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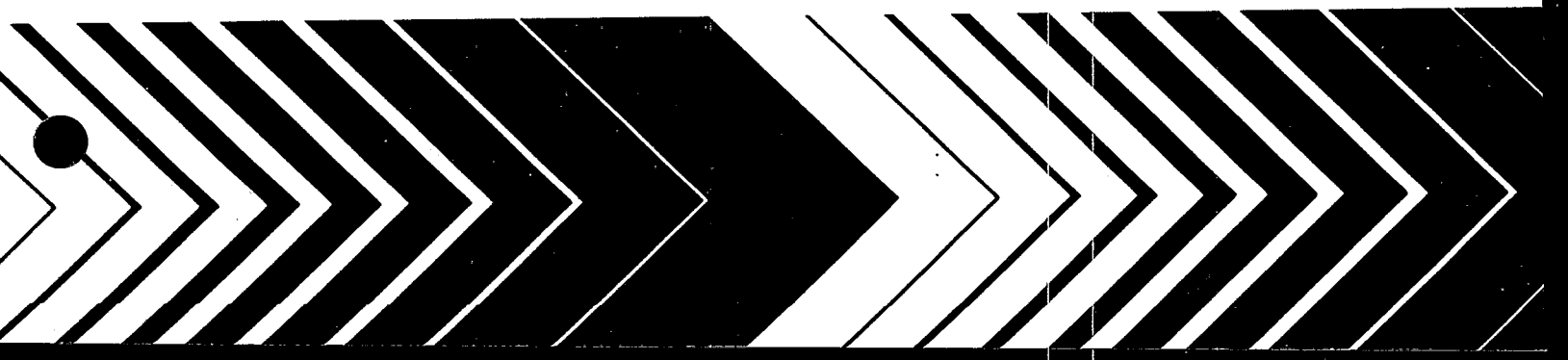
Technical Notes on Drinking Water Methods



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TECHNICAL NOTES

on

DRINKING WATER METHODS

U. S. Environmental Protection Agency
Office of Water
Office of Ground Water and Drinking Water
Office of Research and Development
Environmental Monitoring Systems Laboratory
Cincinnati, OH 45268

DISCLAIMER

This manual has been reviewed by the Technical Support Division, Office of Water and the Environmental Monitoring Systems Laboratory - Cincinnati, U.S. Environmental Protection Agency, and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

FOREWORD

Compliance with National Primary and Secondary Drinking Water Regulations requires that analyses of samples be conducted by a certified laboratory. A certification condition is that an approved method be used. The Office of Water's (OW) Technical Support Division (TSD) prepares the analytical methods parts of drinking water regulations. The Office of Research and Development's (ORD) Environmental Monitoring Systems Laboratory at Cincinnati, Ohio (EMSL-Cincinnati) conducts research to develop and evaluate analytical methods for the determination of contaminants in many media including drinking water. EMSL-Cincinnati also regularly publishes methods for use in drinking water compliance monitoring.

This joint OW/ORD publication, Technical Notes on Drinking Water Methods, was prepared to add modifications, clarifications, options or improvements to methods that have been previously approved and published. To allow the public to use these changes without waiting for incorporation in the next revision of a method, EPA has elected to describe the changes in this document. The Office of Water will approve these changes in a 1994 rulemaking by incorporating Technical Notes on Drinking Water Methods into the drinking water regulations. Procedures described herein supersede or complement procedures described in the approved methods. When a method is revised, relevant procedures from this document will be included in the revised method.

We are pleased to provide these technical notes and believe they will be of considerable value to public and private laboratory, regulatory and certification personnel.

Alan A. Stevens, Director
Technical Support Division
Office of Water

Thomas Clark, Director
Environmental Monitoring Systems
Laboratory - Cincinnati

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ACKNOWLEDGMENTS

We appreciate the many constructive comments and informative questions from our customers, the analytical and certification laboratory community. Their information provided the basis for the options, clarifications and method modifications that are approved and described in these technical notes.

Many people in the Office of Research and Development's Environmental Monitoring Systems Laboratory - Cincinnati (EMSL-Cincinnati) and in the Office of Ground Water and Drinking Water's Technical Support Division (TSD) in Cincinnati contributed to these notes. The EPA scientists in these groups used information from their many contacts with the public, and their years of experience with drinking water analysis to produce this publication. Technical Notes was developed and edited by Richard Reding of TSD who wishes to especially acknowledge the contributions of Thomas Behymer, James Eichelberger, Theodore Martin, Jean Munch, James O'Dell, John Pfaff, Jody Shoemaker and Nancy Ulmer from EMSL-Cincinnati, Patricia Snyder Fair, Marianne Feige, Edward Glick, David Munch and Kent Sorrell from TSD, and Patrick Clark from the Risk Reduction Engineering Laboratory in Cincinnati. Carol Madding, TSD, contributed technical notes and helped with the editorial design. In addition, the names of the developers of the methods and instrumentation that are the subject of this publication can be found in the acknowledgment and reference sections of the EPA method or EPA methods manual.

The administrative personnel of EMSL-Cincinnati, in particular Diane Schirmann, Patricia Hurr, and Helen Brock, provided outstanding support to this effort. The editor also thanks the administrators and managers of the Environmental Protection Agency who supported the development and preparation of this document. Special appreciation is due to Herbert J. Brass, Chief of the Drinking Water Quality Assessment Branch, TSD, and William L. Budde, Director of the Chemistry Research Division, EMSL-Cincinnati, for their cooperation and support during this project.

INTRODUCTION

Richard Reding

This document, Technical Notes on Drinking Water Methods, describes method modifications that were developed after an approved method had been published. Most of the modifications were formerly footnoted in the drinking water regulations, or were described in a proposed rule (58 FR 65622, December 15, 1993). Because this document is incorporated by reference in drinking water regulations, it is a mandatory part of the analytical procedures required to conduct compliance monitoring and to obtain laboratory certification. Laboratories can use this publication as a guide to analytical methods approved under the Safe Drinking Water Act (SDWA), to obtain information on the latest approved modifications to these methods, and to contact EPA with questions about drinking water methods. Since EPA method manuals are printed in a looseleaf format, the format of Technical Notes allows readers to insert pages containing a method change in the manual containing the affected EPA analytical method.

Methods approved for monitoring under National Primary Drinking Water Regulations are in Section I of this document. Methods for which approval will be withdrawn in 1996 are in Section II, and methods for monitoring under National Secondary Drinking Water Regulations are contained in Section III. Mandatory method modifications are described in Section IV. The modifications include a protocol for monitoring chlorine residuals continuously as required under the Surface Water Treatment Rule, requirements for mandatory manual distillation of samples collected for determination of cyanide, and use of another derivatizing reagent with EPA Methods 515.1 and 515.2. Technical notes on optional procedures and recommended modifications to compliance methods are described in Section V. These notes include guidance on how to make analyses of asbestos and dioxin more cost-effective, and when to omit use of mercuric chloride in some EPA pesticide methods. The remainder of this introduction provides guidance on methods selection and on the laboratory certification aspects of approved methods.

SELECTION OF METHODS FOR OTHER CHEMICALS

EPA believes that some water systems wish to measure chemicals that are not included in drinking water regulations, and need advice on what method to use. The December 1993 Proposal noted that while EPA only approves methods for contaminants regulated under the SDWA, the Agency encourages laboratories to use these methods for voluntary monitoring of other contaminants, "if the method description specifically includes these contaminants." This recommendation does not preclude use of other methods, including test kits, for voluntary monitoring. Analysts always should carefully evaluate the performance of any method when using it for samples other than compliance monitoring samples, or for contaminants not regulated under the SDWA.

LABORATORY CERTIFICATION

When using an approved method to obtain certification or to conduct compliance monitoring, EPA strongly encourages users of methods that are published in an EPA manual to follow instructions contained in the introductions to these manuals, unless the instructions conflict with statements in this document, or in the drinking water regulations. Although "must" can be argued to be a stronger word than "should" in requiring adherence to method procedures, some approved methods use these terms interchangeably. Analytical methods for drinking water are written to be prescriptive enough to provide uniformity of data quality, and flexible enough to allow analysts to exercise judgment, skill and initiative to improve the overall quality and efficiency of compliance monitoring. The Agency does not believe that semantical differences between "must" or "should" limits the authority of certification officials to enforce provisions of the methods.

SECTION I. APPROVED DRINKING WATER METHODS FOR COMPLIANCE MONITORING

To make this document a more complete source of current methods information, the approved methods which are specified in regulations at 40 CFR Part 141, are listed in this section. Methods for which approval will be withdrawn in 1996 are in Section II. Recommended methods for secondary contaminant monitoring, which are specified in regulations at 40 CFR Part 143, are listed in Section III.

METHODS FOR COLIFORM SAMPLING

To comply with the provisions of the Total Coliform Rule, public water systems must conduct analyses in accordance with one of the analytical methods in the following table. Total coliform methods, except for the Colisure Test, are contained in the 18th edition of Standard Methods for the Examination of Water and Wastewater, 1992, American Public Health Association, 1015 Fifteenth Street NW, Washington, D.C. 20005. Preparation of the EC medium and the nutrient agar are described in Standard Methods, p. 9-52, para. 1a, and pp. 9-47 to 9-48, respectively. A description of the Colisure Test may be obtained from the Millipore Corporation, Technical Services Department, 80 Ashby Road, Bedford, MA 01730. The phone number is (800) 645-5476.

Organism	Methodology	Citation
Total Coliforms[1]	Total Coliform Fermentation Technique[2,3,4]	9221A, B
	Total Coliform Membrane Filter Technique	9222A, B, C
	Presence-Absence (P-A) Coliform Test[4,5]	9221D
	ONPG-MUG Test[6]	9223
	Colisure Test[7]	

Footnotes

[1] The time from sample collection to initiation of analysis may not exceed 30 hours.
[2] Lactose broth, as commercially available, may be used in lieu of lauryl tryptose broth, if the system conducts at least 25 parallel tests between this medium and lauryl tryptose broth using the water normally tested, and this comparison demonstrates that the false-positive rate for total coliforms, using lactose broth, is less than 10 percent.
[3] If inverted tubes are used to detect gas production, the media should cover these tubes at least one-half to two-thirds after the sample is added.
[4] No requirement exists to run the completed phase on 10 percent of all total coliform-positive confirmed tubes.
[5] Six-times formulation strength may be used if the medium is filter-sterilized rather than autoclaved.
[6] The ONPG-MUG Test is also known as the Autoanalysis Colilert System.
[7] The Colisure Test must be incubated for 28 hours before examining the results. If examination at 28 hours is not convenient, then results may be examined at any time between 28 hours and 48 hours.

METHODS FOR INORGANIC CHEMICALS AND OTHER PARAMETERS

Analysis for the following contaminants shall be conducted in accordance with the methods in the following Table, or their equivalent as determined by EPA. The monitoring requirements for these contaminants are specified at §§ 141.23, 141.41, and 141.80 - 141.91. Criteria for analyzing arsenic, barium, beryllium, cadmium, calcium, chromium, copper, lead, nickel, selenium and thallium with digestion or directly without digestion, and other mandatory procedures are contained in Section IV of this Technical Notes document. Guidance on conducting asbestos analysis is described in Section V of Technical Notes.

Contaminant	Methodology	EPA	ASTM[1]	SM[2]	Other
Antimony	ICP-Mass Spectrometry	200.8[3]			
	Hydride-Atomic Absorption		D-3697-92		
	Atomic Absorption; Platform	200.9[3]			
	Atomic Absorption; Furnace			3113B	
Arsenic	Inductively Coupled Plasma	200.7[3]		3120B	
	ICP-Mass Spectrometry	200.8[3]			
	Atomic Absorption; Platform	200.9[3]			
	Atomic Absorption; Furnace		D-2972-93C	3113B	
	Hydride Atomic Absorption		D-2972-93B	3114B	
Asbestos	Transmission Electron Microscopy	100.1[4]			
	Transmission Electron Microscopy	100.2[5]			
Barium	Inductively Coupled Plasma	200.7[3]		3120B	
	ICP-Mass Spectrometry	200.8[3]			
	Atomic Absorption; Direct			3111D	
	Atomic Absorption; Furnace			3113B	
Beryllium	Inductively Coupled Plasma	200.7[3]		3120B	
	ICP-Mass Spectrometry	200.8[3]			
	Atomic Absorption; Platform	200.9[3]			
	Atomic Absorption; Furnace		D-3645-93B	3113B	

Contaminant	Methodology	EPA	ASTM[1]	SM[2]	Other
Cadmium	Inductively Coupled Plasma	200.7[3]			
	ICP-Mass Spectrometry	200.8[3]			
	Atomic Absorption; Platform	200.9[3]			
	Atomic Absorption; Furnace			3113B	
Chromium	Inductively Coupled Plasma	200.7[3]		3120B	
	ICP-Mass Spectrometry	200.8[3]			
	Atomic Absorption; Platform	200.9[3]			
	Atomic Absorption; Furnace			3113B	
Cyanide	Manual Distillation followed by			4500-CN-C	
	Spectrophotometric, Amenable		D2036-91B	4500-CN-G	
	Spectrophotometric				
	Manual		D2036-91A	4500-CN-E	I-3300-85[6]
	Semi-automated	335.4[7]			
	Selective Electrode			4500CN-F	
Fluoride	Ion Chromatography	300.0[7]	D4327-91	4110B	
	Manual Distill.; Color. SPADNS			4500F-B,D	
	Manual Electrode		D1179-93B	4500F-C	
	Automated Electrode				380-75WE[8]
	Automated Alizarin			4500F-E	129-71W[8]
Mercury	Manual, Cold Vapor	245.1[3]	D3223-91	3112B	
	Automated, Cold Vapor	245.2[9]			
	ICP-Mass Spectrometry	200.8[3]			
Nickel	Inductively Coupled Plasma	200.7[3]		3120B	
	ICP-Mass Spectrometry	200.8[3]			
	Atomic Absorption; Platform	200.9[3]			
	Atomic Absorption; Direct			3111B	
	Atomic Absorption; Furnace			3113B	
Nitrate	Ion Chromatography	300.0[7]	D4327-91	4110B	B-1011[10]
	Automated Cadmium Reduction	353.2[7]	D3867-90A	4500-NO_3-F	
	Ion Selective Electrode			4500-NO_3-D	601[11]
	Manual Cadmium Reduction		D3867-90B	4500-NO_3-E	

Contaminant	Methodology	EPA	ASTM[1]	SM[2]	Other
Nitrite	Ion Chromatography	300.0[7]	D4327-91	4110B	B-1011[10]
	Automated Cadmium Reduction	353.2[7]	D3867-90A	4500-NO_3-F	
	Manual Cadmium Reduction		D3867-90B	4500-NO_3-E	
	Spectrophotometric			4500-NO_2-B	
Selenium	Hydride-Atomic Absorption		D3859-93A	3114B	
	ICP-Mass Spectrometry	200.8[3]			
	Atomic Absorption; Platform	200.9[3]			
	Atomic Absorption; Furnace		D3859-93B	3113B	
Thallium	ICP-Mass Spectrometry	200.8[3]			
	Atomic Absorption; Platform	200.9[3]			
Lead	Atomic absorption; furnace		D3559-90D	3113B	
	ICP-Mass spectrometry	200.8[3]			
	Atomic absorption; platform	200.9[3]			
Copper	Atomic absorption; furnace		D1688-90C	3113B	
	Atomic absorption; direct aspiration		D1688-90A	3111B	
	ICP	200.7[3]		3120B	
	ICP - Mass spectrometry	200.8[3]			
	Atomic absorption; platform	200.9[3]			
pH	Electrometric	150.1[9]	D1293-84	4500-H^+-B	
		150.2[9]			
Conductivity	Conductance		D1125-91A	2510B	
Calcium	EDTA titrimetric		D511-93A	3500-Ca-D	
	Atomic absorption; direct aspiration		D511-93B	3111B	
	Inductively-coupled plasma	200.7[3]		3120B	
Alkalinity	Titrimetric		D1067-92B	2320B	
	Electrometric titration				I-1030-85[6]

Contaminant	Methodology	EPA	ASTM[1]	SM[2]	Other
Ortho-phosphate unfiltered, no digestion or hydrolysis	Colorimetric, automated, ascorbic acid	365.1[7]		4500-P-F	
	Colorimetric, ascorbic acid, single reagent		D515-88A	4500-P-E	
	Colorimetric, phosphomolybdate; automated-segmented flow; automated discrete				I-1601-85[6] I-2601-90[6] I-2598-85[6]
	Ion Chromatography	300.0[7]	D4327-91	4110	
Silica	Colorimetric, molybdate blue; automated-segmented flow				I-1700-85[6] I-2700-85[6]
	Colorimetric		D859-88		
	Molybdosilicate			4500-Si-D	
	Heteropoly blue			4500-Si-E	
	Automated method for molybdate-reactive silica			4500-Si-F	
	Inductively-coupled plasma	200.7[3]		3120B	
Temperature	Thermometric			2550B	
Sodium	Inductively-coupled plasma	200.7[3]			
	Atomic absorption; direct aspiration			3111B	

Footnotes

[1] Annual Book of ASTM Standards, Vols. 11.01 and 11.02, American Society for Testing and Materials, 1916 Race Street, Philadelphia, PA 19103.

[2] 18th edition of Standard Methods for the Examination of Water and Wastewater, 1992, American Public Health Association, 1015 Fifteenth Street NW, Washington, D.C. 20005.

[3] "Methods for the Determination of Metals in Environmental Samples - Supplement I", EPA-600/R-94/111, May 1994. Available at NTIS, PB94-184942.

[4] Method 100.1, "Analytical Method For Determination of Asbestos Fibers in Water," EPA-600/4-83-043, September 1983. Available at NTIS, PB83-260471.

[5] Method 100.2, "Determination Of Asbestos Structures Over 10 μm in Length in Drinking Water," EPA/600/R-94/134, June 1994. Available at NTIS, PB94-201902.

[6] Available from Books and Open-File Reports Section, U.S. Geological Survey, Federal Center, Box 25425, Denver, CO 80225-0425.

[7] "Methods for the Determination of Inorganic Substances in Environmental Samples," EPA-600/R-93/100, August 1993. Available at NTIS, PB94-121811.

[8] Industrial Method No. 129-71W, "Fluoride in Water and Wastewater," December 1972, and Method No. 380-75WE, "Fluoride in Water and Wastewater," February 1976, Technicon Industrial Systems, Tarrytown, NY 10591.

[9] Methods 150.1, 150.2 and 245.2 are available from USEPA, EMSL-Cincinnati, OH 45268. The identical methods are also in "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79/020, March 1983.

[10] Method B-1011, "Waters Test Method for Determination of Nitrite/Nitrate in Water Using Single Column Ion Chromatography," Millipore Corporation, Waters Chromatography Division, 34 Maple Street, Milford, MA 01757.

[11] Technical Bulletin 601 "Standard Method of Test for Nitrate in Drinking Water," July 1994, PN 221890-001, ATI Orion, 529 Main Street, Boston, MA 02129. This method is identical to Orion WeWWG/5880, which is approved for nitrate analysis. ATI Orion republished the method in 1994, and renumbered it as 601, because the 1985 manual "Orion Guide to Water and Wastewater Analysis," which contained WeWWG/5880, is no longer available.

METHODS FOR ORGANIC CHEMICALS

Analyses for regulated organic contaminants under the monitoring requirements specified at §§141.24 and 141.30 shall be conducted using the following EPA methods or their equivalent as approved by EPA. Other mandatory and optional procedures for conducting these methods are described in Sections IV and V, respectively, of this document.

Contaminant	Method
Benzene	502.2, 524.2
Carbon tetrachloride	502.2, 524.2, 551
Chlorobenzene	502.2, 524.2
1,2-Dichlorobenzene	502.2, 524.2
1,4-Dichlorobenzene	502.2, 524.2
1,2-Dichloroethane	502.2, 524.2
cis-Dichloroethylene	502.2, 524.2
trans-Dichloroethylene	502.2, 524.2
Dichloromethane	502.2, 524.2
1,2-Dichloropropane	502.2, 524.2
Ethylbenzene	502.2, 524.2
Styrene	502.2, 524.2
Tetrachloroethylene	502.2, 524.2, 551
1,1,1-Trichloroethane	502.2, 524.2, 551
Trichloroethylene	502.2, 524.2, 551
Toluene	502.2, 524.2
1,2,4-Trichlorobenzene	502.2, 524.2
1,1-Dichloroethylene	502.2, 524.2
1,1,2-Trichloroethane	502.2, 524.2
Vinyl chloride	502.2, 524.2
Xylenes (total)	502.2, 524.2
2,3,7,8-TCDD (dioxin)	1613
2,4-D	515.2, 555, 515.1
2,4,5-TP (Silvex)	515.2, 555, 515.1
Alachlor	505[1], 507, 525.2, 508.1
Atrazine	505[1], 507, 525.2, 508.1
Benzo(a)pyrene	525.2, 550, 550.1
Carbofuran	531.1, 6610
Chlordane	505, 508, 525.2, 508.1
Dalapon	552.1, 515.1
Di(2-ethylhexyl)adipate	506, 525.2
Di(2-ethylhexyl)phthalate	506, 525.2
Dibromochloropropane (DBCP)	504.1, 551
Dinoseb	515.2, 555, 515.1
Diquat	549.1
Endothall	548.1
Endrin	505, 508, 525.2, 508.1
Ethylene dibromide (EDB)	504.1 551
Glyphosate	547, 6651
Heptachlor	505, 508, 525.2, 508.1
Heptachlor Epoxide	505, 508, 525.2, 508.1

Contaminant	Method
Hexachlorobenzene	505, 508, 525.2, 508.1
Hexachlorocyclopentadiene	505, 525.2, 508, 508.1
Lindane	505, 508, 525.2, 508.1
Methoxychlor	505, 508, 525.2, 508.1
Oxamyl	531.1, 6610
PCBs (as decachlorobiphenyl)[2]	508A
(as Aroclors)	505, 508
Pentachlorophenol	515.2, 525.2, 555, 515.1
Picloram	515.2, 555, 515.1
Simazine	505[1], 507, 525.2, 508.1
Toxaphene	505, 508, 525.2
Total Trihalomethanes	502.2, 524.2, 551

Footnotes

1 A nitrogen-phosphorous detector should be substituted for the electron capture detector in Method 505 (or another approved method should be used) to determine alachlor, atrazine and simazine, if lower detection limits are required.

[2] PCBs are qualitatively identified as Aroclors and measured for compliance purposes as decachlorobiphenyl using Method 508A.

Methods 502.2, 505, 507, 508, 508A, 515.1 and 531.1 are in Methods for the Determination of Organic Compounds in Drinking Water, EPA-600/4-88-039, December 1988, Revised, July 1991. Methods 506, 547, 550, 550.1 and 551 are in Methods for the Determination of Organic Compounds in Drinking Water - Supplement I, EPA/600-4-90/020, July 1990. Methods 515.2, 524.2, 548.1, 549.1, 552.1 and 555 are in Methods for the Determination of Organic Compounds in Drinking Water - Supplement II, EPA/600/R-92/129, August 1992. Method 1613 is titled, "Tetra-Through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS," EPA 821-B-94-005, October 1994. These documents are available from the National Technical Information Service, (NTIS) PB91-231480, PB91-146027, PB92-207703 and PB95-104774, U.S. Department of Commerce, 5285 Port Royal Road, Springfield, Virginia 22161. The toll-free number is 800-553-6847. EPA Methods 504.1, 508.1 and 525.2 are available from USEPA EMSL-Cincinnati, Cincinnati, OH 45268. The phone number is (513)-569-7586. Method 6651 is contained in the 18th edition of Standard Methods for the Examination of Water and Wastewater, 1992, and Method 6610 is contained in the Supplement to the 18th edition of Standard Methods for the Examination of Water and Wastewater, 1994, American Public Health Association, 1015 Fifteenth Street NW, Washington, D.C. 20005.

METHODS FOR UNREGULATED CONTAMINANTS

Regulations specified in §141.40 require monitoring for certain contaminants to which maximum contaminant levels do not apply. These chemicals are called "unregulated" contaminants, and presently include sulfate, 34 volatile organic chemicals (VOCs) and 13 synthetic organic chemicals (SOCs).

1. Analysis for the 34 unregulated VOCs listed under paragraphs (e) and (j) of §141.40 shall be conducted using the following recommended methods, or their equivalent as determined by EPA.

VOC Contaminants	Method
Chloroform	502.2, 524.2, 551
Bromodichloromethane	502.2, 524.2, 551
Bromoform	502.2, 524.2, 551
Chlorodibromomethane	502.2, 524.2, 551
Bromobenzene	502.2, 524.2
Bromochloromethane	502.2, 524.2
Bromomethane	502.2, 524.2
n-Butylbenzene	502.2, 524.2
sec-Butylbenzene	502.2, 524.2
tert-Butylbenzene	502.2, 524.2
Chloroethane	502.2, 524.2
Chloromethane	502.2, 524.2
o-Chlorotoluene	502.2, 524.2
p-Chlorotoluene	502.2, 524.2
Dibromomethane	502.2, 524.2
m-Dichlorobenzene	502.2, 524.2
Dichlorodifluoromethane	502.2, 524.2
1,1-Dichloroethane	502.2, 524.2
1,3-Dichloropropane	502.2, 524.2
2,2-Dichloropropane	502.2, 524.2
1,1-Dichloropropene	502.2, 524.2
1,3-Dichloropropene	502.2, 524.2
Fluorotrichloromethane	502.2, 524.2
Hexachlorobutadiene	502.2, 524.2
Isopropylbenzene	502.2, 524.2
p-Isopropyltoluene	502.2, 524.2
Naphthalene	502.2, 524.2
n-Propylbenzene	502.2, 524.2
1,1,2,2-Tetrachloroethane	502.2, 524.2
1,1,1,2-Tetrachloroethane	502.2, 524.2
1,2,3-Trichlorobenzene	502.2, 524.2
1,2,3-Trichloropropane	502.2, 524.2, 504.1
1,2,4-Trimethylbenzene	502.2, 524.2
1,3,5-Trimethylbenzene	502.2, 524.2

METHODS FOR UNREGULATED CONTAMINANTS (CONT.)

2. Analysis for the 13 unregulated SOCs listed under paragraph (n)(11) of §141.40 shall be conducted using the following recommended methods.

SOC Contaminants	Method
Aldicarb	531.1, 6610
Aldicarb sulfone	531.1, 6610
Aldicarb sulfoxide	531.1, 6610
Aldrin	505, 508, 525.2, 508.1
Butachlor	507, 525.2
Carbaryl	531.1, 6610
Dicamba	515.1, 515.2, 555
Dieldrin	505, 508, 525.2, 508.1
3-Hydroxycarbofuran	531.1, 6610
Methomyl	531.1, 6610
Metolachlor	507, 525.2, 508.1
Metribuzin	507, 525.2, 508.1
Propachlor	508, 525.2, 508.1

Other mandatory and optional procedures for conducting analyses of unregulated VOCs and SOCs are described in Sections IV and V, respectively, of this Technical Notes document. Sources for EPA Methods 502.2, 504.1, 505, 507, 508, 508.1, 515.1, 515.2, 524.2, 525.2, 531.1 and 551 and Standard Method 6610 are referenced above under methods for organic chemicals.

3. Analysis for the unregulated inorganic contaminant listed under paragraph (n)(12) of §141.40 shall be conducted using the following recommended methods.

Contaminant	Analytical Method[1] EPA	ASTM	SM
Sulfate	300.0	D4327-91	4110
	375.2	D516-90	4500-SO_4-F
			4500-SO_4-E

1. Sources for the Standard Methods and ASTM sulfate methods are referenced above under methods for inorganic chemicals. The EPA methods are contained in "Methods for the Determination of Inorganic Substances in Environmental Samples," EPA/600/R-93/100, August 1993, which is available at NTIS, PB94-121811.

METHODS FOR FILTRATION AND DISINFECTION

1. Microbiological, pH, and Turbidity Methods

To comply with provisions of the Surface Water Treatment Rule monitoring under Subpart H of 40 CFR Part 141, public water systems must conduct analyses of total coliforms, fecal coliforms, heterotrophic bacteria, turbidity, and temperature in accordance with one of the following analytical methods, and by using mandatory procedures for turbidimeter calibration, which are specified in Section IV of this Technical Notes document. Approved methods for pH are described above under "Methods for Inorganic Contaminants."

Organism	Methodology	Citation[1]
Total Coliforms[2]	Total Coliform Fermentation Technique[3,4,5]	9221A, B, C
	Total Coliform Membrane Filter Technique	9222A, B, C
	ONPG-MUG Test[6]	9223
Fecal Coliforms[2]	Fecal Coliform MPN Procedure[7]	9221E
	Fecal Coliform Membrane Filter Procedure	9222D
Heterotrophic bacteria[2]	Pour Plate Method	9215B
Turbidity	Nephelometric Method	2130B
	Nephelometric Method	180.1[8]
	Great Lakes Instruments	Method 2[9]
Temperature		2550

Footnotes

[1] Except where noted, all methods refer to the 18th edition of Standard Methods for the Examination of Water and Wastewater, 1992, American Public Health Association, 1015 Fifteenth Street NW, Washington, D.C. 20005.
[2] The time from sample collection to initiation of analysis may not exceed 8 hours.
[3] Lactose broth, as commercially available, may be used in lieu of lauryl tryptose broth, if the system conducts at least 25 parallel tests between this medium and lauryl tryptose broth using the water normally tested, and this comparison demonstrates that the false-positive rate for total coliforms, using lactose broth, is less than 10%.
[4] Media should cover inverted tubes at least one-half to two-thirds after the sample is added.
[5] No requirement exists to run the completed phase on 10 percent of all total coliform-positive confirmed tubes.
[6] The ONPG-MUG Test is also known as the Autoanalysis Colilert System.

[7] A-1 Broth may be held up to 3 months in a tightly closed screwcap tube at 4°C.
[8] "Methods for the Determination of Inorganic Substances in Environmental Samples," EPA-600/R-93-100, August 1993. Available at NTIS, PB94-121811.
[9] GLI Method 2, "Turbidity," November 2, 1992, Great Lakes Instruments, Inc., 8855 North 55th Street, Milwaukee, Wisconsin 53223.

2. Disinfectant Residual Methods

Public water systems must measure residual disinfectant concentrations with one of the analytical methods in the following table. The methods are contained in the 18th edition of Standard Methods. Corrections to SM-4500-Cl-E and 4500-Cl-G, and procedures for conducting continuous measurements of chlorine residuals are described in the Technical Notes in Section IV of this document.

Residual[1]	Methodology	Methods
Free Chlorine[2]	Amperometric Titration	4500-Cl D
	DPD Ferrous Titrimetric	4500-Cl F
	DPD Colorimetric	4500-Cl G
	Syringaldazine (FACTS)	4500-Cl H
Total Chlorine[2]	Amperometric Titration	4500-Cl D
	Amperometric Titration (low level measurement)	4500-Cl E
	DPD Ferrous Titrimetric	4500-Cl F
	DPD Colorimetric	4500-Cl G
	Iodometric Electrode	4500-Cl I
Chlorine Dioxide	Amperometric Titration	4500-ClO_2 C
	DPD Method	4500-ClO_2 D
	Amperometric Titration	4500-ClO_2 E
Ozone	Indigo Method	4500-O_3 B

Footnotes

[1] If approved by the State, residual disinfectant concentrations for free chlorine and combined chlorine also may be measured by using DPD colorimetric test kits.
[2] Free and total chlorine residuals may be measured continuously by adapting a specified chlorine residual method for use with a continuous monitoring instrument provided the chemistry, accuracy, and precision of the measurement remain same. Instruments used for continuous monitoring must be calibrated with a grab sample measurement at least every 5 days, or with a protocol approved by the State.

SECTION II. METHODS TO BE WITHDRAWN ON JULY 1, 1996

For convenience and clarity, the methods to be withdrawn on July 1, 1996 are specified in this document in lieu of listing them in the drinking water regulations at 40 CFR Part 141. The following methods may be used to obtain certification and to analyze drinking water compliance samples until July 1, 1996. However, if the rule, which promulgates this withdrawal action, is published after January 1, 1995, the withdrawal date becomes 18 months after publication of the final rule in the *Federal Register*.

ANALYTICAL METHODS TO BE WITHDRAWN FOR INORGANIC CONTAMINANTS

In addition to methods cited at §141.23(k)(1), the methods in the following table only are approved until July 1, 1996 for analyses for antimony, arsenic, barium, beryllium, cadmium, cyanide, fluoride, mercury, nickel, nitrate, nitrite, selenium, sodium and thallium. These methods were previously specified at §141.23(k)(1), except arsenic, fluoride and sodium, which were previously specified at §141.23(k)(2), §141.23(k)(3) and §141.41(c), respectively.

Contaminant	Methodology	EPA[1]	ASTM[2]	SM[3]
Antimony[4]	Atomic Absorption; Furnace	204.2		
Arsenic[4]	Atomic Absorption; Furnace	206.2		
	Hydride-Atomic Absorption	206.3		
	Spectrophotometric	206.4	D-2972-88A	307B
Barium[4]	Atomic Absorption; Direct	208.1		
	Atomic Absorption; Furnace	208.2		
Beryllium[4]	Atomic Absorption; Furnace	210.2		
Cadmium[4]	Atomic Absorption; Furnace	213.2		
Chromium[4]	Atomic Absorption; Furnace	218.2[5]		
Cyanide	Manual Distillation followed by Spectrophotometric Manual	335.2[6]		
	Amenable, Spectrophotometric	335.1		
Fluoride	Manual Distill.; Color. SPADNS	340.1		
	Manual Electrode	340.2		
	Automated Alizarin	340.3		

Mercury[4]	Manual, Cold Vapor	245.1		
Nickel[4]	Atomic Absorption; Direct	249.1		
	Atomic Absorption; Furnace	249.2		
Nitrate	Manual Cadmium Reduction	353.3		
	Automated Hydrazine Reduction	353.1		
Nitrite	Manual Cadmium Reduction	353.3		
	Spectrophotometric	354.1		
Selenium[4]	Atomic Absorption; Furnace	270.2[5,7]		
Thallium[4]	Atomic Absorption; Furnace	279.2		
Sodium	Atomic Absorption; Direct	273.1		
	Atomic Absorption; Furnace	273.2		
	Flame Photometric		D1428-64a	320A

Footnotes

1 "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020, March 1983. Available at NTIS, publication order number PB84-128677.

2 Annual Book of ASTM Standards, Part 31, American Society for Testing and Materials, 1916 Race Street, Philadelphia, PA 19103.

3 Methods 320A and 307B are contained in the 14th (1975) and 16th (1985) editions, respectively, of Standard Methods for the Examination of Water and Wastewater, American Public Health Association, 1015 Fifteenth Street, Washington, D.C. 20005.

4 Several spectrochemical techniques are approved for the determination of metal and metalloid contaminants in drinking water. These techniques are: inductively coupled plasma-atomic emission spectrometry; inductively coupled plasma-mass spectrometry; direct aspiration flame, graphite furnace, and platform graphite furnace atomic absorption spectrometry. To conduct these measurements, samples must not be filtered prior to either sample digestion or "direct analysis." Samples are acid preserved with nitric acid to pH less than 2, held for 16 hours, and the pH verified to be less than 2 before sample processing is started. In addition, the turbidity of the acidified sample must be measured with an approved method, and after preservation is complete. If turbidity is greater than 1 nephelometric turbidity unit (NTU), sample digestion is required using the digestion procedure described in the approved method (except the perchloric acid digestion in SM 3114B must not be used). If the acid preserved sample contains turbidity less than 1 NTU, the sample may be analyzed by "direct analysis" without digestion. However, irrespective of the turbidity of the sample, when determining mercury by cold vapor atomic absorption (CVAA), or antimony, arsenic, or selenium (Sb, As, and Se) by gaseous hydride atomic absorption, sample aliquots must be digested prior to analysis. Digestion is necessary, because organomercury compounds that may be present in drinking water and performance samples cannot be analyzed by CVAA unless converted to inorganic

mercury, and because Sb, As, and Se each must be converted to a specific valence state prior to reduction and generation of the hydride for analysis.

5 For the determination of chromium by graphite furnace analysis, an appropriate volume of 30% hydrogen peroxide (1-mL of 30% H_2O_2 per 100 mL of sample or standard) should be added to the calibration standards and the sample prior to analysis. The addition of hydrogen peroxide ensures that chromium in the sample and calibration standards is in the same valence state [Cr(III)]. This provides uniform signal response in conventional off-the-wall graphite furnace determinations of chromium. Also, calcium concentrations ranging from 10 to 50 mg/L have demonstrated a nonuniform suppressive (less than 20%) matrix effect in conventional off-the-wall nonpyrolytic graphite furnace determinations of chromium. If calcium is present at these concentrations in the chromium sample, use of the matrix modifier magnesium nitrate is highly recommended (cf. SM 3113A).

6 The distillation procedure in EPA Method 335.2 should not be used, and the sodium hydroxide absorber solution final concentration must be adjusted to 0.25 N before colorimetric analysis.

7 For graphite furnace determinations of selenium when nickel nitrate is used as the matrix modifier, an appropriate volume of 30% hydrogen peroxide (2-mL 30% H_2O_2 per 100 mL of sample or standard) should be added to both the calibration standards and samples prior to analysis. It has been demonstrated that the addition of hydrogen peroxide enhances the absorption signal response in conventional off-the-wall graphite furnace determinations of selenium. If digestion of the sample is required, because sample turbidity is greater than 1 NTU, hydrogen peroxide is added to the sample at the time of digestion. Nickel nitrate (Ni conc. of 0.1%) either is added to an aliquot of the processed sample and calibration standards at the time of analysis or may be added directly in the furnace (20 μg Ni per 20 μL injection).

ANALYTICAL METHODS TO BE WITHDRAWN FOR LEAD, COPPER, AND CORROSIVITY

In addition to the methods cited at §141.23(k)(1), the methods in the following table are approved until July 1, 1996 for analyses for lead, copper, conductivity, calcium, alkalinity, orthophosphate and silica. These methods were previously specified on June 30, 1994 (59 FR 33863) at §141.89(a).

Contaminant	Methodology	EPA[1]
Lead[2]	Atomic absorption; furnace technique	239.2
Copper[2]	Atomic absorption; furnace technique	220.2
	Atomic absorption; direct aspiration	220.1
Conductivity	Conductance	120.1
Calcium[2]	EDTA titrimetric	215.2
	Atomic absorption; direct aspiration	215.1
Alkalinity	Titrimetric	310.1
Orthophosphate (unfiltered, no digestion or hydrolysis)	Colorimetric, ascorbic acid, two reagent	365.3
	Colorimetric, ascorbic acid, single	365.2
Silica	Colorimetric	370.1

Footnotes

[1] "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020, March 1983. Available at NTIS as PB84-128677.

[2] To conduct these measurements samples must not be filtered prior to either sample digestion or "direct analysis." Samples are acid preserved with nitric acid to pH less than 2, held for 16 hours, and the pH verified to be less than 2 before sample processing is started. In addition, the turbidity of the acidified sample must be measured using an approved method, and after acid preservation is complete. If turbidity is greater than 1 nephelometric turbidity unit (NTU), sample digestion is required using the digestion procedure described in the approved method. If the acid preserved sample contains turbidity less than 1 NTU, the sample may be analyzed by "direct analysis" without digestion. When digestion is required, the total recoverable technique as defined in the method must be used.

ANALYTICAL METHODS TO BE WITHDRAWN FOR ORGANIC CONTAMINANTS

In addition to methods cited at §141.24(e), the methods specified in the following table may be used until July 1, 1996 for analysis of the contaminants specified below. Methods 502.1, 503.1 and 524.1 are contained in Methods for the Determination of Organic Compounds in Drinking Water, EPA/600/4-88/039, December 1988, Revised, July 1991, which is available from the National Technical Information Service (NTIS), PB91-231480, U.S. Department of Commerce, 5285 Port Royal Road, Springfield, Virginia 22161. The phone number is 800-553-6847. Methods 501.1 and 501.2 for analysis of total trihalomethanes in accordance with the monitoring requirements specified at §141.30 will be printed at 40 CFR 141.30, Appendix C until July 1, 1995.

Contaminant	EPA Method
Benzene	503.1, 524.1
Carbon tetrachloride	502.1, 524.1
Chlorobenzene	502.1, 503.1, 524.1
1,2-Dichlorobenzene	502.2, 524.1
1,4-Dichlorobenzene	502.1, 503.1, 524.1
1,2-Dichloroethane	502.1, 524.1
cis-Dichloroethylene	502.1, 524.1
trans-Dichloroethylene	502.1, 524.1
Dichloromethane	502.1, 524.1
1,2-Dichloropropane	502.1, 524.1
Ethylbenzene	503.1, 524.1
Styrene	503.1, 524.1
Tetrachloroethylene	502.1, 503.1, 524.1
1,1,1-Trichloroethane	502.1, 524.1
Trichloroethylene	502.1, 503.1, 524.1
Toluene	503.1, 524.1
1,2,4-Trichlorobenzene	503.1
1,1-Dichloroethylene	502.1, 524.1
1,1,2-Trichloroethane	502.1, 524.1
Vinyl chloride	502.1, 524.1
Xylenes (total)	503.1, 524.1
Total Trihalomethanes	501.1, 501.2

ANALYTICAL METHODS TO BE WITHDRAWN FOR UNREGULATED VOCS

In addition to methods cited at §141.40(g), EPA Methods 502.1, 503.1 and 524.1 may be used until July 1, 1996 for analysis of the unregulated VOC contaminants that are listed in §141.40(e) and (j), if the contaminant is listed in the analytical scope of the method. These VOC methods are contained in the EPA manual described above for organic contaminants.

METHOD TO BE WITHDRAWN FOR FILTRATION AND DISINFECTION

In addition to methods cited at §141.74(a)(5), Standard Method 408F (Leuco Crystal Violet) may only be used until July 1, 1996 for analysis of free chlorine and combined chlorine (chloramines). This method is contained in the 16th edition of Standard Methods for the Examination of Water and Wastewater, 1985, American Public Health Association, 1015 Fifteenth Street NW, Washington, D.C. 20005.

SECTION III. RECOMMENDED METHODS FOR SECONDARY DRINKING WATER CONTAMINANTS

Analyses of aluminum, chloride, copper, fluoride, foaming agents, iron, manganese, odor, silver, sulfate, total dissolved solids (TDS) and zinc to determine compliance under §143.3 may be conducted with the methods in the following Table. Criteria for analyzing aluminum, copper, iron, manganese, silver, and zinc samples with digestion or directly without digestion, and other mandatory procedures are contained in the Technical Notes in Section IV of this document. Measurement of pH may be conducted with one of the methods listed above in Section I under "Methods for Inorganic Chemicals."

Contaminant	EPA	ASTM[1]	SM[2]	Other
Aluminum	200.7[3] 200.8[3] 200.9[3]		3120B 3113B 3111D	
Chloride	300.0[4]	D4327-91	4110 4500-Cl^--D	
Color			2120B	
Copper	200.7[3] 200.8[3] 200.9[3]	D1688-90A D1688-90C	3120B 3111B 3113B	
Fluoride	300.0[4]	D4327-91 D1179-93A D1179-93B	4110 4500F-B,D 4500F-C 4500F-E	129-71W[5] 380-75WE[5]
Foaming Agents			5540C	
Iron	200.7[3] 200.9[3]		3120B 3111B 3113B	
Manganese	200.7[3] 200.8[3] 200.9[3]		3120B 3111B 3113B	
Odor			2150B	
Silver	200.7[3] 200.8[3] 200.9[3]		3120B 3111B 3113B	I-3720-85[6]
Sulfate	300.0[4] 375.2[4]	D4327-91	4110 4500-SO_4-F 4500-SO_4-C,D	

Contaminant	EPA	ASTM[1]	SM[2]	Other
TDS			2540C	
Zinc	200.7[3] 200.8[3]		3120B 3111B	

Footnotes

[1] Annual Book of ASTM Standards, Vols. 11.01 and 11.02, American Society for Testing and Materials, 1916 Race Street, Philadelphia, PA 19103.
[2] 18th edition of Standard Methods for the Examination of Water and Wastewater, 1992, American Public Health Association, 1015 Fifteenth Street NW, Washington, D.C. 20005.
[3] "Methods for the Determination of Metals in Environmental Samples - Supplement I," EPA-600/R-94-111, May 1994. Available at NTIS, PB94-184942.
[4] "Methods for the Determination of Inorganic Substances in Environmental Samples," EPA-600/R-93-100, August 1993. Available at NTIS, PB94-121811.
[5] Industrial Method No. 129-71W, "Fluoride in Water and Wastewater," December 1972, and Method No. 380-75WE, "Fluoride in Water and Wastewater," February 1976, Technicon Industrial Systems, Tarrytown, NY 10591.
[6] Available from Books and Open-File Reports Section, U.S. Geological Survey, Federal Center, Box 25425, Denver, CO 80225-0425.

SECTION IV. MANDATORY METHOD MODIFICATIONS

This section contains several mandatory method modifications in a series of Technical Notes. Each Technical Note is on a separate sheet to allow users to remove it, and place it with the applicable compliance method(s). The parenthetical number (R), which appears adjacent to method citations in this section, refers to the publication in Section VI (References) that contains the referenced method.

STANDARD METHOD (SM) 4500-Cl-E (R12), CHLORINE RESIDUALS

This Technical Note corrects a typographical error in SM 4500-Cl-E, "Low Level Amperometric Titration" (R12). This method is currently approved at §141.74(a) for measurement of chlorine residuals. When the method is republished, the Standard Methods Committee will correct an error[1] in the numerical factor in the denominator of the formula in part 5 of the method. The formula is on page 4-43 of the 18th edition of Standard Methods. The correct formula must have a factor of 0.00564, which is 10 times greater than the factor printed in the incorrect formula.

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[1] Letter from Andrew D. Eaton, "Error in 4500-Cl E," June 4,1993, American Public Health Association, 1015 Fifteenth Street NW, Washington, D.C. 20005.

STANDARD METHOD (SM) 4500-Cl-G (R12), CHLORINE RESIDUALS

This Technical Note recognizes and corrects an error in SM 4500-Cl-G (R12). This DPD method is currently approved at §141.74(a) for measurement of chlorine residuals. The method as published omits instructions that would allow measurement of total residual chlorine in drinking water samples. The Standard Methods Committee has determined[1] that an editorial omission, not a technical change, occurred in recent versions of this method. The error will be corrected in the next (19th) edition of Standard Methods.

The simplified procedure, which uses DPD chemistry, was omitted from SM 4500-Cl-G (18th ed., para. 4, p. 4-46). EPA corrects the Standard Method error, by printing a correction to paragraph four below. The correction also applies to the 16th edition version of this method, SM 408E.

Simplified Procedure for Total Chlorine

"To obtain monochloramine and dichloramine together as combined chlorine omit step 4d in SM 4500-Cl-G (monochloramine determination). To obtain total chlorine in one reading add the full amount of potassium iodide at the start with the specified amounts of buffer reagent and DPD indicator. Read color after 2 minutes."

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[1] Letter from Andrew D. Eaton, "Inquiry on Chlorine Residual 4500-Cl (18th Edition)," October 26, 1993, American Public Health Association, 1015 Fifteenth Street NW, Washington, D.C. 20005.

PROTOCOL FOR CONTINUOUS CHLORINE RESIDUAL MONITORING

In this Technical Note EPA provides specifications for continuous monitoring of chlorine residuals. These instructions were inadvertently omitted from the Surface Water Treatment Rule (54 FR 27486, June 29, 1989). EPA will permit a grab sample method, which is approved for chlorine residual monitoring at §141.74(a), to be adapted for continuous monitoring of free or total chlorine residuals provided the chemistry, accuracy, and precision of the method are unchanged. Instruments used for continuous monitoring must be calibrated with a grab sample measurement at least every 5 days, or with a protocol approved by the State. If the State also approves, calibration may include minor changes in the reagent mix provided the overall chemistry of the method is not changed. Approved grab sampling methods for chlorine residual measurement are listed below.

Residual[1]	Methodology	Methods
Free Chlorine	Amperometric Titration	4500-Cl D
	DPD Ferrous Titrimetric	4500-Cl F
	DPD Colorimetric	4500-Cl G
	Syringaldazine (FACTS)	4500-Cl H
Total Chlorine	Amperometric Titration	4500-Cl D
	Amperometric Titration (low level measurement)	4500-Cl E
	DPD Ferrous Titrimetric	4500-Cl F
	DPD Colorimetric	4500-Cl G
	Iodometric Electrode	4500-Cl I

[1] If approved by the State, residual disinfectant concentrations for free chlorine and combined chlorine also may be measured by using DPD colorimetric test kits.

SPECTROPHOTOMETRIC DETERMINATIONS OF CYANIDE

Mandatory Manual Distillation in Cyanide Methods

In this Technical Note EPA emphasizes that spectrophotometric measurements of cyanide in water samples always require a manual digestion of the sample to prepare the sample for measurement of cyanide. EPA believes emphasis is needed, because some laboratories seem to be unaware of this requirement. All approved spectrophotometric methods for cyanide are specified at 40 CFR 141.23(k)(1) under the phrase, "Manual distillation followed by." Standard Method SM-4500-CN-C (R12), which describes the mandatory manual distillation procedure, is cited in the rules immediately after this phrase.

"Amenable" spectrophotometric methods also require distillation prior to either free or total cyanide measurements. The approved amenable, manual and automated spectrophotometric methods for cyanide are ASTM D2036-91B and D2036-91A (R11); SM 4500-CN-F and 4500-CN-G (R12); EPA Methods 335.1, 335.2 and 335.3 (R14), EPA 335.4 (R4); and USGS I-3300-85 (R19). (Note: EPA Methods 335.1 and 335.2 will be withdrawn on July 1, 1996, and Method 335.3 has been replaced by Method 335.4).

To avoid manual distillation, laboratories can use a selective electrode method for cyanide, which is discussed below.

Selective Electrode Method, SM 4500-CN-F (R12)

EPA regulates free, not total, cyanide. If SM 4500-CN-F is used to determine free cyanide, distillation is not required. However, to maintain a constant ionic strength background for the electrode measurement, samples and standards must contain the same concentration of sodium hydroxide.

Reduced Volume Cyanide Distillation

In 1994 EPA Method 335.3 was replaced with Method 335.4. The technical differences between the methods are minor; both methods require manual distillation of the sample. However, EPA improved the automation of procedures in Method 335.4, and added an optional, reduced volume distillation procedure. Method 335.4 does not contain the discussion in Method 335.3 of an alternate ultraviolet (UV) digestion procedure, because EPA never approved this optional UV procedure, and because EPA believes that UV digestion will underestimate cyanide concentrations in the drinking water sample.

In this Technical Note, EPA is approving reduced volume distillation for all spectrophotometric cyanide methods. Criteria for reduced volume distillation are as follows.

> *"Reduction in digestion or distillation volumes is acceptable* ***provided all sample-to-reagent ratios are maintained, and provided the final sample volume is sufficient for instrumental measurement of cyanide.*** *Reduced volume distillation apparatus, when employed as described, can be considered an acceptable minor modification to approved cyanide methodology."*

EPA Method 335.2 (R14)

This method will be withdrawn on July 1, 1996. This Technical Note amends Method 335.2 as follows. The sodium hydroxide absorber solution final concentration must be adjusted to 0.25 N before colorimetric analysis. The distillation procedure that is described in the method should not be used, because it uses a secondary scrubber that does not work well.

TURBIDIMETER CALIBRATION (R4, R9, R12)

EPA Method 180.1 (R4), SM 2130B (R12) and GLI Method 2 (R9) are approved at §141.74(a) for measurement of turbidity. This Technical Note specifies that calibration of the turbidimeter must be made either by the use of a formazin standard as specified in the approved method or with a styrene divinylbenzene polymer standard (Amco AEPA-1 Polymer). This reagent is commercially available from Advance Polymer Systems, Inc., 3696 Haven Avenue, Redwood City, California 94063.

SAMPLE DIGESTION FOR DETERMINATION OF METAL CONTAMINANTS

This Technical Note describes when and how a sample must be digested for accurate compliance measurements of metals in drinking water samples. Several spectrochemical techniques are approved for the determination of metal and metalloid contaminants in drinking water. These techniques are: inductively coupled plasma-atomic emission spectrometry; inductively coupled plasma-mass spectrometry; direct aspiration flame, graphite furnace, and platform graphite furnace atomic absorption spectrometry. To conduct these measurements, samples must not be filtered prior to either sample digestion or "direct analysis." Samples are acid preserved with nitric acid to pH less than 2. Preservation is complete after the acidified sample has been held for 16 hours. Before sample processing is started, sample pH must be verified to be less than 2.

To determine whether digestion of the sample is required, the turbidity of the acidified sample must be measured using an approved method and only after preservation is complete. If turbidity is greater than 1 nephelometric turbidity unit (NTU), sample digestion is required using the digestion procedure described in the approved method (see exception below for SM 3114B). If the acid preserved sample contains turbidity less than 1 NTU, the sample may be analyzed by "direct analysis" without digestion.

However, irrespective of the turbidity of the sample, when determining mercury by cold vapor atomic absorption (CVAA), or antimony (Sb), arsenic (As) or selenium (Se) by gaseous hydride atomic absorption, sample aliquots must be digested prior to analysis. Digestion of the sample, which is described in the applicable method[1], is necessary, because organomercury compounds that may be present in drinking water and performance samples cannot be analyzed by CVAA unless converted to inorganic mercury, and because Sb, As, and Se each must be converted to a specific valence state prior to reduction and generation of the hydride for analysis.

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[1]SM 3114B Exception - When determining arsenic or selenium using gaseous hydride SM 3114B (R12), the perchloric acid digestion should never be used. See the Technical Note on "SM 3114B, Arsenic and Selenium" for additional instructions and explanations.

STANDARD METHOD 3114B (R12), ARSENIC AND SELENIUM

This Technical Note describes an important safety warning when using sample digestion procedures that are described in SM 3114B (R12). Determination of arsenic and selenium by gaseous hydride atomic absorption requires digestion of the sample prior to analysis. SM 3114B describes two digestion procedures. One procedure, referred to as the "total recoverable" preparation, uses perchloric acid in the final stage of digestion. This perchloric acid digestion procedure is not required by EPA, and should be avoided, because of potential danger when using perchloric acid, and because a special fume hood is required. When using method SM 3114B, the digestion procedure described in paragraph 4.d, *Preparation of samples and standards for total arsenic and selenium*, that specifies the use sulfuric acid and potassium persulfate should be utilized. This warning is not applicable to the ASTM gaseous hydride methods for arsenic and selenium, because the methods do not allow use of perchloric acid digestion.

ASTM D3859-93B (R11) AND STANDARD METHOD 3113B (R12), SELENIUM

This Technical Note concerns graphite furnace determinations of selenium with ASTM D3859-93B (R11) or SM 3113B (R12). When nickel nitrate is used as the matrix modifier, an appropriate volume of 30% hydrogen peroxide (2-mL 30% H_2O_2 per 100 mL of sample or standard) should be added to both the calibration standards and samples prior to analysis. It has been demonstrated that the addition of hydrogen peroxide enhances the absorption signal response in conventional off-the-wall graphite furnace determinations of selenium. If digestion of the sample is required, because sample turbidity is greater than 1 NTU, hydrogen peroxide is added to the sample at the time of digestion. Nickel nitrate (Ni conc. of 0.1%) either is added to an aliquot of the processed sample and calibration standards at the time of analysis or may be added directly in the furnace (20 μg Ni per 20 μL injection).

STANDARD METHOD 3113B (R12), CHROMIUM

This Technical Note describes procedures for correctly conducting a graphite furnace determination of chromium in a drinking water sample using SM 3113B (R12). The method requires that an appropriate volume of 30% hydrogen peroxide (1-mL of 30% H_2O_2 per 100 mL of sample or standard) be added to the calibration standards and the sample prior to analysis. The addition of hydrogen peroxide ensures that chromium in the sample and calibration standards is in the same valence state, chromium [III]. This provides uniform signal response in conventional off-the-wall graphite furnace determinations of chromium.

Calcium concentrations ranging from 10 to 50 mg/L have demonstrated a nonuniform suppressive (less than 20%) matrix effect in conventional off-the-wall nonpyrolytic graphite furnace determinations of chromium. If calcium is present at these concentrations in the chromium sample, use of the matrix modifier magnesium nitrate is highly recommended (cf. SM 3113A).

METHODS 502.2 (R16) AND 524.2 (R3), SORBENT TRAPS

This Technical Note describes under what conditions an alternate trap may be used in EPA Methods 502.2, Rev. 2.0 (R16) and 524.2, Rev. 4.0 (R3). Both methods allow use of alternative sorbents to trap volatile organic compounds, provided all quality assurance criteria specified in the method are met. This option is already included in Method 524.2 in Sect. 6.2.2, but an explicit requirement not to change other method conditions is missing. EPA notes that some alternate traps may not work under Method 502.2 or 524.2 conditions, because the purge and desorption procedures specified in the methods are optimized for the trap media specified in the methods. **These procedures may not be changed.** Specifically, the purge time, purge gas flow rate, and the desorption time specified in the method may not be changed, because EPA has no data to show that reliable or reproducible results can be obtained if purging or desorption times or flows differ from the specified limits.

The purging and desorption conditions for these methods were designed to achieve analytical maximum efficiency. The purge time and purge gas flow rate required to efficiently purge the target analytes from the water sample are largely independent of the sorbent trapping material. Decreasing the purging or desorption times or gas flows will decrease purging efficiency and/or recovery of target analytes, which will have a negative impact on method precision. Since many of the potential alternate sorbents may be thermally stable at temperatures higher than 180°C, alternate traps may be desorbed and baked out at higher temperatures than those described in the current method revisions. If higher temperatures are used, the analyst should monitor the data for analyte and trap decomposition.

This Technical Note amends Method 502.2, Rev. 2.0 by adding the following sentence to the end of Sect. 6.2.2.

> *"The use of alternative sorbents is acceptable provided the data acquired meets all quality control criteria described in Section 10, and provided the purge and desorption procedures specified in Section 11 of the method are not changed."*

Method 524.2, Rev. 4.0 is amended by changing the last sentence in Sect. 6.2.2 to read as follows.

> *"The use of alternative sorbents is acceptable provided the data acquired meets all quality control criteria described in Section 9, and provided the purge and desorption procedures specified in Section 11 of the method are not changed."*

EPA METHODS 502.2, REV. 2.0 (R16), 524.2, REV. 4.0 (R3), AND 551 (R15) IN SAMPLE ACIDIFICATION

This Technical Note clarifies that **samples must be acidified at the time of collection, but after they have been dechlorinated.** Acidification must not be delayed until the samples are received in the laboratory. These instructions supersede instructions implied or explicit that may be contained in the methods.

METHOD 506 (R15), ERRATA IN SUMMARY

This Technical Note corrects minor errors in the introductory sections of Method 506 (R15), and emphasizes that clean sodium chloride is essential to an accurate analysis. Method 506 is used to determine adipates and phthalates in drinking water samples. The summary in Section 2 of Method 506 incorrectly refers to use of a ternary solvent mixture to conduct the liquid-liquid extraction of the sample; the correct procedure is methylene chloride followed by hexane. The method summary also omits a disk elution solvent. Section 2 is amended to correct these errors, and now reads in entirety as follows.

> *"A measured volume of sample, approximately 1-L, is extracted with methylene chloride followed by hexane using a glass separatory funnel. The solvent extract is isolated, dried and concentrated to a volume of 5 mL or less. The extract is further concentrated by using a gentle stream of nitrogen gas to reduce the sample volume to 1 mL or less.*
>
> *Alternatively, a measured volume of sample is extracted with a liquid-solid extraction (LSE) cartridge or disk. The LSE media are eluted with acetonitrile followed by methylene chloride (disk extraction) or with methylene chloride only (cartridge extraction). The eluant is concentrated using a gentle stream of nitrogen gas or clean air to reduce the volume to 1 mL or less.*
>
> *The analytes in the extract are separated by means of capillary gas chromatography using temperature programming. The chromatographically separated phthalate and adipate esters are measured with a photoionization detector, which is operating at 10 eV."*

EPA strongly encourages laboratories to clean the sodium chloride that is added to the sample by carefully following the heating and storage instructions, which are described at Sect. 7.5 of the method. This will reduce the background contamination measured in the laboratory reagent blank samples.

METHOD 508 (R16), DCPA AND HEXACHLOROCYCLOPENTADIENE

This Technical Note approves Method 508, Rev. 3.0 (R16) for compliance measurement of hexachlorocyclopentadiene, provided the method performance criteria specified in Section 9 of Method 508.1 (R6) are met. This Note also corrects a missing entry in the table of analytes in Sect. 1.1 of Method 508; the CAS Registry number for DCPA (dacthal) is 1861-32-1.

METHODS 515.1 (R16) AND 515.2 (R3), USE OF TMSD

This Technical Note allows and describes use of trimethylsilyldiazomethane (TMSD) as an alternative derivatizing reagent in Methods 515.1, Rev. 4.0 (R16) and 515.2, Rev. 1.0 (R3). EPA is approving TMSD, because some laboratories prefer not to use the other approved derivatizing reagent, Diazald. Since TMSD increases gas chromatographic background, the method surrogate, 2,4-dichlorophenylacetic acid, cannot be used at concentrations of 1 µg/L or lower. Also, Diazald, not TMSD, must be used if dalapon is to be determined, because dalapon is not amenable to esterification with TMSD. If dalapon recovered from the drinking water sample is incompletely esterified, dalapon concentrations will be underestimated. Laboratories wishing to avoid use of Diazald may use Method 552.1 to determine dalapon, and Method 515.1 or 515.2 or 555 for the other chlorinated acid herbicides.

Steps, which replace or augment the calibration and extract esterification (Sect. 11.4) method descriptions when TMSD is used, are described below. The following procedure was written for Method 515.2, which uses liquid-solid extraction (LSE). Analysts using TMSD with liquid-liquid extraction (LLE) Method 515.1 should omit steps specific to LSE, and include appropriate LLE steps from Method 515.1. In particular, the amounts of TMSD, acetic acid, and internal standards to be added may have to be adjusted when the TMSD procedure is adapted for use with Method 515.1. These adjustments may be necessary, if the concentration ratio of original sample to final extract is different in the two methods.

USE OF TRIMETHYLSILYLDIAZOMETHANE TO ESTERIFY ACID HERBICIDES IN METHOD 515.2[1,2]

1. INTRODUCTION

Trimethylsilyldiazomethane (TMSD) is available from a commercial supplier (currently the Aldrich Chemical Company is the sole supplier) as a 2 molar solution in hexane. TMSD is stable during storage in this solution. It should be noted that the gas chromatographic background is somewhat increased when TMSD is used as the derivatizing reagent instead of the generated diazomethane. Although no method analyte is affected by this increased background, the recommended surrogate, 2,4-dichlorophenylacetic acid, is masked by an interfering peak. This renders the surrogate useless at 1 µg/L or lower. Any compound found suitable when TMSD is used is acceptable as a surrogate.

Trimethylsilyldiazomethane can be used to efficiently methylate the following acid herbicides:

Chemical	CAS Registry Number
Acifluorofen	50594-66-6
Bentazon	25057-89-0
Chloramben	133-90-4
Dacthal	1861-32-1
Dicamba	1918-00-9
Dichlorprop	120-36-5
Dinoseb	88-85-7
3,5-Dichlorobenzoic acid	51-36-5
2,4-D	94-75-7
2,4-DB	94-82-6
5-Hydroxydicamba	7600-50-2
Pentachlorophenol	87-86-5
Picloram	1918-02-1
2,4,5-TP (Silvex)	93-72-1
2,4,5-T	93-76-5

TMSD may not be used to esterify dalapon.

The following procedures to methylate the herbicides must be followed.

2. CALIBRATION OF THE GAS CHROMATOGRAPH/ELECTRON CAPTURE DETECTION (GC/ECD) SYSTEM

Calibrate the GC/ECD system using fortified reagent water samples, and use two sets of calibration solutions to prevent coelution. The presence of coeluting analytes makes **confirmation** of positives **mandatory** before taking action on a result. Follow the procedure described below using TMSD to methylate the herbicides. Five concentration levels are recommended.

3. PROCEDURE

Carry out the hydrolysis, clean-up, and extraction of the method analytes as described in Method 515.2 up to Sect. 11.2.4, or in Method 515.1 up to Sect. 11.4. Users of Method 515.1 should begin below where the 2 M TMSD solution is added.

Elute the herbicides from the disk by passing two 2 mL aliquots of methyl tertiary butyl ether (MTBE) through the disk into the collection tube. Rinse the sample container with 4 mL of MTBE and pass it through the disk into the tube.

Transfer the MTBE extract from the collection tube into an anhydrous sodium sulfate drying tube which has been pre-wetted with 1 mL MTBE. Be sure to discard any water layer.

Before the extract passes completely through the sodium sulfate, add an additional 2 mL of MTBE as a rinse.

Concentrate the dried extract to approximately 4 mL. Add methanol (approx. 1 mL) to the extract to yield a 20% (v/v) methanol in MTBE solution. Adjust the volume to 5 mL with MTBE. (TMSD produces the most efficient methylation of the herbicides in a 20% methanol, 80% MTBE solution.)

Add 50 µL of the 2 M TMSD solution to each 5 mL sample extract. (Verify this volume if Method 515.1 is used.)

Place the tube containing the extract into a heating block at 50°C and heat the extract for 1 hour.

Allow the extract to cool to room temperature, then add 100 µL of 2 M acetic acid in methanol to react any excess TMSD. (Verify this volume if Method 515.1 is used.)

Fortify the extract with 100 µL of the internal standard solution (Method 515.2, Sect. 7.17; Method 515.1, Sect. 7.19) to yield a concentration of 0.020 µg/mL. (Verify this if Method 515.1 is used.)

Proceed with the identification and measurement of the analytes using GC/ECD according to the procedures described in the method.

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[1] "Use of Trimethylsilyldiazomethane as a Substitute Reagent for the Esterification of Phenoxy Herbicides," J. Collins and W.J. Bashe, Technology Applications, Inc., July 27, 1993 [Project performed under EPA Contract 68-C1- 0022, J.W. Eichelberger, Work Assignment Manager]

[2] Amounts of TMSD, acetic acid, internal standards and other reagents may have to be adjusted when the TMSD procedure is adapted for use with Method 515.1. These adjustments will be necessary, if the concentration ratio of original sample to final extract is different in the two methods.

METHOD 524.2, REV. 4.0 (R3) QUALITY ASSURANCE, VOC DATA

This Technical Note corrects or clarifies quality assurance steps in Method 524.2, Rev. 4.0 (R3), and provides data for two VOCs that was omitted in the published method.

Changes in Quality Assurance Procedures

EPA is changing some instructions in Sections 9 (quality control) and 10 (calibration) of Method 524.2 that may be conflicting or confusing. The changes described in this Note also apply to Method 502.2, Rev. 2.0 (R16) to the extent that the same problems are in the quality control (Section 10) and calibration (Section 9).

Section 9.3, Initial Demonstration of Accuracy --

EPA has been asked to make the accuracy criteria (±20%), which are part of an initial demonstration of capability (IDC), in Sect. 9.3.3 of Method 524.2 the same as the accuracy criteria (±30%) in the section on continuing calibration checks (Sect. 10.3.5). These criteria will not be changed. EPA specified different criteria, because the IDC and Continuing Calibration measurements are evaluating different controls. EPA believes the IDC measurement, which requires analysis of a series of laboratory fortified blanks, should be more accurate than the Continuing Calibration measurement. To explain this difference in accuracy criteria, and to remove an incomplete reference to the SDWA, Sect. 9.3.3 is revised in this Note.

Section 9.3.3 is superseded in its entirety as follows:

"Some analytes, particularly early eluting gases and late eluting higher molecular weight compounds, will be measured with less accuracy and precision than other analytes. However, the accuracy and precision for all analytes must fall within the limits expressed below. If these criteria are not met for an analyte of interest, take remedial action and repeat the measurements for that analyte until satisfactory performance is achieved. For each analyte, the mean accuracy must be 80-120% (i.e. an accuracy of ± 20%). The precision of the recovery (accuracy) for each analyte must be less than twenty percent (<20%). These criteria are different than the ± 30% response factor criteria specified in Sect. 10.3.5. The criteria differ, because the measurements in Sect. 9.3.3 as part of the initial demonstration of capability should be more stringent than the continuing calibration measurements in Sect. 10.3.5."

Section 9.6 LFB Criteria --

This step in Method 524.4 requires a single laboratory fortified blank (LFB) to be measured with each batch of samples, and with an accuracy that is specified in Sect. 9.3.3 (i.e. ±20%), whereas Sect. 10.3.5 requires the same sample be analyzed with an accuracy of ±30%. EPA is removing this conflict by changing the accuracy requirement to be ±30% in Sect. 9.6.

Section 9.6 is superseded in its entirety as follows:

"Use the procedures and criteria in Sects. 10.3.4 and 10.3.5 to evaluate the accuracy of the measurement of the laboratory fortified blank (LFB), which must be analyzed with each batch of samples that is processed as a group within a work shift. If more than 20 samples are in a work shift batch, analyze one LFB per 20 samples. Prepare the LFB with the concentration of each analyte that was used in the Sect. 9.3.3 analysis. If the acceptable accuracy for this measurement (±30%) is not achieved, the problem must be solved before additional samples may be reliably analyzed.

Since the calibration check sample in Sect. 10.3.5 and the LFB are made the same way and since procedural standards are used, the sample analyzed here may also be used as the calibration check in Sect. 10.3.5. Add the results of the LFB analysis to the control charts to document data quality."

Section 9.5 LRB Analysis --

This step in Method 524.2 states that a field reagent blank may be used in lieu of a laboratory reagent blank (LRB). This is not correct. An LRB must always be analyzed with each batch (as defined at Sect. 9.6) of 20 samples. This Note amends Sect. 9.5 by deleting the erroneous second sentence.

Section 9.5 is superseded in its entirety as follows:

"LABORATORY REAGENT BLANKS (LRB) -- With each batch of samples processed as a group within a work shift, analyze a LRB to determine the background system contamination."

Section 9.7 FRB Analysis --

This step in Method 524.2 states that a "field reagent blank should be analyzed" with each set of samples. This may cause unnecessary work. A field reagent blank is collected as a precaution against false positive results that may occur if the sample is contaminated in the field. Thus, a field reagent blank analysis is only required when contamination is detected in the compliance sample. This Note clarifies when the samples must be analyzed by amending the first sentence in Sect. 9.7.

Section 9.7 is superseded in its entirety as follows:

"If a water sample is contaminated with an analyte, verify that it is not a sampling error by analyzing a field reagent blank. The results of these analyses will help define contamination resulting from field sampling, storage and transportation activities. If the field reagent blank shows unacceptable contamination, the analyst should identify and eliminate the contamination."

Section 10, Calibration --

There can be a conflict between the instructions in Sect. 9.6 in Method 524.2, which define a batch as 20 samples, and Sect. 10.1, which requires calibration every 8 hours. Since a typical chromatographic run exceeds 35 minutes, 20 samples are measured in about 11, not 8, hours. This Note removes the potential conflict by explaining when calibration must be checked.

Section 10.1 is superseded in its entirety as follows:

"Demonstration and documentation of acceptable initial calibration is required before any samples are analyzed. In addition, acceptable performance must be confirmed intermittently throughout analysis of samples by performing continuing calibration checks. These checks are required at the beginning of each work shift, but no less than every 12 hours. Additional periodic calibration checks are good laboratory practice. Since this method uses procedural standards, the analysis of the laboratory fortified blank, which is required in Sect. 9.6, may be used here as the calibration check sample."

Performance Data for cis-and-trans 1,3-dichloropropene

EPA omitted performance data for two unregulated VOCs, cis-1,3-dichloropropene and trans-1,3-dichloropropene. The following table replaces Table 7 in Method 524.2, Rev. 4.0.

TABLE 7. ACCURACY AND PRECISION DATA FROM SEVEN DETERMINATIONS OF METHOD ANALYTES IN REAGENT WATER USING WIDE BORE CAPILLARY COLUMN NUMBER 4

Compound	True Conc. (µg/L)	Mean Conc. Detected (ug/L)	Rel. Std. Dev. (%)	Method Detect. Limit (µg/L)
Acetone	1.0	1.6	5.7	0.28
Acrylonitrile	1.0	0.81	8.7	0.22
Allyl chloride	1.0	0.90	4.7	0.13
2-Butanone	2.0	2.7	5.6	0.48
Carbon disulfide	0.20	0.19	15	0.093
Chloroacetonitrile	1.0	0.83	4.7	0.12
1-Chlorobutane	1.0	0.87	6.6	0.18
t-Dichloro-2-butene	1.0	1.3	8.7	0.36
1,1-Dichloropropanone	5.0	4.2	7.7	1.0
c-1,3-Dichloropropene	0.20	0.20	3.1	0.020
t-1,3-Dichloropropene	0.10	0.11	14	0.048
Diethyl ether	1.0	0.92	9.5	0.28
Ethyl methacrylate	0.20	0.23	3.9	0.028
Hexachloroethane	0.20	0.18	10	0.057
2-Hexanone	1.0	1.1	12	0.39
Methacrylonitrile	1.0	0.92	4.2	0.12
Methylacrylate	1.0	1.2	12	0.45
Methyl iodide	0.20	0.19	3.1	0.019
Methylmethacrylate	1.0	1.0	13	0.43
4-Methyl-2-pentanone	0.40	0.56	9.7	0.17
Methyl-tert-butylether	0.40	0.52	5.6	0.090
Nitrobenzene	2.0	2.1	18	1.2
2-Nitropropane	1.0	0.83	6.2	0.16
Pentachloroethane	0.20	0.23	20	0.14
Propionitrile	1.0	0.87	5.3	0.14
Tetrahydrofuran	5.0	3.9	13	1.6

EPA METHOD 531.1 (R16) AND SM 6610 (R8), STORAGE OF SAMPLES

This Technical Note removes the requirement in Methods 531.1, Rev. 3.0 (R16) and SM 6610 (R8) to freeze the samples. Sect. 8.2.4 of Method 531.1 requires buffered samples to be stored at minus 10°C. EPA realizes that this is impractical and unnecessary. After reviewing time storage data, EPA concluded that samples buffered to a pH of 3 or less may be stored at 4°C. The data supporting this conclusion is contained in Table 6610:II of SM 6610.

To reflect this change this Note supersedes Sect. 8.2.4 of EPA Method 531.1 in its entirety as follows. Users of the Standard Method should make appropriate changes to the procedures, which are described in Paragraph 2 (Sampling and Storage) of SM 6610.

> *"Samples must be iced or refrigerated at 4°C from time of collection until analysis is begun. Although, preservation study results of up to 28 days indicate method analytes are not labile in water samples when sample pH is adjusted to 3 or less, and samples are shipped and stored at 4°C, analyte lability may be affected by the matrix. Therefore, the analyst must verify that the preservation technique is applicable to the samples under study."*

METHOD 551 (R15), PENTANE

This Technical Note allows optional use of pentane as the extraction solvent for some of the analytes in EPA Method 551 (R15). Since a change in the extraction solvent in any method is a change in the chemistry of the method, an alternative solvent must be validated and approved by EPA for each method analyte. EPA has approved only methyl t-butyl ether (MTBE) and pentane for use as extraction solvents in Method 551. Pentane may not be used to extract chloral hydrate; MTBE is approved for all Method 551 analytes.

EPA METHOD 549.1 (R3), SAMPLE CONTAINERS

This Technical Note clarifies that the amber sample bottle specified in Section 6 (Equipment and Supplies) of Method 549.1, Rev. 1.0 (R3), can be made of any type of plastic. The bottle does not have to be PVC as stated in the method.

ALTERNATIVE LIQUID-SOLID EXTRACTION CARTRIDGES AND DISKS

This Technical Note provides criteria for judging the equivalency of liquid-solid extraction (LSE) cartridges and disks for use in methods that allow use of LSE technology. This Note supersedes the phrase "or equivalent" that is used in some methods to describe selection of alternative LSE cartridges or disks. Although EPA welcomes innovative LSE technology, EPA will not approve technology that compromises the reliability of the analysis.

Liquid-solid extraction is performed using various sorbents that are either packed into a cartridge or enmeshed in a disk of inert support material. EPA methods describe the cartridge or disk that was used to develop the LSE procedure, and to produce the data which is published in the method. If a product is mentioned in the methods, it is for information purposes only.

EPA believes various LSE cartridges and disks may be used, provided they meet all quality control requirements of the method, and provided they contain a sorbent that uses the same physicochemical principles as the cartridge or disk that is described in the approved LSE method. To demonstrate that alternative LSE cartridges and disks meet all quality control criteria, the analyst must be aware of the chemistry of the method. For example, in evaluating Method 552.1 the recovery of the free acid (not a chemical derivative) from the water sample must be tested with the alternative LSE cartridge or disk.

In judging LSE disk media, both the sorbent and the support must be evaluated. In the case of sorbents, similarities in polarity are not sufficient. For example, a C_{18}-Silica sorbent may not perform the same as a styrene divinylbenzene copolymer sorbent. Thus, these sorbents would not be considered to be equivalent. In judging supports, any physical support used to hold the sorbent is acceptable provided the support is inert and compatible with the solutions or solvents required in the conditioning and elution steps of the method. However, any sorbent conditioning or elution steps, which are specified in the method must not be modified or eliminated to accommodate the support material. For example, Method 552.1 was developed and validated with ion exchange cartridges to determine dalapon and haloacetic acids. To efficiently extract the acids, the ion exchange resin must be activated with a sodium hydroxide rinse. In judging the equivalency of an alternative disk EPA would still require the rinse, because EPA has no data to support making the rinse optional.

SECTION V. RECOMMENDED METHOD MODIFICATIONS

This section contains several optional procedures and recommended modifications to compliance methods. Each optional or recommended procedure is on a separate page to allow users to remove it, and place it with the applicable method(s). The parenthetical number (R), which appears adjacent to method citations in this section, refers to the publication in Section VI (References) that contains the referenced method.

METHOD 100.1 (R18), ASBESTOS GUIDANCE

This Technical Note does not change Method 100.1 (R18). It describes how to make some steps in the method specifically applicable to the drinking water standard of asbestos fibers greater than 10 μm in length. This guidance is needed because the asbestos method was not designed specifically for measuring fibers greater than 10 μm in length, and because laboratories may not wish to use an ozone/UV generator to prepare the sample for analysis.

EPA METHOD 100.1
DETERMINATION OF ASBESTOS FIBERS IN WATER

OGWDW GUIDANCE AND CLARIFICATION FOR DRINKING WATER

1. Approximately 800 mL of sample should be taken in 1-L bottles. Glass sampling bottles are preferable to plastic. If plastic bottles are used, polyethylene is better than polypropylene. Do not use acid or mercuric chloride as preservatives. Before collecting the sample, the water must be allowed to run until the temperature has stabilized, indicating that the water is representative of the main water line. Samples must be taken in duplicate. Store samples in the dark at 4°C.

2. To avoid use of the ozone, ultraviolet (UV) generator, samples must be filtered on the polycarbonate (PC) filter in the laboratory within 48 hours of collection. If the holding time is exceeded, the sample must be treated to break down microbiological contaminants. This is done immediately prior to filtration by treating the sample in the original container with ozone, UV-light, and resonicating it to disperse the fibers.

3. Up to 5 samples may be composited. Sample compositing must be done in the laboratory on samples which are less than 48-hours-old or have been individually ozone/UV treated in their original sample containers. Samples must be sonicated and equal amounts withdrawn to make up the composite. It may also be prudent to filter an aliquot of each individual sample for analysis in case the composite sample exceeds 1/5 of the MCL (1.4 MFL >10 μm long). If this is not done, the original samples can only be filtered if they are less than 48-hours-old and have been resonicated or have been retreated with ozone-UV and resonicated.

4. Only 0.1 μm pore size PC filter membranes may be used. Filters must be taken from a lot which has been prescreened for background contamination. This is particularly important if fibers less than 10 μm are to be counted because PC filters may be contaminated with asbestos fibers shorter than 10 μm. The PC filter must be backed by a methyl cellulose ester (MCE) filter to diffuse the vacuum across the membrane. Use $\leq$5 μm pore size MCE membrane as the backing filter.

5. A filtration apparatus with straight vertical sides is preferred to one with tapered sides to avoid loss of fibers settling on tapered sides of the funnel.

6. States agencies **may choose to require** the counting of fibers less than 10 μm long to help judge the condition of asbestos/cement pipes. Certification lists must identify whether labs count all fibers or only those over 10 μm, and whether the lab is certified by a state or EPA region.

7. A calibrated magnification of at least 10,000X ± 5% is adequate for counting fibers over 10 μm in length. A minimum spot size of 250 nm or smaller is required for this analysis.

8. For compliance analysis of asbestos in drinking water samples, an analytical sensitivity ≤200,000 fibers per liter (0.2MFL) is required, subject to the following stopping rules:

   a. Analysis may be terminated at the completion of the grid opening during examination of which an analytical sensitivity of 0.2MFL is achieved, or at the completion of the grid opening which contains the 100th asbestos fiber <u>over 10 μm in length</u>, whichever occurs first.

   b. A minimum of 4 grid openings must be counted, even if this results in counting more than 100 asbestos fibers over 10 μm in length.

   c. The grid openings examined must be drawn about equally from a minimum of 3 specimen grids.

9. Counting rules:

   a. Count fibers with an aspect ratio ≥3:1.

   b. Count a fiber bundle as a single fiber with a width equal to an estimate of the mean bundle width, and length equal to the <u>maximum</u> length.

   c. Count individual asbestos fibers and bundles within clusters and matrices, as long as they meet the definitions of fibers and bundles as described in 9A and 9B.

   d. Count the fibers which intersect the top and left sides of the grid opening and record as twice their visible length. Do not record fibers intersecting the bottom and right sides of the grid opening.

   e. Count only one end of the fiber to avoid possibly counting a fiber more than once.

10. Fiber identification criteria:

    a. Each fiber suspected to be chrysotile must first be examined by electron diffraction following the procedure in Figure 15 of the EPA method. If the characteristic electron diffraction (ED) pattern is observed, the fiber shall be classified as CD (chrysotile identified by diffraction pattern). If no pattern is observed or the pattern is not distinctive, the fiber shall be examined by EDXA (energy dispersive x-ray analysis) and classified according to the EPA method. Only chrysotile fibers classified as CD, CMQ (chrysotile identified by morphology and semi-quantitative EDXA) or CDQ (chrysotile identified by morphology, electron diffraction and semi-quantitative EDXA) shall be included in the calculation of the concentration for the purposes of this regulation.

    b. Each fiber suspected to be amphibole must first be examined by electron diffraction following the procedure in Figure 18 of the EPA Method. Each fiber must be examined by EDXA. If a random orientation electron diffraction pattern showing a 0.53 nm layer spacing is obtained, and the elements and peak areas of the EDXA spectrum correspond to those of a known amphibole asbestos, the fiber shall be classified as ADQ (amphibole identified by diffraction and semi-quantitative EDXA). If the random orientation electron diffraction pattern cannot be obtained, is incomplete, or is not recognizable as a non-amphibole pattern, but the elements and the peak areas of the EDXA spectrum correspond to those of a known amphibole asbestos, the fiber shall be classified as AQ (amphibole identified by semi-quantitative EDXA). Only amphibole fibers classified as ADQ, AQ, AZQ (amphibole identified by zone axis electron diffraction and semiquantitative EDXA) and AZZQ (amphibole identified by 2 zone axes electron diffraction and semi-quantitative EDXA) shall be included in the calculation of asbestos concentration.

11. It is not necessary to calculate the mass concentration of asbestos for this regulation. Concentrations must be reported in MFL>10 μm. When no asbestos fibers greater than 10 μm are found, report <0.2 MFL>10 μm.

METHOD 502.2 (R16), USE OF THE PID

This Technical Note clarifies when a photoionization detector (PID) is not required. Method 502.2, Rev. 2.0 (R16) requires the use of a PID to measure volatile organic compounds (VOCs) that cannot be measured with an electrolytic conductivity detector. If only halogenated analytes, such as the trihalomethanes, are to be measured, a PID is not needed. This option will allow laboratories to use this VOC method for determination of total trihalomethanes as specified at §141.30 without the expense of a PID.

METHODS 502.2 (R16), 524.2 (R3) AND 551 (R15) SAMPLE DECHLORINATION

This Technical Note provides guidance to help laboratories correctly dechlorinate samples for compliance with the total trihalomethane (TTHM) monitoring requirements under 40 CFR 141.30 using EPA Method 502.2, Rev. 2.0 (R16) or 524.2, Rev. 4.0 (R3) or 551 (R15), or when VOCs and THMs are to be measured in the same sample. This guidance also applies to use of EPA Methods 502.1, 503.1 and 524.1 (R16). These methods are not approved for THM analysis under 40 CFR 141.30, but some laboratories may wish to use these methods for analysis of samples other than compliance samples.

This guidance supersedes the discussion on ascorbic acid contained in the introduction (p. 3) to the 1991 EPA manual (R16). The Agency believes revised guidance is warranted because laboratories may be confused by the variety of preservation procedures described in the five methods. The reagent available to dechlorinate samples varies with the method used, or with the analyte to be measured.

Laboratories must carefully follow the preservation procedure described in each method, **especially the order in which reagents are added to the sample.** Each method allows use of one or more dechlorination reagents depending on the analyte to be measured. These reagents remain available for use, but **EPA strongly recommends use of sodium thiosulfate** as the dechlorination reagent, because the Agency has more performance data demonstrating the effectiveness of this chemical than for other dechlorination reagents.

One exception to this recommendation is ascorbic acid must be used when vinyl chloride and other gases are measured with a mass spectrometer, because sodium thiosulfate in an acidified sample generates a gas that interferes with the analysis. **EPA cautions that samples dechlorinated with ascorbic acid must be acidified immediately, as directed in the method.** Other exceptions, such as for analysis of haloacetonitriles are described in Section 8 of EPA Method 551 (R15).

METHOD 504.1 (R5), CHROMATOGRAPHIC INTERFERENCES

Although this Technical Note discusses misidentifications that may occur when measuring 1,2-dibromoethane (EDB) or dibromochloropropane (DBCP) with Method 504.1 (R5), the guidance and warnings provided here are applicable to the interpretation of analytical results from any method. Volatile organic chemicals (VOCs) or trihalomethanes (THMs) can cause chromatographic interference problems if these chemicals are in the sample, and coelute on the column used to separate and identify EDB or DBCP. Interferences can lead to false positive results, if a coeluting VOC or THM is misidentified as EDB or DBCP.

Since any method, even one that uses a selective detector, is subject to false positive results, any result that exceeds an action concentration must be rigorously confirmed to avoid unnecessary action. Method 504.1 uses an electron capture detector that is very sensitive and stable. Although this detector is excellent at detecting very low concentrations of halogenated compounds, it is subject to many interferences.

Sections 4.3 and 6.6.2 in Method 504.1 note that a common THM disinfection by-product in chlorinated water supplies, dibromochloromethane, can elute close to EDB. This means in the initial demonstration of capability, a laboratory must determine the retention time of dibromochloromethane or other compounds that might coelute with the method analytes. A relative response factor and retention time for each possible interfering analyte should be determined. These retention times can be determined by using procedures in Method 551 to prepare and analyze THM and VOC standards for analysis on a Method 504.1 chromatographic column. This information can be obtained more easily if a DB-1 column is used in Method 504.1 and the retention times are compared to the THM and VOC retention times obtained with the DB-1 column used in Method 551.

Confirmation procedures must be followed before taking action on a result. Confirmation of potential Method 504.1 or Method 551 chromatographic interferences can be obtained with an inexpensive purge-and-trap analysis (EPA Method 502.2 (R16) or 524.2 (R3)). These methods can identify interfering trihalomethanes, or VOCs that might occur with EDB if the source of EDB were unleaded gasoline (cf. Sect. 2.3). Although Method 524.2 is not as sensitive as Method 504.1, EDB can be measured at concentrations greater than 0.06 µg/L. Other confirmation procedures, which are described in Method 504.1, are: analysis on a second column with dissimilar retention times (Sect. 6.6.2), and changing the temperature program to provide sufficient separation between EDB and dibromochloromethane (Sect. 9.1.2).

EPA emphasizes that knowledge of probable contaminants in a sample, and of method interferences are key parts of quality assurance and good data interpretation when using <u>any</u> analytical method. Laboratories reporting data must realize that interpreters of occurrence data are often unfamiliar with weaknesses in an analytical method, and that officials may enforce on the data as provided by the laboratory. EPA strongly encourages data reviewers to

question the plausibility, not just the possibility, of a result, and not assume that a laboratory has always eliminated analytical error. A skeptical approach is especially important when initial sample results are being interpreted.

METHODS 505, 507, 508 (R16), INTERCHANGE OF DETECTORS

This Technical Note clarifies under what conditions a laboratory may use either an electron-capture detector (ECD) or a nitrogen-phosphorous detector (NPD) in EPA Methods 505, Rev. 2.0; 507, Rev. 2.0; or 508, Rev. 3.0 (R16). Laboratories may wish to use a different detector to decrease method detection limits. For example, use of an NPD in Method 505 can increase the sensitivity of the analysis for alachlor, atrazine and simazine. Section 6.8.3 of Methods 507 and 508 and Sect. 10.4 of Methods 505, 507 and 508 allow use of an ECD or NPD detector provided the initial demonstration of capability criteria are met. These criteria are specified in Section 10 of each method.

Section 6.8.3 of Methods 507 and 508 note that a mass spectrometer might be used. This Note withdraws this recommendation, which was made before Method 525.2 was available. EPA no longer recommends use of a mass spectrometer with Methods 507 and 508, because important tuning and calibration procedures for the mass spectrometer are not described in either method, and because Method 525.2 thoroughly describes these procedures. Method 525.2 is approved for determination of all Method 507 and 508 analytes, except PCBs as the seven Aroclors.

EPA METHODS 507, 508, 515.1 (R16), MERCURIC CHLORIDE

This Technical Note removes the requirement to use mercuric chloride, because concerns have been raised about the environmental hazards and costs associated with disposal of mercuric compounds. Mercuric chloride is used as a biocide in EPA Methods 507, Rev. 2.0; 508, Rev. 3.0; and 515.1, Rev. 4.0 (R16). Since drinking water usually exhibits limited biological activity, EPA is removing the requirement under Sect. 8.2 of Methods 507, 508, and 515.1 to use mercuric chloride as a bactericide. To minimize the possibility of occasional false-negative results, the Agency would still require the use of mercuric chloride in any drinking water sample that might be expected to exhibit biological degradation of a target pesticide.

There are also environmental and economic concerns about addition of acid to drinking water samples in the VOC methods (Methods 502.2, 524.2, and 551). However, EPA will not remove this requirement, because EPA has data that demonstrates microbiological degradation of VOCs in drinking water samples.

EPA METHOD 1613, DIOXIN (R17)

This Technical Note does not change Method 1613 (R17). It describes how to make some steps in the method specifically applicable to measurement of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD). Guidance is needed because Method 1613 was written to determine many isomers of dioxins and furans, but under the Safe Drinking Water Act, EPA only regulates the 2,3,7,8-TCDD isomer. Also, information to determine if the drinking water sample needs to be filtered is not clearly provided in Method 1613. Using this guidance will substantially decrease the cost of Method 1613, because it eliminates many costly steps that are not required when only TCDD is to be determined.

EPA METHOD 1613

OGWDW GUIDANCE AND CLARIFICATION FOR ANALYSIS OF 2,3,7,8-TETRACHLORODIBENZO-p-DIOXIN (TCDD) IN DRINKING WATER

1. The only isotopically labeled compounds which are necessary for calibration and quantitation in addition to the native 2,3,7,8-TCDD are $^{13}C_{12}$ 2,3,7,8-TCDD (the spiking compound), $^{37}Cl_4$ 2,3,7,8-TCDD (the clean-up standard), and $^{13}C_{12}$ 1,2,3,4-TCDD (the internal standard).

2. During calibration, selected ion current profiles of only the compounds in item 1 above need be obtained according to directions in Sect. 7 of the method by monitoring the exact masses specified for these compounds in Table 3 of the method at >10,000 resolving power. The relative abundances must meet the criteria specified in the method. There must be at least baseline resolution in the chromatogram between the 1,2,3,4-TCDD and the 2,3,7,8-TCDD isomers.

3. If the sample is colorless, odorless, has a turbidity of one (1) NTU or less and consists of a single phase, filtration is not required, and the sample may be analyzed according to Sect. 11.1 of the method. Turbidity must be measured with an approved method. Any sample containing multiple phases, or having a turbidity of more than one (>1) NTU must be filtered. The filter particulate must be analyzed according to Sect. 11.2 of the method.

4. Since drinking water samples are relatively free from interferences, the optional clean-up steps described in the method probably will not be needed for most samples.

SECTION VI. EPA CONTACTS AND METHOD REFERENCES

OBTAINING METHODS AND TECHNICAL ASSISTANCE

For assistance in obtaining copies of EPA methods, or for answers to technical questions about drinking water methods please contact:

U.S. EPA, Environmental Monitoring Systems Laboratory
Chemistry Research Division (MC 564)
Cincinnati, OH 45268-0001
Telephone: 513 569-7586

CERTIFICATION AND REGULATORY ASSISTANCE

For answers to questions about laboratory certification, the EPA Labcert Bulletin, and the regulatory status of drinking water methods please contact:

U.S. EPA, Technical Support Division
Drinking Water Quality Assessment Branch (MC 140)
ATTN: Methods and Laboratory Certification
Cincinnati, OH 45268-0001
Telephone: 513 569-7938

REFERENCES

R1. Approved EPA Methods 200.7, 200.8, 200.9, and 245.1 are contained in "Methods for the Determination of Metals in Environmental Samples - Supplement I," May 1994, NTIS PB94-184942.

R2. EPA Method 100.2, "Determination of Asbestos Structures over 10 μm in Length in Drinking Water," June 1994, NTIS PB94-201902.

R3. Approved EPA Methods 515.2, 524.2, 548.1, 549.1, 552.1 and 555 are contained in "Methods for the Determination of Organic Compounds in Drinking Water - Supplement II," August 1992, NTIS PB92-207703.

R4. Approved EPA Methods 180.1, 300.0, 335.4, 353.2 and recommended Method 375.2 are contained in "Methods for the Determination of Inorganic Substances in Environmental Samples," August 1993, NTIS PB94-121811.

R5. EPA Method 504.1, "1,2-Dibromoethane (EDB), 1,2-Dibromo-3-chloropropane (DBCP), and 1,2,3-Trichloropropane (123TCP) in Water by Microextraction and Gas Chromatography," 1993.

R6. EPA Method 508.1, Rev. 1.0, "Determination of Chlorinated Pesticides, Herbicides, and Organohalides by Liquid-Solid Extraction and Electron Capture Gas Chromatography," 1994.

R7. EPA Method 525.2, Rev. 1.0, "Determination of Organic Compounds in Drinking Water by Liquid-Solid Extraction and Capillary Column Gas Chromatography/Mass Spectrometry," March 1994.

R8. Method 6610 "Carbamate Pesticides" is contained in Standard Methods for the Examination of Water and Wastewater 18th Edition Supplement, 1994 may be purchased from the American Public Health Association, 1015 Fifteenth Street NW, Washington, D.C. 20005.

R9. GLI Method 2, "Turbidity" is available free from Great Lakes Instruments, Inc., November 2, 1992.

R10. Orion Technical Bulletin 601 "Standard Method of Test for Nitrate in Drinking Water," July 1994 is identical to Orion WeWWG/5880, which had previously been approved for nitrate analysis at 40 CFR 141.23(k)(1). ATI Orion republished this method in 1994, and renumbered it as 601, because the 1985 manual "Orion Guide to Water and Wastewater Analysis," which contained WeWWG/5880, is no longer available. Technical Bulletin 601 is available free from ATI Orion, 529 Main Street, Boston, MA 02129. Laboratories wishing to use the Orion method should be aware that SM 4500-NO_3-D, which is published in the 18th edition of Standard Methods for the Examination of Water and Wastewater, is equivalent to Orion 601.

R11. The American Society for Testing and Materials (ASTM) annually reprints all of the methods contained in the Annual Book of ASTM Methods, Vols. 11.01 and 11.02, including methods that have not been editorially or technically revised. Thus, it is permissible to use any edition that contains the EPA-approved version of the method that is approved. The Annual Book of ASTM Methods may be purchased from ASTM, 1916 Race Street, Philadelphia, PA 19103.

R12. Eighteenth edition of Standard Methods for the Examination of Water and Wastewater, 1992 may be purchased from the American Public Health Association, 1015 Fifteenth Street NW, Washington, D.C. 20005.

R13. EPA Method 245.2, "Mercury, Automated Cold Vapor Technique," Environmental Monitoring Systems Laboratory, Cincinnati, OH 45268, 1974. Also contained in reference 14.

R14. "Methods for Chemical Analysis of Water and Wastes," EPA, March 1983, NTIS PB84-128677.

R15. Approved EPA Methods 506, 547, 550, 550.1 and 551 are contained in "Methods for the Determination of Organic Compounds in Drinking Water -- Supplement I," July 1990, NTIS PB91-146027.

R16. Approved EPA Methods 502.2, 505, 507, 508, 508A, 515.1 and 531.1, and Methods 502.1, 503.1, and 524.1, which will be withdrawn are contained in "Methods for the Determination of Organic Compounds in Drinking Water," December 1988, Revised July 1991, NTIS PB91-231480.

R17. EPA Method 1613, Revision B, "Tetra-through-Octa- Chlorinated Dioxins and Furans by Isotope-Dilution HRGC/HRMS," October 1994, NTIS PB95-104774.

R18. EPA Method 100.1, "Analytical Method for the Determination of Asbestos Fibers in Water," September 1983, NTIS PB83-260471.

R19. Methods I-3300-85, I-1030-85, I-1601-85, I-2598-85, I-1700-85 and I-2700-85 in Techniques of Water Resources Investigations of the U.S. Geological Survey, Book 5, Chapter A-1, 3rd ed., U.S. Geological Survey, Books and Open File Reports Section, Box 25425, Federal Center, Denver, CO 80225-0425, 1989.

R20. "Waters Test Method for Determination of Nitrite/Nitrate in Water Using Single Column Ion Chromatography," Method B-1011 is available free from Millipore Corporation, Waters Chromatography Division, 34 Maple Street, Milford, MA 01757.

R21. Industrial Method No. 129-71W, "Fluoride in Water and Wastewater," December 1972, and Method No. 380-75WE, "Fluoride in Water and Wastewater," February 1976 are available free from Technicon Industrial Systems, Tarrytown, NY 10591.

R22. Method I-2601-90 in Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory--Determination of Inorganic and Organic Constituents in Water and Fluvial Sediments, Open File Report 93-125 is available from U.S. Geological Survey, Books and Open File Reports Section, Box 25425, Federal Center, Denver, CO 80225-0425, 1993.

References R1 to R4 are available for a fee through the National Technical Information Service (NTIS), which is located at U.S. Department of Commerce, 5285 Port Royal Road, Springfield, Virginia 22161; the toll-free number is (800)-553-6847. Until references R5 to R7 are published in "Methods for the Determination of Organic Compounds in Drinking Water - Supplement III," these methods are available free from EPA-EMSL-Cincinnati, Cincinnati, OH 45268. The phone number is (513) 569-7586. The "Supplement III" manual is expected to be published by EMSL-Cincinnati in late 1995.

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