify that the sample was in his/her possession or secured in the laboratory at all times, from the moment it was received from the custodian until the analyses were performed.

9.2.3 Sample Plan Implementation

Prior to implementing a sampling plan, it is often strategic to walk through the sampling plan mentally, starting with the preparation of equipment until the time when samples are received at the laboratory. This mental excursion should be in as much detail as can be imagined, because the small details are the ones most frequently overlooked. By employing this technique, items not included on the equipment list may be discovered, as well as any major oversight that could cause the sampling effort to fail. During this review of the sampling plan, an attempt should be made to anticipate what could go wrong. A solution to anticipated problems should be found, and, if necessary, materials needed for solving these problems should be added to the equipment list.

The remainder of this section discusses examples of sampling strategies for different situations that may be encountered.

Containers

Prior to discussing the sampling of containers, the term must be defined. The term container, as used here, refers to receptacles that are designed for transporting materials, e.g., drums and other smaller receptacles, as opposed to stationary tanks. Weighted bottles, Coliwasas, drum thiefs, or triers are the sampling devices that are chosen for the sampling of containers. (See Section 9.2.2.4 for a full discussion of sampling equipment.)

The sampling strategy for containers varies according to (1) the number of containers to be sampled and (2) access to the containers. Ideally, if the waste is contained in several containers, every container will be sampled. If this is not possible due to the large number of containers or to cost factors, a subset of individual containers must be randomly selected for sampling. This can be done by assigning each container a number and then randomly choosing a set of numbers for sampling.

Access to a container will affect the number of samples that can be taken from the container and the location within the container from which samples can be taken. Ideally, several samples should be taken from locations displaced both vertically and horizontally throughout the waste. The number of samples required for reliable sampling will vary depending on the distribution of the waste components in the container. At a minimum with an unknown waste, a sufficient number and distribution of samples should be taken to address any possible vertical anomalies in the waste. This is because contained wastes have a much greater tendency to be nonrandomly heterogeneous in a vertical rather than a horizontal direction due to (1) settling of solids and the denser phases of liquids and (2) variation in the content of the waste as it enters the container. Bags, paper drums, and open-headed steel drums (of which the entire top can be removed) generally do not restrict access to the waste and therefore do not limit sampling.

When access to a container is unlimited, a useful strategy for obtaining a representative set of samples is a three-dimensional simple random sampling strategy in which the container is divided by constructing an imaginary three-dimensional grid (see Figure 9-20), as follows. First, the top surface of the waste is divided into a grid whose section either approximate the size of the sampling device or are larger than the sampling device if the container is large. (Cylindrical containers can be divided into imaginary concentric circles, which are then further divided into grids of equal size.) Each section is assigned a number. The height of the container is then divided into imaginary levels that are at least as large as the vertical space required by the chosen sampling device. These imaginary levels are then assigned numbers. Specific levels and grid locations are then selected for sampling using a random-number table or random-number generator. (an alternative means of choosing random sampling locations using circumference and diameter dimensions is discussed in Section 9.2.2.1.)

Another appropriate sampling approach is the two-dimensional simple random sampling strategy, which can usually yield a more precise sampling when fewer samples are collected. This strategy involves (1) dividing the top surface of the waste into an imaginary grid as in the three-dimensional strategy, (2) selecting grid sections for sampling using random-number tables or random-number generators, and (3) sampling each selected grid point in a vertical manner along the entire length from top to bottom using a sampling device such as a drum thief or Coliwasa.

Some containers, such as drums with bung openings, limit access to the contained waste and restrict sampling to a single vertical plane. Samples taken in this manner can be considered representative of the entire container only if the waste is known to be homogenous or if no horizontal stratification has occurred. Precautions must be taken when sampling any type of steel drum because the drum may explode or expel gases and/or pressurized liquids. An EPA/NEIC manual, "Safety Manual for Hazardous Waste Site Investigation," addresses these safety precautions.

Tanks

Tanks are essentially large containers. The considerations involved in sampling tanks are therefore similar to those for sampling containers. As with containers, the goal of sampling tanks is to acquire a sufficient number of samples from different locations within the waste to provide analytical data that are representative of the entire tank contents.

The accessibility of the tank contents will affect the sampling methodology. If the tank is an open one, allowing unrestricted access, then usually a representative set of samples is best obtained using the three-dimensional simple random sampling strategy, as described for containers (see also Section 9.2.2.1). This strategy involves dividing the tank contents into an imaginary three-dimensional grid. As a first step, the top surface of the waste is divided into a grid whose sections either approximate the size of the sampling device or are larger than the sampling device if the tank is large.

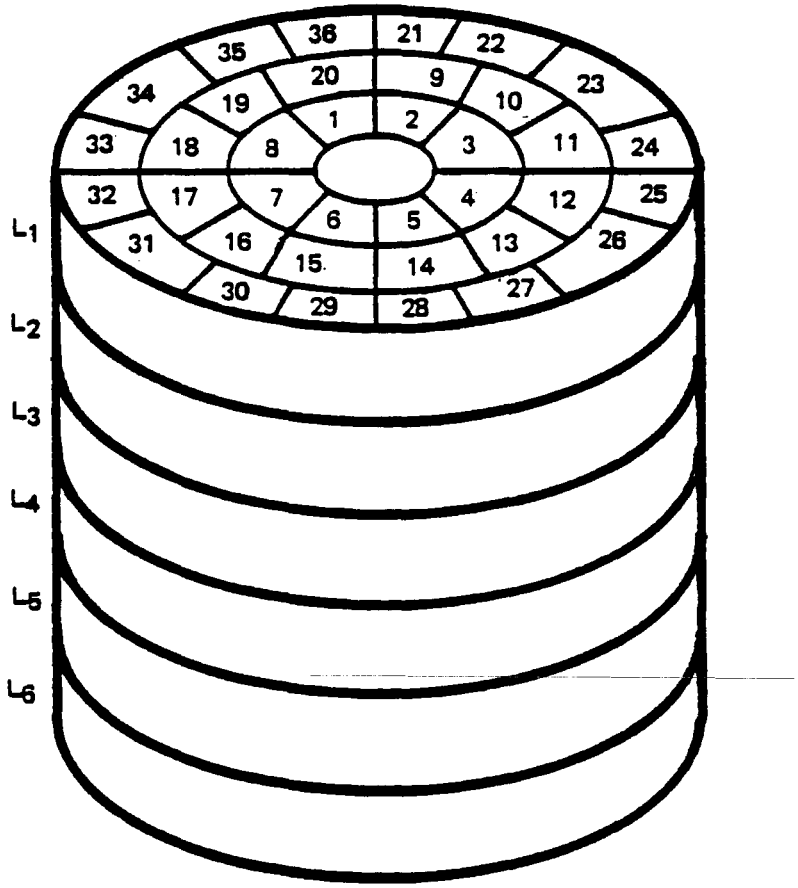

Figure 9-20. Container divided into an imaginary three-dimensional grid.

(Cylindrical tanks can be divided into imaginary concentric circles, which are then further divided into grids of equal size.) Each section is assigned a number. The height of the tank is then divided into imaginary levels that are at least as large as the vertical space required by the chosen sampling device. These imaginary levels are assigned numbers. Specific levels and grid locations are then selected for sampling using a random-number table or random-number generator.

A less comprehensive sampling approach may be appropriate if information regarding the distribution of waste components is known or assumed (e.g., if vertical compositing will yield a representative sample). In such cases, a two-dimensional simple random sampling strategy may be appropriate. In this strategy, the top surface of the waste is divided into an imaginary grid; grid sections are selected using random-number tables or random-number generators; and each selected grid point is then sampled in a vertical manner along the entire length from top to bottom using a sampling device such as a weighted bottle, a drum thief, or Coliwasa. If the waste is known to consist of two or more discrete strata, a more precise representation of the tank contents can be obtained by using a stratified random sampling strategy, i.e., by sampling each stratum separately using the two- or three-dimensional simple random sampling strategy.

Some tanks permit only limited access to their contents, which restricts the locations within the tank from which samples can be taken. If sampling is restricted, the sampling strategy must, at a minimum, take sufficient samples to address the potential vertical anomalies in the waste in order to be considered representative. This is because contained wastes tend to display vertical, rather than horizontal, nonrandom heterogeneity due to settling of suspended solids or denser liquid phases. If access restricts sampling to a portion of the tank contents (e.g., in an open tank, the size of the tank may restrict sampling to the perimeter of the tank; in a closed tank, the only access to the waste may be through inspection ports), then the resulting analytical data will be deemed representative only of the accessed area, not of the entire tank contents unless the tank contents are known to be homogeneous.

If a limited access tank is to be sampled, and little is known about the distribution of components within the waste, a set of samples that is representative of the entire tank contents can be obtained by taking a series of samples as the tank contents are being drained. This should be done in a simple random manner by estimating how long it will take to drain the tank and then randomly selecting times during drainage for sampling.

The most appropriate type of sampling device for tanks depends on the tank parameters. In general, subsurface samples (i.e., pond samplers) are used for shallow tanks, and weighted bottles are usually employed for tanks deeper than 5 ft. Dippers are useful for sampling pipe effluents.

Waste Piles

In waste piles, the accessibility of waste for sampling is usually a function of pile size, a key factor in the design of a sampling strategy for a waste pile. Ideally, piles containing unknown wastes should be sampled using a three-dimensional simple random sampling strategy. This strategy can be employed only if all points within the pile can be accessed. In such cases, the pile should be divided into a three-dimensional grid system, the grid sections assigned numbers, and the sampling points then chosen using random-number tables or random-number generators.

If sampling is limited to certain portions of the pile, then the collected sample will be representative only of those portions, unless the waste is known to be homogenous.

In cases where the size of a pile impedes access to the waste, a set of samples that are representative of the entire pile can be obtained with a minimum of effort by scheduling sampling to coincide with pile removal. The number of truckloads needed to remove the pile should be estimated and the truckloads randomly chosen for sampling.

The sampling devices most commonly used for small piles are thiefs, triers, and shovels. Excavation equipment, such as backhoes, can be useful for sampling medium-sized piles.

Landfills and Lagoons

Landfills contain primarily solid waste, whereas lagooned waste may range from liquids to dried sludge residues. Lagooned waste that is either liquid or semisolid is often best sampled using the methods recommended for large tanks. Usually, solid wastes contained in a landfill or lagoon are best sampled using the three-dimensional random sampling strategy.

The three-dimensional random sampling strategy involves establishing an imaginary three-dimensional grid of sampling points in the waste and then using random-number tables or random-number generators to select points for sampling. In the case of landfills and lagoons, the grid is established using a survey or map of the area. The map is divided into two two-dimensional grids with sections of equal size. (An alternative way of choosing random sampling locations is presented in the second example described in Section 9.2.2.1) These sections are then assigned numbers sequentially.

Next, the depth to which sampling will take place is determined and subdivided into equal levels, which are also sequentially numbered. (The lowest sampling depth will vary from landfill to landfill. Usually, sampling extends to the interface of the fill and the natural soils. If soil contamination is suspected, sampling may extend into the natural soil.) The horizontal and vertical sampling coordinates are then selected using random-number tables or random-number generators. If some information is known about the nature of the waste, then a modified three-dimensional strategy may be more appropriate. For example, if the landfill consists of several cells, a more precise measurement may be obtained by considering each cell as a stratum and employing a stratified three-dimensional random sampling strategy (see Section 9.1).

Hollow-stem augers combined with split-spoon samplers are frequently appropriate for sampling landfills. Water-driven or water-rinsed coring equipment should not be used for sampling because the water can rinse chemical components from the sample. Excavation equipment, such as backhoes, may be useful in obtaining samples at various depths; the resulting holes may be useful for viewing and recording the contents of the landfill.

9.2.4 Sample Compositing

The compositing of samples, is usually done for cost-saving reasons, involves the combining of a number of samples or aliquots of a number of samples collected from the same waste. The disadvantage of sample compositing is the loss of concentration variance data, whereas the advantage is that, for a given analytical cost, a more representative (i.e., more accurate) sample is obtained.

It is usually most expedient and cost effective to collect component samples in the field and to composite aliquots of each sample later in the laboratory. Then, if after reviewing the data any questions arise, the samples can be recomposited in a different combination, or each component sample can be analyzed separately to determine better the variation of waste composition over time and space, or to determine better the precision of an average number. The fact that this recompositing of samples can occur without the need to resample often results in a substantial cost savings.

To ensure that recompositing can be done at a later date, it is essential to collect enough sample volume in the field so that, under normal circumstances, enough component sample will remain following compositing to allow for a different compositing scheme or even for an analysis of the component samples themselves.

The actual compositing of samples requires the homogenization of all component samples to ensure that a representative subsample is aliquoted. The homogenization procedure, and the containers and equipment used for compositing, will vary according to the type of waste being composited and the parameters to be measured. Likewise, the composite sample itself will be homogenized prior to the subsampling of analytical aliquots.

9.2.5 References

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APPENDIX

COMPANY REFERENCES

The following listing of frequently-used addresses is provided for the convenience of users of this manual. No endorsement is intended or implied.

Ace Glass Company
1342 N.W. Boulevard
P.O. Box 688
Vineland, NJ 08360
(609) 692-3333

Aldrich Chemical Company
Department T
P.O. Box 355
Milwaukee, WI 53201

Alpha Products
5570 - T W. 70th Place
Chicago, IL 60638
(312) 586-9810

Barneby and Cheney Company
E. 8th Avenue and N. Cassidy Street
P.O. Box 2526
Columbus, OH 43219
(614) 258-9501

Bio - Rad Laboratories
2200 Wright Avenue
Richmond, CA 94804
(415) 234-4130

Burdick & Jackson Lab Inc.
1953 S. Harvey Street
Muskegon, MO 49442

Calgon Corporation
P.O. Box 717
Pittsburgh, PA 15230
(412) 777-8000

Conostan Division
Conoco Speciality Products, Inc.
P.O. Box 1267
Ponca City, OK 74601
(405) 767-3456

Corning Glass Works
Houghton Park
Corning, NY 14830
(315) 974-9000

Dohrmann, Division of Xertex Corporation
3240 - T Scott Boulevard
Santa Clara, CA 95050
(408) 727-6000
(800) 538-7708

E. M. Laboratories, Inc.
500 Executive Boulevard
Elmsford, NY 10523

Fisher Scientific Co.
203 Fisher Building
Pittsburgh, PA 15219
(412) 562-8300

General Electric Corporation
3135 Easton Turnpike
Fairfield, CT 06431
(203) 373-2211

Graham Manufactory Co., Inc.
20 Florence Avenue
Batavia, NY 14020
(716) 343-2216

Hamilton Industries
1316 18th Street
Two Rivers, WI 54241
(414) 793-1121

ICN Life Sciences Group
3300 Hyland Avenue
Costa Mesa, CA 92626

Johns - Manville Corporation
P.O. Box 5108
Denver, CO 80217

Kontes Glass Company
8000 Spruce Street
Vineland, NJ 08360

Millipore Corporation
80 Ashby Road
Bedford, MA 01730
(617) 275-9200
(800) 225-1380

National Bureau of Standards
U.S. Department of Commerce
Washington, DC 20234
(202) 921-1000

Pierce Chemical Company
Box 117
Rockford, IL 61105
(815) 968-0747

Scientific Glass and Instrument, Inc.
7246 - T Wynnwood
P.O. Box 6
Houston, TX 77001
(713) 868-1481

Scientific Products Company
1430 Waukegon Road
McGaw Park, IL 60085
(312) 689-8410

Spex Industries
3880 - T and Park Avenue
Edison, NJ 08820

Waters Associates
34 - T Maple Street
Milford, MA 01757
(617) 478-2000
(800) 252-4752

Whatman Laboratory Products, Inc.
Clifton, NJ 07015
(201) 773-5800