ORIGINAL PC 8

R08-7/R08-13 SDWA

From: <Fair.Pat@epamail.epa.gov>
To: MCCAMBM@ipcb.state.il.us
Date: 6/30/2008 12:48:07 PM
Subject: here it is

see page 14 (24th page of the file)

(See attached file: Tech Notes.pdf)

E-MAIL EXCHANGE WITH USEPA TO LOCATE & IDENTIFY METHODS

From: Mike McCambridge
To: Fair.Pat@epamail.epa.gov
Date: 6/30/2008 5:37:42 PM
Subject: Re: here it is

Thank you for forwarding the reference. I have checked the lists of discontinued methods, those recommended for further use, and those still in use. I have noted two apparent discrepancies that I hope you can clarify.

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Please clarify these issues to me if you are able to do so. Alternatively, let me know if you cannot do so at this time.

Michael J. McCambridge
Attorney
Illinois Pollution Control Board
312-814-6924

>>> <Fair.Pat@epamail.epa.gov> 6/30/2008 12:42 PM >>>

see page 14 (24th page of the file)

(See attached file: Tech Notes.pdf)

From: Mike McCambridge
To: Fair.Pat@epamail.epa.gov
Date: 7/1/2008 11:10:39 AM
Subject: Re: here it is

Thanks. No great rush.

Michael J. McCambridge
Attorney
Illinois Pollution Control Board
312-814-6924

>>> <Fair.Pat@epamail.epa.gov> 7/1/2008 6:24 AM >>>
Mike,

I'll check into your questions, but I can't guarantee that I'll resolve them. There isn't any one here who was involved in putting Technical Notes together, so I will need to do some research. I'll let you know what I find out; it may be next week before I get back to you.

Pat

"Mike McCambridge" <mccambridge@ipcb.state.il.us> To Pat Fair/CI/USEPA/US@EPA
cc
06/30/2008 06:37 PM Subject Re: here it is

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(See attached file: Tech Notes.pdf)

From: <Fair.Pat@epamail.epa.gov>
To: MCCAMBM@ipcb.state.il.us
Date: 7/1/2008 2:35:08 PM
Subject: Re: here it is

Mike,

I have found the answers to your questions:

1. Prior to the Dec 5, 1994 rule, the citation for EPA Method 245.1 (issued in 1974) was "Methods of Chemical Analysis of Water and Wastes," EPA Environmental and Monitoring and Support Laboratory, Cincinnati, OH 45268 (EPA-600/4-79-020). March 1983. Available from ORD Publications, CERI, EPA, Cincinnati, OH 45268. The method was updated to the version (Revision 3.0) that is published in "Methods for Determination of Metals in Environmental Samples, Supplement I" (EPA-600/R-94-111) May 1994 which was approved in the Dec 5, 1994 rule.

2. A similar situation exists for EPA 502.2. The original citation was "Methods for the Determination of Organic Compounds in Drinking Water," ORD Publications, CERI, EPA/600/4-88/039, December 1988. The manual was revised in July 1991 and the methods in the revised manual were approved in the Dec 5, 1994 rule. Method 502.2, Revision 2.0 (1989) replaced Revision 1.0 (1986).

Also note that there has been another change to EPA 502.2. The version that is now cited is Revision 2.1 (1995) which is published in "Methods for the Determination of Organic Compounds in Drinking Water, Supplement III" EPA/600/R-95-131, August 1995. The previous version was withdrawn effective June 1, 2001.

Hope this helps.
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Michael J. McCambridge
Attorney
Illinois Pollution Control Board
312-814-6924

>>> <Fair.Pat@epamail.epa.gov> 7/1/2008 2:34 PM >>>
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From: <Fair.Pat@epamail.epa.gov>
To: MCCAMBM@ipcb.state.il.us
Date: 7/1/2008 2:40:12 PM
Subject: Re: here it is

Are you adding references to the new appendix that includes optional alternative methods? Just curious...

"Mike McCambridge" <mccambridge@ipcb.state.il.us> 07/01/2008 03:37 PM

To: Pat Fair/CI/USEPA/US@EPA
cc:
Subject: Re: here it is

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>>> <Fair.Pat@epamail.epa.gov> 6/30/2008 12:42 PM >>>

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(See attached file: Tech Notes.pdf)

From: Mike McCambridge
To: Fair.Pat@epamail.epa.gov
Date: 7/1/2008 2:59:32 PM
Subject: Re: here it is

I am uncertain how best to deal with the appendix listing of alternative methods. It is possible that the listing itself may be added to the Illinois rules as an appendix. It is also possible that references in the various federally derived provisions that restrict the selection of methods (i.e., the State counterparts to 40 C.F.R. 141.23(e)(1), 141.24(k)(1), etc.) will require a reference to the listing of alternative methods. I should have a clearer picture as I continue my work on the proposal, after I have dealt with the USEPA March 12, 2007 amendments.

Michael J. McCambridge
Attorney
Illinois Pollution Control Board
312-814-6924

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(See attached file: Tech Notes.pdf)

From: Mike McCambridge
To: Fair.Pat@epamail.epa.gov
Date: 7/8/2008 12:57:19 PM
Subject: Waters Methods

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312-814-6924

Mike McCambridge - Re: Waters Methods

From: <Fair.Pat@epamail.epa.gov>
To: "Mike McCambridge" <mccambridge@ipcb.state.il.us>
Date: 7/8/2008 2:19 PM
Subject: Re: Waters Methods

Mike,

I'm working off site today, so I don't have access to the references I need to answer your questions. I should have copies of the methods that were added to 40 CFR 141 as part of the 2007 methods update rule. If these Waters methods are prior to that, I might not be able to help you. Unfortunately, I don't know who might have them other than Waters.

I'll see what I can find tomorrow and get back to you.

Pat

-----"Mike McCambridge" <mccambridge@ipcb.state.il.us> wrote: -----

> To: Pat Fair/CI/USEPA/US@EPA
> From: "Mike McCambridge" <mccambridge@ipcb.state.il.us>
> Date: 07/08/2008 01:57PM
> Subject: Waters Methods
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From: Mike McCambridge
To: Fair.Pat@epamail.epa.gov
Date: 7/8/2008 2:29:21 PM
Subject: Re: Waters Methods

Whatever you can do for me when you get back. I have continued to look into this today. I am convinced that Method 6500 added to SW-846 in Update IV in the end of 2007 is the method you have called "Method D6508" from Waters. See 73 Fed. Reg. 486 (Jan. 3, 2008); http://www.epa.gov/SW-846/pdfs/6500.pdf. If this is true, I will likely cite the SW-846 version of the method, since it is much easier to obtain than the method from Waters. As described, Waters initially acted like I spoke a foreign language when I asked for "Method D6508." As for Method B-1011, it seems to distill down to me needing the title to the document in which the method appears.

Talk to you when you return.

Michael J. McCambridge
Attorney
Illinois Pollution Control Board
312-814-6924

>>> <Fair.Pat@epamail.epa.gov> 7/8/2008 2:18 PM >>>
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From: <Fair.Pat@epamail.epa.gov>
To: MCCAMBM@ipcb.state.il.us
Date: 7/10/2008 7:46:26 AM
Subject: Re: Waters Methods

Mike,

Here's Waters 6508 method that was approved for drinking water. Aren't you limited to methods that are listed as approved for drinking water? Based on the info at the top of the method, I'm guessing this may now be an ASTM method. It was evaluated under the ATP program, so EPA was given the method prior to the ASTM process. I don't know this for sure and it will be something I investigate as we begin putting together our next Expedited Methods Approval FR action. (If it is the same method, we'll probably list it in Appendix A.)

(See attached file: Waters Method D 6508, Rev 2_EPA-HQ-OW-2003-0070-0063.pdf)

As for the other method, it was approved prior to the 2007 methods rule. I don't have a copy of it, because I wasn't involved in the earlier methods rules. However, I have asked our ATP coordinator to see if it is in the ATP file. When I hear back from him, I'll let you know.

Hope this helps,
Pat

"Mike McCambridge" <mccambridge@ipcb.state.il.us> 07/08/2008 03:29 PM

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From: Mike McCambridge
To: Fair.Pat@epamail.epa.gov
Date: 7/10/2008 5:07:33 PM
Subject: Re: Waters Methods

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Can you help on this one too?

Michael J. McCambridge
Attorney
Illinois Pollution Control Board
312-814-6924

>>> <Fair.Pat@epamail.epa.gov> 7/10/2008 7:43 AM >>>
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(See attached file: Waters Method D 6508, Rev 2_EPA-HQ-OW-2003-0070-0063.pdf)

As for the other method, it was approved prior to the 2007 methods rule. I don't have a copy of it, because I wasn't involved in the earlier methods rules. However, I have asked our ATP coordinator to see if it is in the ATP file. When I hear back from him, I'll let you know.

Hope this helps,
Pat

"Mike McCambridge" <mccambridge@ipcb.state.il.us> 07/08/2008 03:29 PM

To: Pat Fair/CI/USEPA/US@EPA
cc:
Subject: Re: Waters Methods

Whatever you can do for me when you get back. I have continued to look into this today. I am convinced that Method 6500 added to SW-846 in Update IV in the end of 2007 is the method you have called "Method

D6508" from Waters. See 73 Fed. Reg. 486 (Jan. 3, 2008); http://www.epa.gov/SW-846/pdfs/6500.pdf. If this is true, I will likely cite the SW-846 version of the method, since it is much easier to obtain than the method from Waters. As described, Waters initially acted like I spoke a foreign language when I asked for "Method D6508." As for Method B-1011, it seems to distill down to me needing the title to the document in which the method appears.

Talk to you when you return.

Michael J. McCambridge
Attorney
Illinois Pollution Control Board
312-814-6924

>>> <Fair.Pat@epamail.epa.gov> 7/8/2008 2:18 PM >>>
Mike,

I'm working off site today, so I don't have access to the references I need to answer your questions. I should have copies of the methods that were added to 40 CFR 141 as part of the 2007 methods update rule. If these Waters methods are prior to that, I might not be able to help you. Unfortunately, I don't know who might have them other than Waters.

I'll see what I can find tomorrow and get back to you.

Pat

-----"Mike McCambridge" <mccambridge@ipcb.state.il.us> wrote: -----

To: Pat Fair/CI/USEPA/US@EPA
From: "Mike McCambridge" <mccambridge@ipcb.state.il.us>
Date: 07/08/2008 01:57PM
Subject: Waters Methods

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The copy of Method B-1011 sent me by Waters is nearly identical to one that I found on the USEPA website. The only difference between the two is that the method from the USEPA website is headed "Waters." The document it appears to include pages 13 through 17 from some reference. It is undated, which means that I cannot use it for an incorporation by reference. Do you have a dated copy of Method B-1011 or a fuller copy of the posted reference that would include the date? It appears that the method is just one cited out of a fuller reference, and I should cite to that fuller reference by its own title. I will also approach Waters with this request.

Your rule cites "Waters Method D6508, Rev. 2," entitled "Test Method for Determination of Dissolved Inorganic Anions in Aqueous Matrices Using Capillary Ion Electrophoresis and Chromate Electrolyte." Waters sent me a document marked "Method 6500," "revision 0," and dated February 2007," and entitled "Dissolved Inorganic Anions In Aqueous Matrices By Capillary Ion Electrophoresis." That document appears to be Method 6500 from SW-846. Is "Waters Method D6508, Rev. 2" the same as Method 6500, rev. 0 from SW-846? If so, why did USEPA cite this as "D6508"? If not, can you forward me a copy of Method D6508 or give me enough information to identify the method to Waters, that I might obtain a copy of the right method?

Michael J. McCambridge
Attorney
Illinois Pollution Control Board
312-814-6924

Mike McCambridge - Re: Waters Methods

From: <Fair.Pat@epamail.epa.gov>
To: "Mike McCambridge" <mccambridge@ipcb.state.il.us>
Date: 7/10/2008 9:31 PM
Subject: Re: Waters Methods

Mike,

I haven't done a one-to-one check of the ASTM method against the Waters method, so I can't say for sure that they are the same. My comment was meant to let you know that I would do that BEFORE we issue the next set of method approvals. If they are the same or only have insignificant differences, then we will include the ASTM method as an approved method. Legally, it won't be an approved drinking water method until we publish a notice in the Federal Register.

It's my opinion that if the Waters methods aren't easily available from Waters, then you can easily justify not including them in your state regulations. Our ATP coordinator wasn't able to find a copy of the nitrate/nitrite method in his files. However, he is still checking on it.

I have the GA Tech method. I can email it to you on Monday. If you need it before then, you can go to the e-docket for the 2007 Methods Update Rule. I know the method is in the docket, because I put it there and it is available for download through the docket site.

I will see if I can find out how we should be referencing the GA Tech method. I thought our information was correct when we went final on the rule.

Hope this helps.
Pat

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> To: Pat Fair/CI/USEPA/US@EPA
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> Date: 07/10/2008 06:07PM
> Subject: Re: Waters Methods
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07/08/2008 03:29

PM

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Michael J. McCambridge
Attorney
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312-814-6924

From: Mike McCambridge
To: Fair.Pat@epamail.epa.gov
Date: 7/11/2008 3:45:30 PM
Subject: Re: Waters Methods

It does, as the stream moves ever onward. Wasn't it Aristotle who said that you cannot step into the same stream twice?

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Michael J. McCambridge
Attorney
Illinois Pollution Control Board
312-814-6924

From: Mike McCambridge
To: Fair.Pat@epamail.epa.gov
Date: 8/6/2008 2:08:48 PM
Subject: Georgia Radium Method

I am having trouble locating the new method for Ra-226 and Ra-228 from the Georgia Institute of Technology that USEPA added on March 12, 2007. The Environmental Resource Center may no longer exist. I need a copy of the method if it is to appear in the Illinois regulations. I must also assure that the availability information is presented correctly.

Can you provide a copy of the method?

Can you provide where the public may obtain the method?

Tomorrow the Board will propose the amendments that will include the March 12, 2007 methods revisions and the June 3, 2008 equivalent methods approvals. Issues will remain regarding Waters Method 6508, rev. 2, which is the same as ASTM D6508-00(2005)e2, since I can get it from ASTM but not from Waters Corp., and the Georgia Radium Method that I now seek.

Michael J. McCambridge
Attorney
Illinois Pollution Control Board
312-814-6924

Mike McCambridge - Re: Georgia Radium Method

From: <Fair.Pat@epamail.epa.gov>
To: "Mike McCambridge" <mccambridge@ipcb.state.il.us>
Date: 8/6/2008 10:04 PM
Subject: Re: Georgia Radium Method

Mike,

I'm on travel this week, so I don't have access to the GA Radium method. I'll send it to you early next week. I seem to remember you saying that the contact information that was given to us for the March 2007 methods rule is no longer applicable. I'll have to see if I can find the correct contact information for you. I know I can give you the method, but I'm sure you still need a source to publish in your regulations.

Pat
-----"Mike McCambridge" <mccambridge@ipcb.state.il.us> wrote: -----

> To: Pat Fair/CI/USEPA/US@EPA
> From: "Mike McCambridge" <mccambridge@ipcb.state.il.us>
> Date: 08/06/2008 12:08PM
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>
> Michael J. McCambridge
> Attorney
> Illinois Pollution Control Board
> 312-814-6924

From: Mike McCambridge
To: Fair.Pat@epamail.epa.gov
Date: 9/11/2008 4:29:42 PM
Subject: Radium Method

I did not receive the e-mail. My IT people tell me that they have no way to recover items caught in their filters; they do not maintain a "spam folder," as appears on both of my personal e-mail accounts.

Try one more time, and use this address. Please CC my personal e-mail account: m.mccambridge@att.net. Also use your EPA address, and give the IT people here a couple of days to make the necessary system adjustments.

I am sending a copy of this e-mail to our IT people, and I will ask them to include your domain as "allowed." It would amaze me if USEPA is blocked as a domain, but anything is possible.

We live in such a nightmare world of spam and malicious e-mail. The best efforts of the most conscientous IT protocol is bound to "gang aft agley," as Rabbie Burns would have it.

If you have trouble, call me.

Michael J. McCambridge
Attorney
Illinois Pollution Control Board
312-814-6924

From: Mike McCambridge
To: Fair.Pat@epamail.epa.gov
Date: 9/15/2008 12:02:52 PM
Subject: Geargia Tech Radium Method

I did receive the method, but only on my personal e-mail account, not on the State system. We must bear this in mind for the future. If you need to contact me, use my personal e-mail (m.mccambridge@att.net) or call me.

Thanks for your efforts.

I have only one minor favor remianing to ask: could you let me know what you learn with regard to availability. I will redouble my efforts to get this information myself, and I will let you know if I learn enything, but I will need that information to complete the incorporation by reference. Perhaps, "U.S. EPA" will get a response before "Pollution Control Board." So far, I have received no responses to calls or e-mails.

Michael J. McCambridge
Attorney
Illinois Pollution Control Board
312-814-6924

From: Mike McCambridge
To: Fair.Pat@epamail.epa.gov; TURLEY, Dawn
Date: 9/17/2008 9:06:17 AM
Subject: Re: Test for IPCB E-mail delivery

It worked, thank goodness.

Thank you both (Pat Fair and Dawn Turley) for all your help.

Michael J. McCambridge
Attorney
Illinois Pollution Control Board
312-814-6924

>>> <Fair.Pat@epamail.epa.gov> 9/17/2008 8:06 AM >>>
I added Mike's name to my email list. I believe the earlier messages that I sent to him were either replies to his messages or I copied/pasted his address from an earlier email. Hope you figure out the problem. You can see if he receives this message, since he's copied on it.

"Dawn TURLEY" <turleyd@ipcb.state.il.us> To Pat Fair/CI/USEPA/US@EPA
09/16/2008 10:17 AM cc
Subject
Re: Test for IPCB E-mail delivery

Thank you for responding so quickly. I am trying to determine why Mike is not getting your e-mails. Would you please remove Mike McCambridges e-mail from your address book and recreate his address to ensure that it's correct?

His address is mccambm@ipcb.state.il.us

Thank you,
Dawn Turley
IPCB Network Support
Phone: 217-782-2415
Fax: 217-524-8508

On 9/15/2008 at 7:25 PM, <Fair.Pat@epamail.epa.gov> wrote:
Dawn,

I received your email.

Pat Fair
-----"Dawn TURLEY" <turleyd@ipcb.state.il.us> wrote: -----

To: Pat Fair/CI/USEPA/US@EPA
From: "Dawn TURLEY" <turleyd@ipcb.state.il.us>
Date: 09/15/2008 02:27PM

Subject: Test for IPCB E-mail delivery

I am the e-mail administrator for the IPCB. Mike McCambridge is having problems receiving your e-mails.
In order to track and resolve the problem, would you please reply to this e-mail and then try to send me a new e-mail?
Thank you,
Dawn Turley
IPCB Network Support
Phone: 217-782-2415
Fax: 217-524-8508

From: <Fair.Pat@epamail.epa.gov>
To: MCCAMBM@ipcb.state.il.us
Date: 10/15/2008 10:30:16 AM
Subject: Source of Radium 226-228 method

Mike,

I finally tracked down the contact information for obtaining the GA Tech method for radium 226 & 228 in drinking water. Here it is:

Robert Rosson
Georgia Tech Research Institute
925 Dalney Road
Atlanta, GA 30332

(404)407-6339
robert.rosson@gtri.gatech.edu

I can't easily update the CFR to reflect this changed contact information. I am going to try to update the information on EPA's drinking water web page, so it will be accurate.

I hope this information helps and is not too late.

Pat Fair

From: Mike McCambridge
To: Fair.Pat@epamail.epa.gov
Date: 10/15/2008 10:32:50 AM
Subject: Re: Source of Radium 226-228 method

Thank you very much. I now have all I need to include the method in the pending update, so that entities in Illinois may opt to use the method.

Michael J. McCambridge
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United States
Environmental Protection
Agency

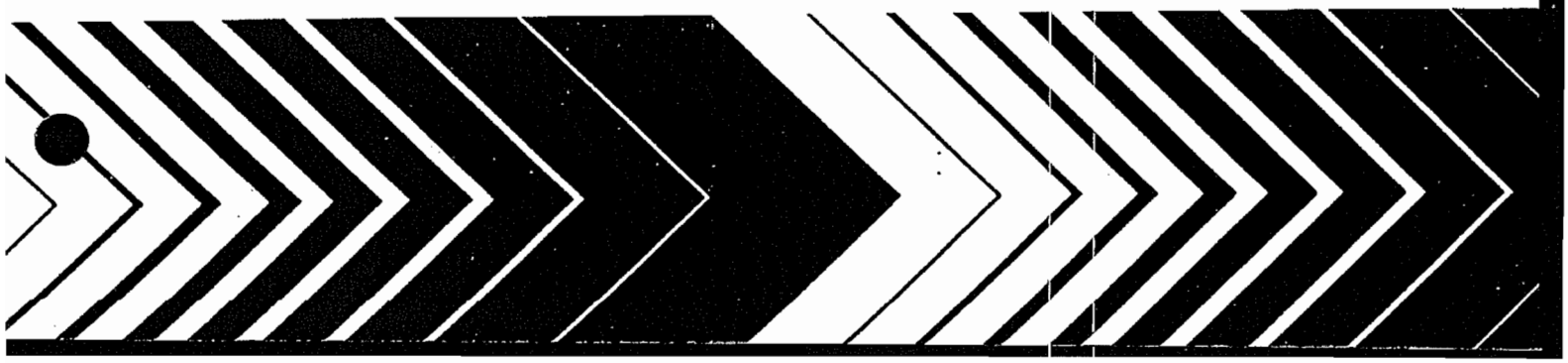
Office of Research and
Development
Washington DC 20460

EPA/600/R-94/173
October 1994

EPA

Technical Notes on Drinking Water Methods

ATT. TO E-MAIL
6-30-08 FR, USEPA
INCL. IN PC 9



EPA/600/R-94/173
October 1994

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.

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Technical Support Division
Office of Water

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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

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.

	Analytical Method[1]		
Contaminant	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 ≤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 $\pm$ 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 $\leq$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 $\geq$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.

*U.S. GOVERNMENT PRINTING OFFICE:1995-650-006/00220

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This ASTM D6508, Rev2 method document has been reviewed by EPA Office of Drinking Water and Wastewater for EPA Tier 3 approval. Added updated QC criteria based upon statistical analysis by Dyncorp.

ATP Case #:	**N00-0002 and D00-0002**
Draft #:	**Second draft with EPA Modifications: ASTM D6508, Rev 2**
Date:	**December 2000**
Method Author:	**Jim Krol**
Telephone:	**508/482-2131**
FAX:	**508/482-3625**

Test Method for Determination of Dissolved Inorganic Anions in Aqueous Matrices Using Capillary Ion Electrophoresis and Chromate Electrolyte

1 Scope

1.1 This test method covers the determination of the inorganic anions fluoride, bromide, chloride, nitrite, nitrate, ortho-phosphate, and sulfate in drinking water, wastewater, and other aqueous matrices using capillary ion electrophoresis (CIE) with indirect UV detection. See Fig. 1 through 6.

1.2 The test method uses a chromate-based electrolyte and indirect UV detection at 254 nm. It is applicable for the determination of inorganic anions in the range of 0.2 to 50 mg/L except for fluoride whose range is 0.2 to 25 mg/L.

1.3 It is the responsibility of the user to ensure the validity of this test method for other anion concentrations and untested aqueous matrices.

Note 1: The highest accepted anion concentration submitted for P&B extend the anion concentration range for the following anions; Chloride to 93 mg/L, Sulfate to 90 mg/L, Nitrate to 72 mg/L, and ortho-phosphate to 58 mg/L.

1.4 This method does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use. For specific hazard statements, see sec. 9.

2 Referenced Documents

2.1 ASTM Standards

D 1066 Practice for Sampling Steam[1]
D 1129 Terminology Relating to Water[1]
D 1193 Specification for Reagent Water[1]
D 2777 Practice for Determination of Precision and Bias of Applicable Methods of Committee D-19 on Water[1]
D 3370 Practices for Sampling Water[1]
D 3856 Guide for Good Laboratory Practices in Laboratories Engaged in Sampling and Analysis of Water[1]
D 5810 Standard Practice of Spiking Samples[1]
D 5847 Standard Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis[1]
D 5905 Standard Specification for Substitute Wastewater[1]
F 488 Test Method for Total Bacterial Count in Water[2]

2.2 EPA 40 CFR Ch.1 (7-1-92 Edition), Pt 136, App. B, page 565 – 567: Definition and Procedure for the Determination of the Method Detection Limit-Revision 1.11.

2.3 Draft Protocol for EPA Approval of New Methods for Organic and Inorganic Analytes in Wastewater and Drinking Water, dated Mar 1999, EPA-821-B-98-003.

3 Terminology

3.1 Definitions - For definitions of terms used in this test method, refer to Terminology D1129.

3.2 Description of Terms Specific to This Test Standard:

3.2.1 Capillary Ion Electrophoresis -- an electrophoretic technique in which an UV absorbing electrolyte is placed in a 50 μm to 75 μm fused silica capillary. Voltage is applied across the capillary causing electrolyte and anions to migrate towards the anode and through the capillary's UV detector window. Anions are separated based upon the their differential rates of migration in the electrical field. Anion detection and quantitation are based upon the principles of indirect UV detection.

3.2.2 Electrolyte -- combination of a UV absorbing salt and an electroosmotic flow modifier placed inside the capillary, used as a carrier for the analytes, and for detection and quantitation. The UV absorbing portion of the salt must be anionic and have an electrophoretic mobility similar to the analyte anions of interest.

3.2.3 Electroosmotic Flow (EOF) -- the direction and velocity of electrolyte solution flow within the capillary under an applied electrical potential (voltage); the velocity and direction of flow is determined by electrolyte chemistry, capillary wall chemistry, and applied voltage.

3.2.4 Electroosmotic Flow Modifier (OFM) -- a cationic quaternary amine in the electrolyte that dynamically coats the negatively charged silica wall giving it a net positive charge. This reverses the direction of the electrolyte's natural electroosmotic flow and directs it towards the anode and detector. This modifier augments anion migration and enhances speed of analysis. Its concentration secondarily effects anion selectivity and resolution. See Fig. 7.

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1) Annual Book of ASTM Standards, Vol. 11.01
2) Annual Book of ASTM Standards, Vol. 11.02

3.2.5 Electrophoretic Mobility -- the specific velocity of a charged analyte in the electrolyte under specific electroosmotic flow conditions. The mobility of an analyte is directly related to the analyte's equivalent ionic conductance and applied voltage, and is the primary mechanism of separation.

3.2.6 Electropherogram -- a graphical presentation of UV detector response versus time of analysis; the x axis is migration time which is used to qualitatively identify the anion, and the y axis is UV response which can be converted to time corrected peak area for quantitation.

3.2.7 Hydrostatic Sampling -- a sample introduction technique in which the capillary with electrolyte is immersed in the sample, and both are elevated to a specific height, typically 10 cm, above the receiving electrolyte reservoir for a preset amount of time, typically less than 60 s. Nanolitres of sample are siphoned into the capillary by differential head pressure and gravity.

3.2.8 Indirect UV Detection -- a form of UV detection in which the analyte displaces an equivalent net charge amount of the highly UV absorbing component of the electrolyte causing a net decrease in background absorbance. The magnitude of the decreased absorbance is directly proportional to analyte concentration. Detector output polarity is reversed in order to obtain a positive mV response.

3.2.9. Midpoint of Peak Width -- CIE peaks are typically asymmetrical with the peak apex shifting with increasing concentration, and peak apex may not be indicative of true analyte migration time. Midpoint of peak width is the midpoint between the analyte peak's start and stop integration, or the peak center of gravity.

3.2.10 Migration Time -- the time required for a specific analyte to migrate through the capillary to the detector. The migration time in capillary ion electrophoresis is analogous to retention time in chromatography.

3.2.11 Time Corrected Peak Area -- normalized peak area; peak area divided by migration time. CE principles state that peak area is dependent upon migration time, i.e. for the same concentration of analyte, as migration time increases (decreases) peak area increases (decreases). Time corrected peak area accounts for these changes.

4 Summary of Test Method

4.1 Capillary ion electrophoresis, see Fig. 7 through Fig. 10, is a free zone electrophoretic technique optimized for the determination of anions with molecular weight less than 200. The anions migrate and are separated according to their mobility in the electrolyte when an electrical field is applied through the open tubular fused silica capillary. The electrolyte's electroosmotic low modifier dynamically coats the inner wall of the capillary changing the surface to a net positive charge. This reversal of wall charge reverses the natural EOF. The modified EOF in combination with a negative power supply augments the mobility of the analyte anions towards the anode and detector achieving rapid analysis times. Cations migrate in the opposite direction towards the cathode and are removed from the sample during analysis. Water and other neutral species move toward the detector at the same rate as the EOF. The neutral species migrate slower than the analyte anions and do not interfere with anion analysis. See Fig. 7 and 8.

4.2 Sample is introduced into the capillary using hydrostatic sampling. The inlet of the capillary containing electrolyte is immersed in the sample and the height of the sample raised 10 cm for 30 s where low nanolitre volumes are siphoned into the capillary. After sample loading, the capillary is immediately immersed back into the electrolyte. The voltage is applied initiating the separation process.

4.3 Anion detection is based upon the principles of indirect UV detection. The UV absorbing electrolyte anion is displaced charge-for-charge by the separated analyte anion. The analyte anion zone has a net decrease in background absorbance. This decrease in UV absorbance is quantitatively proportional to analyte anion concentration. See Fig. 9. Detector output polarity is reversed to provide positive mV response to the data system, and to make the negative absorbance peaks appear positive.

4.4 The analysis is complete once the last anion of interest is detected. The capillary is automatically vacuum purged by the system of any remaining sample, and replenished with fresh electrolyte. The system is now ready for the next analysis.

5 Significance and Use

5.1 Capillary ion electrophoresis provides a simultaneous separation and determination of several inorganic anions using nanolitres of sample in a single injection. All anions present in the sample matrix will be visualized yielding an anionic profile of the sample.

5.2 Analysis time is less than 5 min with sufficient sensitivity for drinking water, and wastewater applications. Time between samplings is less than 7 minutes allowing for high sample throughput.

5.3 Minimal sample preparation is necessary for drinking water and wastewater matrices. Typically only a dilution with water is needed.

5.4 This test method is intended as an alternative to other multi-analyte methods and various wet chemistries for the determination of inorganic anions in water and wastewater. Compared to other multi-analyte methods the major benefits of CIE are speed of analysis, simplicity, and reduced reagent consumption and operating costs.

6 Interferences

6.1 Analyte identification, quantitation, and possible comigration occur when one anion is in significant excess to other anions in the sample matrix. For two adjacent peaks, reliable quantitation can be achieved when the concentration differential is less than 100:1. As the resolution between two anion peaks increase so does the tolerated concentration differential. In samples containing 1000 mg/L Cl, 1 mg/L SO_4 can be resolved and quantitated, however, the high Cl will interfere with Br and NO_2 quantitation.

6.2 Dissolved carbonate, detected as HCO_3^{-1}, is an anion present in all aqueous samples, especially alkaline samples. Carbonate concentrations greater than 500 mg/L will interfere with PO_4 quantitation.

6.3 Monovalent organic acids, except for formate, and neutral organics commonly found in wastewater migrate later in the electropherogram, after carbonate, and do not interfere. Formate, a common organic acid found in environmental samples, migrates shortly after fluoride but before phosphate. Formate concentrations greater than 5 mg/L will interfere with fluoride identification and quantitation. Inclusion of 2 mg/L formate into the Mixed Anion Working Solution aids in fluoride and formate identification and quantitation.

6.4 Divalent organic acids usually found in wastewater migrate after phosphate. At high concentrations, greater than 10 mg/L, they may interfere with phosphate identification and quantitation.

6.5 Chlorate also migrates after phosphate and at concentrations greater than 10 mg/L will interfere with phosphate identification and quantitation. Inclusion of 5 mg/L chlorate into the Mixed Anion Working Solution aids in phosphate and chlorate identification and quantitation.

6.6 As analyte concentration increases, analyte peak shape becomes asymmetrical. If adjacent analyte peaks are not baseline resolved, the data system will drop a perpendicular between them to the baseline. This causes a decrease in peak area for both analyte peaks and a low bias for analyte amounts. For optimal quantitation, insure that adjacent peaks are fully resolved, if they are not, dilute the sample 1:1 with water.

6.7 Samples containing high levels of TOC, total organic carbon, may effect the observed analyte migration times. The TOC binds to the capillary surface decreasing the EOF and increasing analyte migration times. Refer to Figure 7. However, the change in EOF does not effect analyte selectivity. Analytes are identified using normalized analyte migration times with respect to a reference peak, chloride, always the first peak in the electropherogram. The surface can be regenerated with a 5 minute wash with 500 mM NaOH.

7 .Apparatus

7.1 Capillary Ion Electrophoresis System -- the system consists of the following components, as shown in Fig. 10, or equivalent:[3]

7.1.1 High Voltage Power Supply -- capable of generating voltage (potential) between 0 and minus 30 kV relative to ground with the capability working in a constant current mode.

7.1.2 Covered Sample Carousel -- to prevent environmental contamination of the samples and electrolytes during a multi-sample batch analysis.

7.1.3 Sample Introduction Mechanism -- capable of hydrostatic sampling technique, using gravity, positive pressure, or equivalent.

7.1.4 Capillary Purge Mechanism -- to purge the capillary after every analysis with fresh electrolyte to eliminate any interference from the previous sample matrix, and to clean the capillary with other reagents, such as sodium hydroxide.

7.1.5 UV Detector -- having the capability of monitoring 254 nm, or equivalent, with a time constant of 0.3 s.

7.1.6 Fused Silica Capillary -- a 75 μm (inner diameter) x 375 μm (outer diameter) x 60 cm (length) having a polymer coating for flexibility, and a non-coated section to act as the cell window for UV detection.[3]

7.1.7 Constant Temperature Compartment -- to keep the samples, capillary, and electrolytes at constant temperature.

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3) Available from Waters, 34 Maple St., Milford, Ma., 01757, 800/252-4752.

7.2 Data System -- computer system that can acquire data at 20 points per second minimum, express migration time in minutes to 3 decimal places, use midpoint of the analyte peak width, or center of gravity, to determine the analyte migration time, use normalized migration times with respect to a reference peak for qualitative identification, use time corrected peak area response for analyte quantitation, and express results in concentration units.[3]

Note 2: It is recommended that integrators or standard chromatographic data processing not be used with this test method.

7.3 Anion Exchange Cartridges in the Hydroxide form.[4]

7.4 Plastic Syringe -- 20 mL, Disposable.

7.5 Vacuum Filtration Apparatus -- capable for filtering 100 mL of reagent through a 0.45 µm aqueous filter.

8 Reagents and Materials

8.1 Purity of Reagents: -- Unless otherwise indicated, it is intended that all reagents shall conform to the reagent grade specification of the Analytical Reagents of the American Chemical Society, where such specifications are available.[5] Other grades may be used, provided it is first ascertained that the reagent is of sufficient high purity to permit its use without lessening the performance or accuracy of the determination. Reagent chemicals shall be used for all tests.

Note 3: Calibration and detection limits of this method are biased by the purity of the reagents.

8.2 Purity of Water:-- Unless otherwise indicated, references to water shall be understood to mean Type I reagent water conforming or exceeding specification D1193. Freshly drawn water should be used for preparation of all stock and working standards, electrolytes, and solutions.[6] Performance and detection limits of this method are limited by the purity of reagent water, especially TOC.

8.3 Reagent Blank: Reagent Water or any other solution used to preserve or dilute the sample.

8.4 Individual Anion Solution, Stock:

Note 4: It is suggested that certified individual 1000 mg/L anion standards be purchased for use with this test method.

Note 5: All weights given are for anhydrous or dried salts. Must account for reagent purity to calculate true value concentration. Certify against NIST traceable standards.

8.4.1 Bromide Solution, Standard (1.0 mL = 1.00 mg Bromide):
Dry approximately 0.5 g of sodium bromide (NaBr) for 6 h at 150°C and cool in a desiccator. Dissolve 0.128 g of the dry salt in a 100 mL volumetric flask with water, and fill to mark with water.

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4) Available from Alltech Associates, P/N 30254, 2051 Waukegan Rd, Deerfield IL., 60015, 847/948-8600.

5) Reagent Chemicals, American Chemical Society Specifications, Am. Chem. Soc., Washington, DC For suggestions on the testing of reagents not listed by the American Chemical Society, see Analar Standards for Laboratory Chemicals, BDH Ltd., Poole, Dorset. U.K., and the United States Pharmacopeia and National Formulary, U.S. Pharmacopoeia Convention, Inc. (USPC), Rockville, Md.

6) Although the reagent water may exceed D1193 specification, the reagent water needs to be periodically tested for bacterial contamination. Bacteria and their waste products may adversely affect system performance. As a guide, ASTM type IA water specifies a total bacteria count of 10 colonies/L. Refer to Test Method F 488 for analysis procedure.

8.4.2 Chloride Solution, Standard (1.0 mL = 1.00 mg Chloride): Dry approximately 0.5 g of sodium chloride (NaCl) for 1 h at 100°C and cool in a desiccator. Dissolve 0.165 g of the dry salt in a 100 mL a volumetric flask with water, and fill to mark with water.

8.4.3 Fluoride Solution, Standard (1.0 mL = 1.00 mg Fluoride): Dry approximately 0.5 g of sodium fluoride (NaF) for 1 h at 100°C and cool in a desiccator. Dissolve 0.221 g of the dry salt in a 100 mL volumetric flask with water, and fill to mark with water.

8.4.4 Formate Solution, Standard (1.0 mL = 1.00 mg Formate): Dissolve 0.151 g of sodium formate in a 100 mL volumetric flask with water, and fill to mark with water.

8.4.5 Nitrate Solution, Standard (1.0 mL = 1.00 mg Nitrate): Dry approximately 0.5 g of sodium nitrate ($NaNO_3$) for 48 h at 105°C and cool in a desiccator. Dissolve 0.137 g of the dry salt in a 100 mL volumetric flask with water, and fill to mark with water.

8.4.6 Nitrite Solution, Standard (1.0 mL = 1.00 mg Nitrite): Dry approximately 0.5 g of sodium nitrite ($NaNO_2$) for 24 h in a desiccator containing concentrated sulfuric acid. Dissolve 0.150 g of the dry salt in a 100 mL volumetric flask with water, and fill to mark with water. Store in a sterilized glass bottle. Refrigerate and prepare monthly.

Note 6: Nitrite is easily oxidized, especially in the presence of moisture. Use only fresh reagent.

Note 7: Prepare sterile bottles for storing nitrite solutions by heating for 1 h at 170°C in an air oven.

8.4.7 Ortho-Phosphate Solution, Standard (1.0 mL = 1.00 mg o-Phosphate): Dissolve 0.150 g of anhydrous dibasic sodium phosphate (Na_2HPO_4) in a 100 mL volumetric flask with water, and fill to mark with water.

8.4.8 Sulfate Solution, Standard (1.0 mL = 1.00 mg Sulfate): Dry approximately 0.5 g of anhydrous sodium sulfate (Na_2SO_4) for 1 h at 110°C and cool in a desiccator. Dissolve 0.148 g of the dry salt in a 100 mL volumetric flask with water, and fill to mark with water

8.5 Mixed Anion Solution, Working: Prepare a 0.2 mg/L and at least 3 different working standards concentrations for the analyte anions of interest bracketing the desired range of analysis, typically between 0.2 and 50 mg/L, and add 2 mg/L formate to all standards. Add an appropriate aliquot of Individual Anion Stock Solution (8.4) to a pre-rinsed 100 mL volumetric flask, and dilute to 100 mL with water.

Note 8: Use 100 µL of Individual Anion Stock Solution (8.4) per 100 mL for 1 mg/L anion.

Note 9: Anions of no interest may be omitted.

Note 10: The mid-range Mixed Anion Solution, Working may be used for the determination of migration times and resolution described in 12.1.

8.6 Calibration Verification Solution (CVS): A solution formulated by the laboratory of mixed analytes of known concentration prepared in water. The CVS solution must be prepared from a different source to the calibration standards.

8.7 Performance Evaluation Solution (PES): A solution formulated by an independent source of mixed analytes of known concentration prepared in water. Ideally, the PES solution should be purchased from an independent source.

8.8 Quality Control Solution (QCS): A solution of known analyte concentrations added to a synthetic sample matrix such as Substitute Wastewater that sufficiently challenges the Test Method.

8.9 Buffer Solution (100 mM CHES / 1 mM Calcium Gluconate): Dissolve 20.73 g of CHES (2-[N-Cyclohexylamino]-Ethane Sulfonic Acid) and 0.43 g of Calcium Gluconate in a 1 L volumetric flask with water, and dilute to 1 L with water. This concentrate may be stored in a capped glass or plastic container for up to 1year.

8.10 Chromate Concentrate Solution (100 mM Sodium Chromate): Dissolve 23.41 g of sodium chromate tetrahydrate ($Na_2CrO_4 \cdot 4\ H_2O$) in a 1 L volumetric flask with water, and dilute to 1 L with water. This concentrate may be stored in a capped glass or plastic container for up to 1 year.

8.11 OFM Concentrate Solution (100 mM Tetradecyltrimethyl Ammonium Bromide): Dissolve 33.65 g of Tetradecyltrimethyl Ammonium Bromide (TTABr) in a 1 L volumetric flask with water, and dilute to 1 L with water. Store this solution in a capped glass or plastic container for up to 1 year.

Note 11: TTABr needs to be converted to the hydroxide form (TTAOH) for use with this test method. TTAOH is commercially available as 100 mM TTAOH [7] which is an equivalent substitute.

8.12 Sodium Hydroxide Solution (500 mM Sodium Hydroxide)-- Dissolve 20 g of sodium hydroxide (NaOH) in a 1 L plastic volumetric flask with water, and dilute to 1 L with water.

8.13 Electrolyte Solution, Working (4.7 mM Chromate / 4 mM TTAOH / 10 mM CHES / 0.1 mM Calcium Gluconate) [8]: Wash the anion exchange cartridge in the hydroxide form (7.3) using the 20 mL plastic syringe (7.4) with 10 mL of 500 mM NaOH (8.12) followed by 10 mL of water. Discard the washings. Slowly pass 4 mL of the 100 mM TTABr Solution (8.11) through the cartridge into a 100 mL volumetric flask. Rinse the cartridge with 20 mL of water, adding the washing to the volumetric flask.

Note 12: The above procedure is used to convert the TTABr to TTAOH, which is used in the electrolyte. If using commercially available 100 mM TTAOH, the above conversion step is not necessary; substitute 0.5 mL of 100 mM TTAOH and continue below

Into the 100 mL volumetric flask add 4.7 mL of Chromate Concentrate Solution (8.10) and 10 mL of Buffer solution (8.9). Mix and dilute to 100 mL with water. The natural pH of the electrolyte should be 9 ± 0.1. Filter and degas using the vacuum filtration apparatus. Store the any remaining electrolyte in a capped glass or plastic container at ambient temperature. The electrolyte is stable for 1 year.

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7) Available from Waters Corp. as IonSelect 100mM OFM Hydroxide Concentrate, 100 mM TTAOH, P/N 49387.
8) Availiable from Waters Corp. as IonSelect High Mobility Anion Electrolyte, P/N 49385.

9 Precautions

9.1 Chemicals used in this test method are typical of many useful laboratory chemicals, reagents and cleaning solutions, which can be hazardous if not handled properly. Refer to Guide D 3856.

9.2 It is the responsibility of the user to prepare, handle, and dispose of chemical solutions in accordance with all applicable federal, state, and local regulations.

9.3 **Warning** -- This capillary electrophoresis method uses high voltage as a means for separating the analyte anions, and can be hazardous if not used properly. Use only those instruments that have all proper safety features.

10 Sampling

10.1 Collect samples in accordance with Practice D 3370.

10.2 Rinse samples containers with sample and discard to eliminate any contamination from the container. Fill to overflowing and cap to exclude air.

10.3 Analyze samples as soon as possible after collection. For nitrite, nitrate, and phosphate refrigerate the sample at 4°C after collection. Warm to room temperature before dilution and analysis.

10.4 At the lab, filter samples containing suspended solids through a pre-rinsed 0.45 μm aqueous compatible membrane filter before analysis.

10.5 If sample dilution is required to remain within the scope of this Test Method, dilute with water only.

11 Preparation of Apparatus

11.1 Set up the CE and data system according to the manufacturer's instructions.

11 2 Program the CE system to maintain a constant temperature of 25° ± 0.5°C; or 5°C above ambient laboratory temperature. Fill the electrolyte reservoirs with fresh chromate electrolyte working solution (8.13), and allow 10 min for thermal equilibration.

11.3 Condition a new capillary (7.1.6) with 500 mM NaOH Solution (8.12) for 5 min followed by water for 5 min. Purge the capillary with electrolyte (8.13) for 3 min.

11.4 Apply 15 kV of voltage and test for current. The current should be 14 ± 1 µA. If no current is observed, then there is a bubble and/or blockage in the capillary. Degas the chromate electrolyte working solution and retry. If still no current, replace the capillary.

11.5 Set the UV detector to 254 nm detection, or equivalent. Zero the detector to 0.000 absorbance. UV offset is less then 0.1 AU.

11.6 Program the CE system for constant current of 14 µA.

11.7 Program the CE system for a hydrostatic sampling of 30 s. Approximately 37nL of sample is siphoned into the capillary. Different sampling times may be used provided that the samples and standards are analyzed identically.

11.8 Program the CE system for a 1 min purge with the chromate electrolyte working solution between each analysis. Using a 15 psi vacuum purge mechanism, one 60 cm capillary volume can be displaced in 30 s.

11.9 Program the data system for an acquisition rate of at least 20 points per s. Program the data system to identify analyte peaks based upon normalized migration time using Cl as the reference peak, and to quantitate analyte peak response using time corrected peak area.

Note 13: Under the analysis conditions Cl is always the first peak in the electropherogram, and can be used as a migration time reference peak.

12 Calibration

12.1 Determination of Migration Times-- Calibrate Daily. The migration time of an anion is dependent upon the electrolyte composition, pH, capillary surface and length, applied voltage, the ionic strength of the sample, and temperature. For every fresh electrolyte determine the analyte migration time, in min to the third decimal place, of the mid-range mixed anion standard working solution (8.5), described in Sec 11. Use the mid-point of analyte peak width as the determinant of analyte migration time.

Note 14: Analyte peak apex may be used as the migration time determinant, but potential analyte misidentification may result with asymmetrical peak shape at high analyte concentrations.

12.2 Analyze the blank (8.3), a 0.2 mg/L, and at least 3 working mg/L solutions (8.5), using the set-up described in sec 11. For each anion concentration (X-axis) plot time corrected peak area response (Y-axis). Determine the best linear calibration line through the data points, or use the linear regression calibration routine (1/X Weighting and Linear Through Zero) available in the data system.

Note 15: Do not use peak height for calibration. Peak area is directly related to migration time, i.e. for the same analyte concentration, increasing migration time gives increasing peak area.

Note 16: EPA recommends calibration at the minimum concentration of 0.2 mg/L plus 3 additional points.

The r^2 (coefficient of determination) values should be greater than 0.995; typical r^2 values obtained from the interlaboratory collaborative are given in Table A2.

12.3 Calibrate daily and with each change in electrolyte, and validate by analyzing the CVS solution (8.6) according to procedure in Sec16.4.

12.4 After validation of linear multiple point calibration, a single point calibration solution can be used between 0.2 and 50 mg/L for recalibration provided the quality control requirements in Sec 16.4 are met.

13 Procedure

13.1 Dilute the sample, if necessary with water, to remain within the scope (Sec 1.2, 1.3) and calibration of this test method. Refer to A1.5.1.

13.2 Analyze all blanks (8.3), standards (8.5), and samples as described in Sec 11 using the quality control criteria described in Sec 16.5 to 16.9. Refer to Fig. 1 through 5 for representative anion standard, detection limit standard, substitute wastewater, drinking water, and wastewater electropherograms.

13.3 Analyze all blanks, calibration standards, samples, and quality control solutions in singlicate. Perform at least one matrix spike analysis in duplicate as part of the QC protocol, Sec 16.7. Optional: Duplicate analyses are preferred due to short analysis times.

Note 17: Collaborative data was acquired, submitted and evaluated as the average of duplicate samplings.

13.4 After 20 sample analyses, or batch, analyze the QCS solution (8.8). If necessary, recalibrate using a single mixed anion standard working solution (8.5), and replace analyte migration time.

Note 18: A change in analyte migration time of the mixed anion standard working solution by more than +5% suggests that components in the previously analyzed sample matrices have contaminated the capillary surface. Refer to sec 6.7. Continue but wash the capillary with NaOH solution (8.12) before the next change in electrolyte.

14 Calculation

14.1 Relate the time corrected peak area response for each analyte with the calibration curve generated in section 12.2 to determine mg/L concentration of analyte anion. If the sample was diluted prior to analysis, then multiply mg/L anion by the dilution factor to obtain the original sample concentration, as follows:

Original Sample mg/L Analyte = (A x SF) where;
A = analyte concentration determined from the calibration curve, in mg/L,
SF = scale or dilution factor.

15 Report Format

15.1 The sample analysis report should contain the sample name, analyte anion name, migration time reported to 3 decimal places, migration time ratio, peak area, time corrected peak area, sample dilution, and original solution analyte concentration. Optional: Report analysis method parameters, date of sample data acquisition, and date of result processing for documentation and validation purposes.

16 Quality Control

16.1 Before this test method is applied to the analysis of unknown samples, the analyst should establish quality control according to procedures recommended in Practice D5847, and Guide D5810.

16.2 The laboratory using this test must perform an initial demonstration of laboratory capability according to procedures outlined in Standard Practice D5847, and Appendix C.

Note 19: Certified Performance Evaluation Solutions (PES) and QC Solutions (QCS and CVS) are commercially available, and recommended.

16.3 Initial Demonstration of Performance: Analyze seven replicates of a Performance Evaluation Solution (PES, 8.7). Calculate analyte concentration mean and standard deviation of the seven replicates and compare to the precision and Initial %Recovery for the analyte in reagent water given in Table 8.

16.3.1 Repeat the 7 replicate analysis protocol before using a freshly prepared QVS solution (8.6) and QCS solution (8.8) for the first time. Calculate the standard deviation and compare with previous results using the student t-test. If no significant difference is noted then use the combined standard deviation to determine the QC limits, for the QVS and QCS solutions.

16.4 Calibration Verification: After calibration, verify the calibration linearity and acceptable instrument performance using a Calibration Verification Solution (8.6) treated as an unknown. If the determined CVS concentrations (8.6) are not within ± 3 standard deviations of the known true values as described in 16.3.1, the calibration solutions may be out of control. Reanalyze, and if analyte concentration still falls outside the acceptable limits, fresh calibration solutions (8.5) are required. Successful CVS analyte concentration must be confirmed after recalibration before continuing with the Test Method.

16.5 Analyze a reagent blank (8.3) with each batch to check for contamination introduced by the laboratory or use of the Test Method.

16.6 Quality Control Solution: Analyze one QCS (8.8) after 20 samples, or batch. The analyte concentrations for the QCS should fall within the lower limit (LL) and upper limits (UL) given in Table 8.

16.7 Matrix Spike Recovery: One Matrix Spike (MS) must be analyzed in duplicate with each batch of samples to test method recovery and relative %difference between them. Spike a portion of one sample from each batch with a known concentration of analyte, prepared in accordance with Guide D3856. The % recovery of the spike should fall within the MS/MSD lower and upper limits, and the Relative %Difference given in Table 8 for the appropriate sample matrix. If it does not, an interference may be present and the data for the set of similar samples matrices must be qualified with a warning that the data are suspect, or an alternate test method should be used. Refer to Guide D5810.

16.7.1 If the known analyte concentration is between 15 and 50 mg/L, then spike the sample solution to increase analyte concentration by 50%.

16.7.2 If the known analyte concentration is between 2 mg/L and 15 mg/L, then spike the sample solution to increase analyte concentration by 100%, but not less than 2 mg/L.

16.7.3 If the known analyte concentration is less than 2 mg/L, then spike the sample solution with 1 mg/L, 5 times the ML.

16.7.4 Calculate the percent recovery of the spike using the following formula:

$$\% \text{ Recovery} = 100\,[A\,(V_S + V) - B\,V_S] / C\,V \quad \text{where}$$

A = Analyte Concentration (mg/L) in Spiked Sample
B = Analyte Concentration (mg/L) in Unspiked Sample
C = Concentration (mg/L) of Analyte in Spiking Solution
V_S = Volume (mL) of Sample Used
V = Volume (mL) Added with Spike.

Evaluate performance according to Practice D5847.

16.8 Method Precision: One unknown sample should be analyzed in triplicate with each batch to test method precision. Calculate the standard deviation and use the F-Test to compare with the single operator precision given in Tables 1 through 7 for the equivalent analyte concentration and matrix type. Evaluate performance according to Practice D5847.

16.9 The laboratory may perform additional quality control as desired or appropriate.

17 Precision and Bias

17.1 The precision and bias data presented in this test method meet the requirements of Practice 2777-98, and are given in Tables 1 through 7. The full Research Report, RR# D19-1165, can be obtained from ASTM Headquarters.

17.2 This test method interlaboratory collaborative was performed by 11 laboratories using one operator each. Four Youden Pair spike concentrations for the 7 analytes anions yielding 8 analyte concentration levels. Test data was submitted for 11 Reagent Waters, 11 Substitute Wastewaters, 15 Drinking Waters, and 13 Wastewater sample matrices.

17.3 All data given in this method was quantitated using non-weighted linear calibration through zero, except where noted.

17.4 The precision, bias, and matrix recovery of this test method per anion analyte in the 4 tested sample matrices are based upon the analyte true value, calculated using weight, volume, and purity. True value spiking solution concentrations are given in Table A4.

17.5 The bias and matrix recovery statements for less than 2 mg/L of chloride, sulfate, and nitrate in naturally occurring sample matrices may be misleading due to spiking of small analyte concentration into a high naturally occurring analyte concentration observed with the matrix blank. The commonly occurring analyte concentrations observed in the sample matrix blanks for the naturally occurring tested matrices are given in Table A5.

17.6 The high nitrate bias and %recovery noted for the 0.5 mg/L NO_3 spike solution are attributed to the spiking solution containing 50 mg/L nitrite and 0.5 mg/L nitrate. Refer to Appendix Table A4, Solution 3. Some of the nitrite converted to nitrate prior to analysis. Similar NO_x conversion effect is observed with the 2 mg/L nitrate and 2 mg/L nitrite spike, Solution 7.

17.7 All collaborative participants used the premade Chromate electrolyte, (IonSelect High Mobility Anion Electrolyte, available from Waters Corp.) Ten laboratories used a Waters CIA Analyzer with Millennium Data Processing Software, and one laboratory used a Agilent CE System with Diode Array Detector that provided equivalent results, although different sampling and detection conditions were necessary for equivalent performance.
Note 20: Refer to reference B1.16 and Agilent (the former HP Company) website for recommended operating conditions.

18 Key Words

Anion
Capillary Electrophoresis
Drinking Water
Ion Analysis
Reagent Water
Substitute Wastewater
Wastewater

Appendix A
Mandatory Information

A1.1 All data presented in the following Tables conform and exceed the requirements of D2777-98. Data from eleven reagent waters, eleven substitute wastewater, fifteen Drinking Water, and thirteen wastewater sample matrices, were tested using a set of 4 Youden Pair concentrations for 7 analyte anions. All submitted individual data points are the average of duplicate samplings.

A1.2 Calibration Linearity

A1.2.1 All laboratories used a provided set of 4 certified, mixed anion calibration solutions in concentrations between 0.5 mg/L and 50 mg/L, formulated in random concentrations given in Table A1. They were prepared from certified, individual 1000 mg/L Stock Standards obtained from APG, Inc, Belpre, Ohio. No dilution was necessary.

Table A1: Collaborative Calibration Standard, mg/L Concentrations

Analyte Anion	Standard 1	Standard 2	Standard 3	Standard 4
Chloride	50	25	0.5	10
Bromide	0.5	25	10	50
Nitrite	25	0.5	50	10
Sulfate	10	25	0.5	50
Nitrate	25	0.5	50	10
Fluoride	5	0.5	10	25
Phosphate	50	25	0.5	10

A1.2.2 A Linear Through Zero; no weighting regression was used to calculate the calibration curve. The range coefficient of determination (r^2) values obtained from the collaborative is shown in Table A2

Table A2: Expected Range of (r^2) Coefficient of Determination

Anion / r^2	Average, n=29	Lowest	Highest
Chloride	0.99987	0.99959	0.99997
Bromide	0.99953	0.99878	0.99996
Nitrite	0.99983	0.99961	0.99999
Sulfate	0.99976	0.99901	0.99999
Nitrate	0.99957	0.99840	0.99999
Fluoride	0.99972	0.99797	0.99999
Phosphate	0.99982	0.99942	0.99999

A1.2.3 EPA requires that 1/X weighting be used for calibration. The P & B data were derived using unweighted calibration. Table A2a shows there is no significant difference in r^2 linearity between these 2 calibration routines.

Table A2a Coefficient of Determination r^2 from a Single Calibration

Analyte Anion	No Weighted Calibration	1/x Weighted Calibration
Chloride	0.99994	0.99996
Bromide	0.99942	0.99923
Nitrite	0.99975	0.99981
Sulfate	0.99971	0.99974
Nitrate	0.99975	0.99974
Fluoride	0.99986	0.99967
Phosphate	0.99999	0.99999

A1.3 Quality Control Solution Preparation

A1.3.1 The Quality Control Solution (QCS) was also used as the Calibration Verification Solution (CVS).

A1.3.2 Quality Control Solution (QCS) was manufactured, analyzed using ion chromatography, and certified by APG as 100X concentrate, to replicate typical Drinking Water concentrations. Required 1:100 dilution with water before analysis. The QCS analyte concentrations, required control limits, and interlaboratory determined control limits based upon n# analyses are given in Table A3.

Table A3: Quality Control Acceptance Limits

Analyte Anion	True Value mg/L	Certified Value mg/L	Required 99% Confidence Interval	Determined QCS Mean ± Std Dev, n = 82
Chloride	48.68	48.61 ± 0.12	43.99 – 52.96	47.64 ±1.53
Bromide	0.00	0.00	0.00	0.00
Nitrite	2.87	2.90 ± 0.07	2.39 – 3.26	2.88 ± 0.19
Sulfate	35.69	35.63 ± 0.25	29.54 – 40.53	35.02 ± 1.21
Nitrate	15.76	15.78 ± 0.15	12.80 – 18.39	15.33 ± 4.35
Fluoride	1.69	1.68 ± 0.01	1.49 – 1.87	1.67 ± 0.09
Phosphate	5.47	5.55 ± 0.12	4.78 – 6.20	5.58 ± 0.28

A1.3.3 A single day's QCS was reprocessed using a 1/X weighting linear calibration and remained within the QC Acceptance Limits.

Table A3a QC Standard Results: Reprocessed Using 1/x Calibration

Analyte Anion	No Weighted Calibration	1/x Weighted Calibration	QC Acceptance 99%Conf Interval
Chloride	48.64 ± 1.06	48.77 ± 1.07	43.99 – 52.96
Nitrite	2.93 ± .03	2.82 ± .03	2.39 – 3.26
Sulfate	34.49 ± .79	34.64 ± .79	29.54 – 40.53
Nitrate	15.28 ± .15	15.23 ± .18	12.80 – 18.39
Fluoride	1.74 ± .02	1.63 ± .02	1.49 – 1.87
Phosphate	5.75 ± .15	5.77 ± .15	4.78 – 6.20

A1.4 Youden Pair Spiking Solution Preparation

A1.4.1 Eight mixed anion, 100X concentrate, spiking solutions were prepared in accordance with Sec 8.3 (Reagents and Materials) of the test method using anhydrous sodium salts. The mg/L concentrations of the eight standards followed the approved Youden Pair design - 0.5 & 0.7, 2 & 3, 15 & 20, 40 & 50 mg/l for all anions except fluoride, which is 0.5 & 0.7, 2 & 3, 7& 10, 20 & 25mg/L. The analyte true value concentrations were randomized among the eight spiking solutions as described in Table A4.

A1.4.2 A ninth solution containing approximately 10 mg/L of each analyte was diluted 1:50 with water, and was used for method detection limit calculations.

Table A4: True Value Youden Pair Spiking mg/L Concentrations

Anion / TV	1	2	3	4	5	6	7	8	9
Chloride	0.71	2.00	2.98	14.92	39.81	19.91	49.76	0.50	10.20
Bromide	2.00	3.01	14.93	39.81	19.91	49.77	0.70	0.51	10.49
Nitrite	2.98	39.61	19.81	14.86	49.52	0.50	2.00	0.70	9.94
Sulfate	39.60	49.51	0.49	0.70	1.98	2.98	14.86	19.81	10.23
Nitrate	14.92	19.19	39.87	49.78	0.50	0.70	2.00	2.98	10.35
Fluoride	2.00	0.71	0.50	3.00	9.99	6.99	19.98	24.99	10.40
Phosphate	49.51	39.60	19.90	0.50	2.98	1.99	0.69	14.86	10.48

These solutions, kept at ambient temperature, were analyzed before and during the collaborative to monitor for accuracy and stability. The mg/L True Value in was used to determine bias, matrix recovery, and the single operator and interlaboratory precision in the P & B tables per the requirement of D 2777.

Solution 3 and 7 exhibited some conversion of nitrite to nitrate before analysis. This conversion is evident in the bias and % Recovery for 0.5 mg/L and 2 mg/l nitrite and nitrate.

A1.5 Sample Matrix Preparation

A1.5.1 All participating laboratories provided and tested reagent water, substitute wastewater, naturally occurring drinking water, and naturally occurring wastewater. Before matrix spiking with the Youden Pair solutions, the sample matrix was evaluated, then appropriately diluted to give the highest anion concentration below 50 mg/L. The diluted sample matrix was used to dilute each Youden Pair spiking solution 1:100.

A1.5.2 Reagent Water was used as-is. Substitute wastewater was diluted 1:20 with water. Naturally occurring drinking water was used as-is or diluted 1:5 with water. Naturally occurring wastewater was diluted between 1:3 and 1:20, except one which required a 1:1000 dilution due to high chloride.

A1.5.3 Due to the anion content of the naturally occurring drinking water and "real" wastewater matrices, some of the reported spike matrix results exceeded the scope of this test method. Linearity and matrix recovery data obtained from the collaborative indicated that these data are acceptable, and extended the useful range of this test method.

A1.5.4 Due to the anion content of the naturally occurring sample matrices given in Table A5, the low concentration bias and recovery may be misleading because of spiking a low anion concentration increment into a large naturally occurring concentration of the same anion.

Table A5: Blank Analyte Concentrations for Naturally Occurring Sample Matrices

Data in mg/L	Chloride	Sulfate	Nitrate
Drinking Water	0.7 to 41.9	0.5 to 33.6	0.2 to 6.5
Substitute Wastewater	20.5 to 25.5	3.2 to 4.0	Not Detected
"Real" Wastewater	0.9 to 43.4	0.5 to 50.4	0.3 to 23.0

A1.6 Test Method Detection Limits:

A1.6.1 Spiking Solution #9, containing 10 mg/L of each analyte, was diluted 1:50 with water and was used for detection limit calculations. Ten laboratories performed seven replicate samplings, and the mean and standard deviation from each laboratory was calculated. The mean time corrected peak area response for the 7 replicates was given the true value of the solution #9, and from a simple proportion, the standard deviation was calculated as mg/L.

$$\text{Std Dev, mg/L} = \frac{(\text{True Value Conc Sol'n \#9, mg/L})(\text{Response Std Dev})}{\text{Ave Response of Sol'n \#9}}$$

A1.6.2 Method detection limits (MDL) were derived using "pooled" EPA protocol and the student t-test at 6 degrees of freedom, as follows;
The method detection limit (MDL) =(3.14)(Std Dev, mg/L).

A1.6.3 The upper and lower confidence limits were calculated as;
95% Confidence Interval: LCL (Lower Confidence Limit) = 0.64 x MDL
UCL (Upper Confidence Limit) = 2.20 x MDL

A1.6.4 Method Detection Limits are given in Table A6.

Table A6: Method Detection Limits

Anion	mg/L Solution Concentration	Method Detection MDL, mg/L	95% Confidence Interval mg/L
Chloride	0.204	0.075	0.048 to 0.165
Bromide	0.210	0.120	0.077 to 0.264
Nitrite	0.199	0.103	0.066 to 0.227
Sulfate	0.205	0.065	0.042 to 0.143
Nitrate	0.207	0.076	0.049 to 0.167
Fluoride	0.208	0.032	0.020 to 0.070
Phosphate	0.210	0.097	0.062 to 0.213

Table 1
Precision, Bias, and Matrix Recovery for Chloride

Matrix	# of Values	True Value	Mean Result	Bias vs True Value	Recovery vs True Value	Interlab Std Dev S(t)	Interlab %RSD	Single Operator Std Dev, S(o)	Analyst %RSD
Reagent	9	0.50	0.55	0.05	110.0	0.11	19.8		
Water	10	0.71	0.69	-0.02	97.2	0.08	11.5	0.05	7.5
	10	2.00	1.97	-0.03	98.5	0.14	6.8		
	9	2.98	2.97	-0.01	99.7	0.11	3.8	0.05	2.1
	10	14.92	14.76	-0.16	98.9	0.61	4.2		
	10	19.91	19.81	-0.10	99.5	0.81	4.1	0.48	2.8
	10	39.81	38.58	-1.23	96.9	1.43	3.7		
	10	49.76	48.70	-1.06	97.9	1.94	4.0	1.36	3.1
Substitute	9	0.50	0.46	-0.04	92.0	0.51	111.1		
Wastewater	9	0.71	0.43	-0.28	60.6	0.69	160.7	0.42	93.8
	9	2.00	1.52	-0.48	76.0	0.68	45.0		
	9	2.98	2.58	-0.40	86.6	0.63	24.5	0.50	24.3
	9	14.92	14.29	-0.63	95.8	1.02	7.1		
	9	19.91	18.93	-0.98	95.1	1.24	6.6	0.60	3.6
	9	39.81	37.34	-2.47	93.8	5.44	14.6		
	9	49.76	47.54	-2.22	95.5	3.13	6.6	4.43	10.4
Drinking	12	0.50	0.63	0.13	126.0	0.67	106.1		
Water	12	0.71	0.75	0.04	105.6	0.34	45.5	0.40	57.2
	12	2.00	2.15	0.15	107.5	0.51	23.6		
	12	2.98	2.95	-0.03	99.0	0.39	13.1	0.47	18.5
	12	14.92	14.54	-0.38	97.5	0.71	4.9		
	12	19.91	19.09	-0.82	95.9	1.11	5.8	0.37	2.2
	12	39.81	38.38	-1.43	96.4	1.56	4.1		
		49.76	47.97	-1.79	96.4	2.19	4.6	1.26	3.9
"Real"	9	0.50	0.42	-0.08	84.0	0.34	81.0		
Wastewater	10	0.71	0.47	-0.24	66.2	0.34	72.6	0.26	59.3
	10	2.00	1.56	-0.44	78.0	0.51	32.7		
	9	2.98	2.78	-0.20	93.3	0.19	6.8	0.37	17.3
	10	14.92	14.29	-0.63	95.8	0.63	4.4		
	10	19.91	18.83	-1.08	94.6	0.78	4.1	0.46	2.8
	9	39.81	37.01	-2.80	93.0	2.78	7.5		
	10	49.76	48.24	-1.52	96.9	3.15	6.5	2.54	6.0

Table 2
Precision, Bias, and Matrix Recovery for Bromide

Matrix	# of Values	True Value	Mean Result	Bias vs True Value	Recovery vs True Value	Interlab Std Dev S(t)	Interlab %RSD	Single Operator Std Dev, S(o)	Analyst %RSD
Reagent	10	0.51	0.60	0.09	117.6	0.19	31.0		
Water	10	0.70	0.83	0.13	118.6	0.23	28.2	0.10	14.6
	10	2.00	2.06	0.06	103.0	0.14	6.6		
	10	3.01	2.88	-0.13	95.7	0.23	7.9	0.15	6.3
	10	14.93	15.00	0.07	100.5	0.58	3.9		
	10	19.91	19.32	-0.59	97.0	0.97	5.0	0.75	4.4
	10	39.81	39.66	-0.15	99.6	1.24	3.1		
	10	49.77	50.04	0.27	100.5	2.94	5.9	1.61	3.6
Substitute	9	0.51	0.67	0.16	131.4	0.19	28.8		
Wastewater	9	0.70	0.96	0.26	137.1	0.21	21.8	0.08	9.3
	9	2.00	2.14	0.14	107.0	0.22	10.2		
	9	3.01	2.72	-0.29	90.4	0.35	12.8	0.17	7.0
	9	14.93	14.70	-0.23	98.5	0.58	3.9		
	9	19.91	18.91	-1.00	95.0	2.62	13.8	1.63	9.7
	9	39.81	38.76	-1.05	97.4	1.11	2.9		
	9	49.77	48.81	-0.96	98.1	1.52	3.1	0.48	1.1
Drinking	13	0.51	0.58	0.07	113.7	0.25	43.4		
Water	13	0.70	0.83	0.13	118.6	0.22	26.5	0.14	19.9
	13	2.00	1.98	-0.02	99.0	0.25	12.5		
	13	3.01	2.56	-0.45	85.0	0.25	9.7	0.15	6.8
	13	14.93	14.63	-0.30	98.0	0.50	3.4		
	13	19.91	19.22	-0.69	96.5	1.10	5.7	0.77	4.6
	13	39.81	38.97	-0.84	97.9	1.99	5.1		
	13	49.77	48.74	-1.03	97.9	1.49	3.1	1.13	2.6
"Real"	11	0.51	0.59	0.08	115.7	0.11	19.3		
Wastewater	12	0.70	0.78	0.08	111.4	0.19	24.4	0.10	14.0
	11	2.00	2.08	0.08	104.0	0.13	6.3		
	12	3.01	2.70	-0.31	89.7	0.41	15.1	0.27	11.5
	12	14.93	15.16	0.23	101.5	0.90	6.0		
	11	19.91	19.46	-0.45	97.7	1.63	8.4	1.09	6.3
	12	39.81	40.24	0.43	101.1	2.27	5.7		
	12	49.77	49.97	0.20	100.4	2.52	5.0	0.91	2.0

Table 3
Precision, Bias, and Matrix Recovery for Nitrite

Matrix	# of Values	True Value	Mean Result	Bias vs True Value	Recovery vs True Value	Interlab Std Dev S(t)	Interlab %RSD	Single Operator Std Dev, S(o)	Analyst %RSD
Reagent	9	0.50	0.62	0.12	124.0	0.16	26.1		
Water	9	0.70	0.72	0.02	102.9	0.08	10.5	0.05	7.1
	10	2.00	1.31	-0.69	65.5	0.25	19.2		
	10	2.98	3.11	0.13	104.4	0.17	5.4	0.13	6.0
	10	14.86	14.70	-0.16	98.9	0.47	3.2		
	10	19.81	19.88	0.07	100.4	0.70	3.5	0.27	1.5
	10	39.61	39.90	0.29	100.7	0.88	2.2		
	10	49.52	48.24	-1.28	97.4	1.34	2.8	1.25	2.8
Substitute	9	0.50	0.37	-0.13	74.0	0.22	59.7		
Wastewater	9	0.70	0.59	-0.11	84.3	0.28	48.1	0.21	43.2
	10	2.00	1.25	-0.75	62.5	0.38	30.8		
	9	2.98	2.62	-0.36	87.9	0.82	31.4	0.43	22.1
	9	14.86	14.40	-0.46	96.9	0.58	4.0		
	10	19.81	19.50	-0.31	98.4	1.66	8.5	0.81	4.8
	10	39.61	39.97	0.36	100.9	2.02	5.0		
	9	49.52	49.09	-0.43	99.1	3.03	6.2	2.11	4.7
Drinking	11	0.50	0.52	0.02	104.0	0.08	14.4		
Water	12	0.70	0.74	0.04	105.7	0.17	23.3	0.09	13.5
	12	2.00	1.30	-0.70	65.0	0.21	15.9		
	12	2.98	2.97	-0.01	99.7	0.14	4.6	0.16	7.4
	11	14.86	14.60	-0.26	98.3	0.40	2.8		
	11	19.81	19.82	0.01	100.1	0.59	3.0	0.26	1.5
	11	39.61	39.35	-0.26	99.3	0.99	2.5		
	12	49.52	49.14	-0.38	99.2	1.93	3.9	0.64	1.5
"Real"	9	0.50	0.55	0.05	110.0	0.13	24.5		
Wastewater	10	0.70	0.73	0.03	104.3	0.24	32.9	0.07	10.8
	9	2.00	1.27	-0.73	63.5	0.18	14.2		
	10	2.98	2.99	0.01	100.3	0.19	6.2	0.15	7.0
	10	14.86	14.55	-0.31	97.9	0.46	3.1		
	10	19.81	19.68	-0.13	99.3	0.71	3.6	0.38	2.2
	9	39.61	39.21	-0.40	99.0	1.03	2.6		
	9	49.52	47.27	-2.25	95.5	3.50	7.4	2.40	5.6

Table 4
Precision, Bias, and Matrix Recovery for Sulfate

Matrix	# of Values	True Value	Mean Result	Bias vs True Value	Recovery vs True Value	Interlab Std Dev S(t)	Interlab %RSD	Single Operator Std Dev, S(o)	Analyst %RSD
Reagent	9	0.49	0.49	0.00	100.0	0.18	37.5		
Water	10	0.70	0.71	0.01	101.4	0.20	29.2	0.05	8.3
	10	1.98	2.04	0.06	103.0	0.19	9.7		
	10	2.98	3.09	0.11	103.7	0.24	7.9	0.06	2.5
	10	14.86	14.67	-0.19	98.7	0.57	4.0		
	10	19.81	19.67	-0.14	99.3	0.73	3.8	0.44	2.6
	10	39.60	39.66	0.06	100.2	0.92	2.4		
	10	49.51	49.27	-0.24	99.5	1.26	2.6	0.49	1.1
Substitute	9	0.49	0.38	-0.11	77.6	0.25	66.9		
Wastewater	9	0.70	0.51	-0.19	72.9	0.08	16.4	0.18	39.3
	9	1.98	1.83	-0.15	92.4	0.29	16.2		
	9	2.98	2.86	-0.12	96.0	0.31	11.2	0.20	8.6
	9	14.86	14.19	-0.67	95.5	1.06	7.7		
	9	19.81	19.23	-0.58	97.1	0.97	5.2	0.46	2.8
	9	39.60	38.45	-1.15	97.1	1.33	3.6		
	9	49.51	47.75	-1.76	96.4	1.43	3.1	0.75	1.8
Drinking	12	0.49	0.41	-0.08	83.7	0.21	52.8		
Water	12	0.70	0.41	-0.29	58.6	0.20	50.3	0.14	34.3
	13	1.98	1.77	-0.21	89.4	0.53	30.3		
	13	2.98	2.68	-0.30	89.9	0.42	16.2	0.27	12.1
	13	14.86	14.25	-0.61	95.9	1.11	8.0		
	12	19.81	19.31	-0.50	97.5	1.39	7.4	1.48	8.9
	12	39.60	38.58	-1.02	97.4	1.96	5.2		
	13	49.51	48.43	-1.08	97.8	2.04	4.3	1.44	3.3
"Real"	10	0.49	0.37	-0.12	75.5	0.39	106.4		
Wastewater	11	0.70	0.16	-0.54	22.9	1.19	765.2	0.47	179.6
	11	1.98	1.57	-0.41	79.3	0.87	55.4		
	11	2.98	2.53	-0.45	84.9	0.64	25.4	0.24	11.9
	11	14.86	14.69	-0.17	98.9	1.26	8.6		
	10	19.81	19.38	-0.43	97.8	0.90	4.6	0.57	3.4
	11	39.60	38.74	-0.86	97.8	1.71	4.4		
	10	49.51	48.36	-1.15	97.7	1.51	3.1	0.47	1.1

Table 5
Precision, Bias, and Matrix Recovery for Nitrate

Matrix	# of Values	True Value	Mean Result	Bias vs True Value	Recovery vs True Value	Interlab Std Dev S(t)	Interlab %RSD	Single Operator Std Dev, S(o)	Analyst %RSD
Reagent	10	0.50	1.02	0.52	204.00	0.08	7.4		
Water	10	0.69	0.71	0.02	102.90	0.08	11.6	0.06	6.4
	11	1.99	2.83	0.84	142.21	0.23	8.1		
	11	2.97	2.89	-0.08	97.31	0.18	6.4	0.14	5.0
	11	14.91	14.77	-0.14	99.06	0.44	3.0		
	11	19.18	19.77	0.59	103.08	0.64	3.2	0.24	1.4
	10	39.86	39.09	-0.77	98.07	1.43	3.7		
	10	49.77	48.93	-0.84	98.31	1.72	3.5	0.62	1.4
Substitute	11	0.50	1.18	0.68	236.00	0.41	34.9		
Wastewater	10	0.69	0.55	-0.14	79.71	0.30	55.3	0.42	4.9
	10	1.99	2.70	0.71	135.68	0.42	15.4		
	10	2.97	2.33	-0.64	78.45	1.10	47.3	0.39	15.4
	9	14.91	14.29	-0.62	95.84	0.78	5.4		
	10	19.18	18.69	-0.49	97.45	1.46	7.8	0.25	1.5
	11	39.86	37.70	-2.16	94.58	1.93	5.1		
	11	49.77	47.78	-1.99	96.00	2.18	4.6	1.62	3.8
Drinking	11	0.50	1.06	0.56	212.00	0.19	18.1		
Water	11	0.69	0.65	-0.04	94.20	0.06	8.7	0.12	14.4
	12	1.99	3.05	1.06	153.27	0.39	12.8		
	11	2.97	3.01	0.04	101.35	0.22	7.2	0.33	10.8
	12	14.91	14.69	-0.22	98.52	0.62	4.2		
	12	19.18	20.05	0.87	104.54	0.88	4.4	0.46	2.7
	12	39.86	39.31	-0.55	98.62	1.67	4.3		
	12	49.77	48.93	-0.84	98.31	1.43	2.9	0.78	1.8
"Real"	11	0.50	0.94	0.44	188.00	0.80	84.7		
Wastewater	10	0.69	0.69	0.00	100.00	0.09	13.3	0.39	47.6
	10	1.99	3.00	1.01	150.75	0.38	12.7		
	10	2.97	3.01	0.04	101.35	0.20	6.6	0.23	7.8
	11	14.91	14.52	-0.39	97.38	0.66	4.6		
	11	19.18	19.26	0.08	100.42	0.77	4.0	0.77	4.6
	11	39.86	39.13	-0.73	98.17	1.78	4.6		
	11	49.77	49.17	-0.60	98.79	2.26	4.6	0.93	2.1

Table 6
Precision, Bias, and Matrix Recovery for Fluoride

Matrix	# of Values	True Value	Mean Result	Bias vs True Value	Recovery vs True Value	Interlab Std Dev S(t)	Interlab %RSD	Single Operator Std Dev, S(o)	Analyst %RSD
Reagent	10	0.50	0.51	0.01	102.00	11.00	11.4		
Water	10	0.71	0.73	0.02	102.82	7.90	8.1	0.02	2.9
	10	2.00	2.05	0.05	102.50	3.60	3.7		
	10	3.00	2.96	-0.04	98.67	4.40	4.6	0.09	3.4
	10	6.99	7.02	0.03	100.43	5.40	5.6		
	10	9.99	9.79	-0.20	98.00	4.60	4.8	0.13	1.6
	10	19.98	19.60	-0.38	98.10	3.80	3.9		
	10	24.99	24.51	-0.48	98.08	4.80	4.9	0.74	3.4
Substitute	10	0.50	0.50	0.00	100.00	0.09	18.0		
Wastewater	10	0.71	0.71	0.00	100.00	0.09	12.0	0.01	2.3
	10	2.00	1.98	-0.02	99.00	0.12	6.0		
	10	3.00	2.94	-0.06	98.00	0.10	3.4	0.06	2.6
	10	6.99	6.92	-0.07	99.00	0.28	4.1		
	9	9.99	9.94	-0.05	99.50	0.46	4.7	0.28	3.3
	10	19.98	19.67	-0.31	98.45	0.94	4.8		
	10	24.99	24.78	-0.21	99.16	1.09	4.4	0.63	2.8
Drinking	13	0.50	0.48	-0.02	96.00	0.06	12.9		
Water	13	0.71	0.68	-0.03	95.77	0.06	9.5	0.02	3.4
	13	2.00	1.96	-0.04	98.00	0.08	3.9		
	13	3.00	2.90	-0.10	96.67	0.10	3.4	0.08	3.5
	13	6.99	6.91	-0.08	98.86	0.25	3.6		
	13	9.99	9.91	-0.08	99.20	0.37	3.7	0.18	2.2
	13	19.98	19.94	-0.04	99.80	0.68	3.4		
	12	24.99	24.27	-0.72	97.12	1.63	6.7	1.30	5.9
"Real"	11	0.50	0.47	-0.03	94.00	0.08	16.9		
Wastewater	11	0.71	0.68	-0.03	95.77	0.08	11.7	0.04	7.6
	11	2.00	1.96	-0.04	98.00	0.12	6.3		
	11	3.00	2.93	-0.07	97.67	0.18	6.2	0.09	3.5
	11	6.99	6.85	-0.14	98.00	0.26	3.8		
	10	9.99	9.56	-0.43	95.70	0.73	7.7	0.44	5.3
	11	19.98	20.06	0.08	100.40	1.23	6.1		
	11	24.99	25.12	0.13	100.52	1.34	5.3	0.32	1.4

Table 7
Precision, Bias, and Matrix Recovery for o-Phosphate

Matrix	# of Values	True Value	Mean Result	Bias vs True Value	Recovery vs True Value	Interlab Std Dev S(t)	Interlab %RSD	Single Operator Std Dev, S(o)	Analyst %RSD
Reagent	10	0.50	0.41	-0.09	82.00	0.12	29.6		
Water	9	0.69	0.51	-0.18	73.91	0.13	26.6	0.03	7.2
	10	1.99	1.88	-0.11	94.47	0.16	8.3		
	10	2.98	2.76	-0.22	92.62	0.14	4.9	0.08	3.2
	10	14.86	14.93	0.07	100.47	0.64	4.3		
	9	19.80	19.76	-0.04	99.80	1.00	5.1	0.85	4.9
	10	39.60	39.79	0.19	100.48	1.38	3.5		
	10	49.51	50.10	0.59	101.19	1.76	3.5	0.72	1.6
Substitute	11	0.50	0.49	-0.01	98.00	0.15	30.0		
Wastewater	10	0.69	0.59	-0.10	85.51	0.17	28.8	0.13	24.4
	11	1.99	1.92	-0.07	96.48	0.28	14.6		
	10	2.98	2.89	-0.09	96.98	0.22	7.6	0.18	7.5
	11	14.86	15.31	0.45	103.03	1.74	11.4		
	11	19.80	19.78	-0.02	99.90	1.16	5.9	0.84	4.8
	11	39.60	39.58	-0.02	99.95	2.72	6.9		
	11	49.51	49.19	-0.32	99.35	3.98	8.1	2.18	4.9
Drinking	12	0.50	0.46	-0.04	92.00	0.14	30.0		
Water	13	0.69	0.55	-0.14	79.71	0.20	36.3	0.07	13.4
	13	1.99	1.89	-0.10	94.97	0.22	11.9		
	13	2.98	2.87	-0.11	96.31	0.24	8.5	0.07	2.8
	12	14.86	15.09	0.23	101.55	0.91	6.1		
	13	19.80	20.28	0.48	102.42	0.96	4.7	1.06	6.0
	13	39.60	40.37	0.77	101.94	2.15	5.3		
	13	49.51	50.75	1.24	102.50	3.14	6.2	1.03	2.3
"Real"	11	0.50	0.43	-0.07	86.00	0.17	39.1		
Wastewater	11	0.69	0.53	-0.16	76.81	0.24	46.5	0.12	25.8
	11	1.99	1.72	-0.27	86.43	0.27	15.8		
	11	2.98	2.52	-0.46	84.56	0.48	19.2	0.30	14.0
	11	14.86	14.93	0.07	100.47	0.91	6.1		
	11	19.80	19.90	0.10	100.51	1.35	6.8	0.91	5.2
	11	39.60	38.98	-0.62	98.43	1.45	3.7		
	10	49.51	48.26	-1.25	97.48	1.80	3.7	0.82	1.9

Table 8
QC Acceptance Criteria

Analyte	Matrix	Precision % RSD	Average %Recovery	Initial LL - UL	Ongoing LL - UL	MS/MSD LL - UL	MS/MSD RPD
Chloride	RW	6.30	98.5	90.8 - 106.2	88.7 - 108.3	89.4 - 107.5	12.0
	DW	10.00	97.0	84.0 - 110.0	81.1 - 113.0	81.9 - 112.5	18.6
	WW	7.00	92.8	83.0 - 102.6	81.4 - 104.2	81.8 - 103.8	13.2
Bromide	RW	10.10	99.7	92.2 - 107.2	86.7 - 112.7	88.5 - 111.0	19.2
	DW	12.70	95.8	85.9 - 105.6	79.8 - 111.8	81.8 - 109.8	23.3
	WW	14.40	99.2	87.2 - 111.2	80.1 - 118.3	82.4 - 116.0	26.9
Nitrite	RW	6.40	100.6	95.1 - 106.0	91.9 - 109.2	92.8 - 108.3	12.1
	DW	4.30	99.6	92.4 - 106.7	91.5 - 107.7	91.8 - 107.4	8.1
	WW	4.90	98.9	91.3 - 106.5	90.2 - 107.6	90.5 - 107.3	9.2
Sulfate	RW	9.40	100.4	90.9 - 109.9	86.9 - 113.9	88.2 - 112.6	17.9
	DW	16.1	95.6	82.6 - 108.6	74.9 - 116.2	77.5 - 113.7	29.7
	WW	19.60	95.3	78.9 - 111.7	70.1 - 120.5	72.6 - 118.0	36.9
Nitrate	RW	8.40	99.5	93.1 - 105.9	88.6 - 110.4	90.0 - 108.9	15.9
	DW	9.40	100.2	93.0 - 107.4	88.0 - 112.4	89.4 - 111.0	17.4
	WW	6.70	99.1	90.7 - 107.6	88.6 - 109.7	89.2 - 109.1	12.4
Fluoride	RW	7.90	99.5	92.2 - 106.7	88.7 - 110.3	89.8 - 109.1	14.9
	DW	4.86	98.3	91.9 - 104.8	90.5 - 106.2	90.9 - 105.7	9.0
	WW	7.90	98.5	90.0 - 107.1	87.0 - 110.1	88.0 - 109.1	14.7
Phosphate	RW	10.60	98.2	91.9 - 104.5	85.4 - 111.0	87.4 - 109.0	20.1
	DW	9.40	100.2	89.3 - 111.1	85.8 - 114.6	87.0 - 113.4	17.4
	WW	16.90	94.6	81.5 - 107.7	73.5 - 115.8	76.1 - 113.1	31.5

All data determined as spike recovery from ASTM method validation and EPA Tier 3 Criteria

Reagent water (RW) data between 0.5 and 50 mg/L, except Fluoride 0.5 and 25 mg/L
consisting of 4 Youden Pairs
Drinking (DW) and Wastewater (WW) data between 2 and 50 mg/L except Fluoride 2 and 25 mg/L
consisting of 3 Youden Pairs

RSD = %Relative Standard Deviation; (std dev / mean)(100)
LL = Lower Limit of %Recovery
UL = Upper Limit of %Recovery
RPD = Relative % Difference between MSD

Appendix B
(Non-mandatory Information)

B.1 Suggested Background References

B1.1 EPA Method 6500, "Dissolved Inorganic Anions in Aqueous Matrices by Capillary Ion Electrophoresis", SW846, Rev 0, January 1998.

B1.2 Method 4140, "Inorganic Anions by Capillary Ion Electrophoresis", Standard Methods for the Examination of Water and Wastewater, 20th Edition, 1998, p 4-12 to 4-20.

B1.3 Krol, Benvenuti, and Romano, "Ion Analysis Methods for IC and CIA and Practical Aspects of Capillary Ion Analysis Theory", Waters Corp, Lit Code WT-139, 1998.

B1.4 Jandik, P., Bonn, G., "Capillary Electrophoresis of Small Molecules and Ions", VCH Publishers, 1993

B1.5 Romano, J., Krol, J, "Capillary Ion Electrophoresis, An Environmental Method for the Determination of Anions in Water", J. of Chromatography, Vol. 640, 1993, p. 403.

B1.6 Romano, J., "Capillary Ion Analysis: A Method for Determining Ions in Water and Solid Waste Leachates", Amer. Lab., May 1993, p. 48.

B1.7 Jones, W., "Method Development Approaches for Ion Electrophoresis", J. of Chromatography, Vol. 640, 1993, p. 387.

B1.8 Jones, W., Jandik, P., "Various Approaches to Analysis of Difficult Sample Matrices for Anions using Capillary Electrophoresis", J. of Chromatography, Vol. 608, 1992, p. 385.

B1.9 Bondoux, G., Jandik, P., Jones, W., "New Approaches to the Analysis of Low Level of Anions in Water", J. of Chromatography, Vol. 602, 1992, p. 79.

B1.10 Jandik, P., Jones, W., Weston, A., Brown, P.,"Electrophoretic Capillary Ion Analysis: Origins, Principles, and Applications", LC·GC, Vol. 9, Number 9, 1991, p. 634.

B1.11 Romano, J., Jackson, P., "Optimization of Inorganic Capillary Electrophoresis for the Analysis of Anionic Solutes in Real Samples", J. of Chromatography, Vol. 546, 1991, p. 411.

B1.12 Jandik, P., Jones, W., "Optimization of Detection Sensitivity in the Capillary Electrophoresis of Inorganic Anions", J of Chromatography, Vol. 546, 1991, p. 431.

B1.13 Jandik, P., Jones, W., "Controlled Changes of Selectivity in the Separation of Ions by Capillary Electrophoresis", J. of Chromatography, Vol. 546, 1991, p 445.

B1.14 Foret, R., et.al., "Indirect Photometric Detection in Capillary Zone Electrophoresis", J. of Chromatography, Vol. 470, 1989, p. 299.

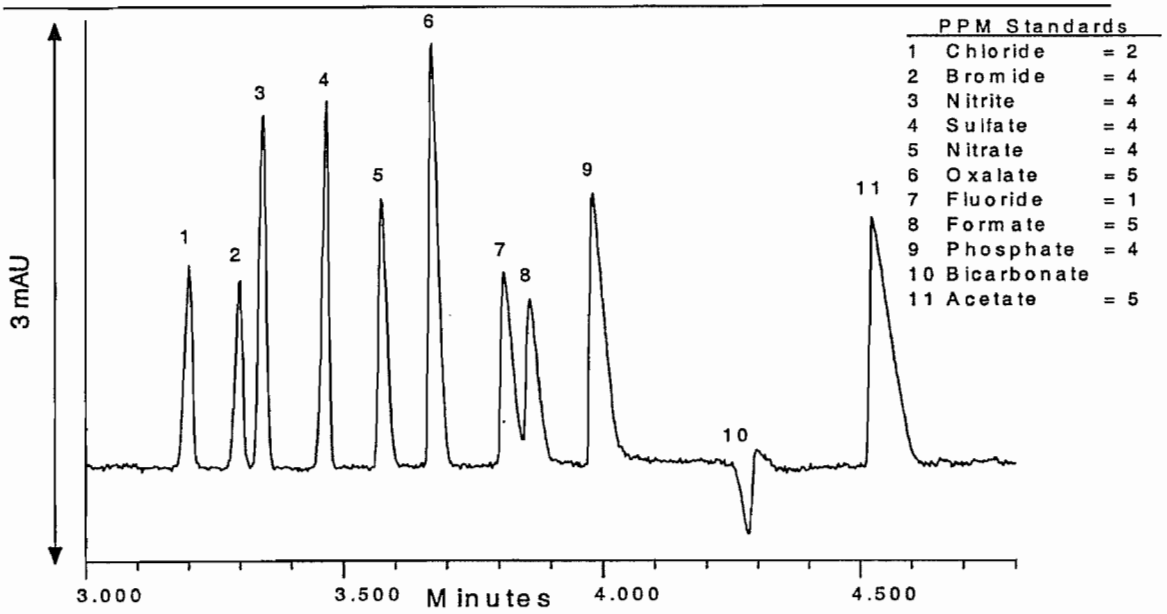
B1.15 Hjerte'n, S. et. al., "Carrier-free Zone Electrophoresis, Displacement Electrophoresis and Isoelectric Focusing in an Electrophoresis Apparatus", J. of Chromatography, Vol. 403, 1987, p. 47.

B1.16 Serwe, M., "New ASTM Standard: Recommended Operating Conditions for the Agilent CE", Agilent Technologies Application Brief, Publication Number 5968-8660E.

Appendix C
Capillary Ion Electrophoresis
Initial Demonstration of Performance
Single Operator

General Inorganic Anion & Organic Acid Analysis with Indirect UV Detection
Basis for EPA Method 6500, ASTM D6508, and Standard Methods 4140

The performance data given in this appendix was provided in the collaborative instruction booklet to evaluate initial demonstration of performance required by the collaborative design.



Analysis Conditions:

Electrolyte:	IonSelect High Mobility Anion Electrolyte, P/N 49385
Capillary:	75 µm (id) x 375 µm (od) x 60 cm (length)
Temperature:	25°C (5°C Above Ambient)
Power Supply:	Negative
Voltage:	15 kV
Current:	14 ± 1 µA (Use Constant Current for Analysis)
Sampling:	Hydrostatic for 30 Seconds
Detection:	Indirect UV at 254 nm, Hg Lamp, 185 or 254 nm Window
Time Constant:	0.3 Seconds, or less
Sampling Rate:	20 Data Points per Second
Analyte MT:	Mid-Point of Analyte Peak Width at Baseline
Quantitation:	Time Corrected Peak Area (Peak Area / MT)

Millennium Data Processing Method:

CIE Processing Method using Mid-Point of Peak Width for Migration Time

Integration
Peak Width = 2.25 - 3.00 Threshold = 100 ± 25
Min Area = 100 Min Height = 50
Inhibit Intg. = 0 to 3 min

Calibration
Averaging = None MT Window = 2%
Update MT = Average Standards
Peak Match = First for Chloride
(Cl is always first in the pherogram, use as a ref peak)
Cl MT Window = 10%
Other Analytes = Closest
Quantitate By = Time Corrected Peak Area
Fit Type = Linear Through Zero

Report
Analyte Name
Analyte Migration Time
Analyte Migration Time Ratio (respect to Cl Ref Peak)
Peak Area
Time Corrected Peak Area
Amounts

Use fresh electrolyte daily; recalibrate with every change in electrolyte.
Clear previous calibration (in Quick Set Page) before recalibration.
Do Not use analyte peak height for quantitation due to asymmetrical peak shapes.

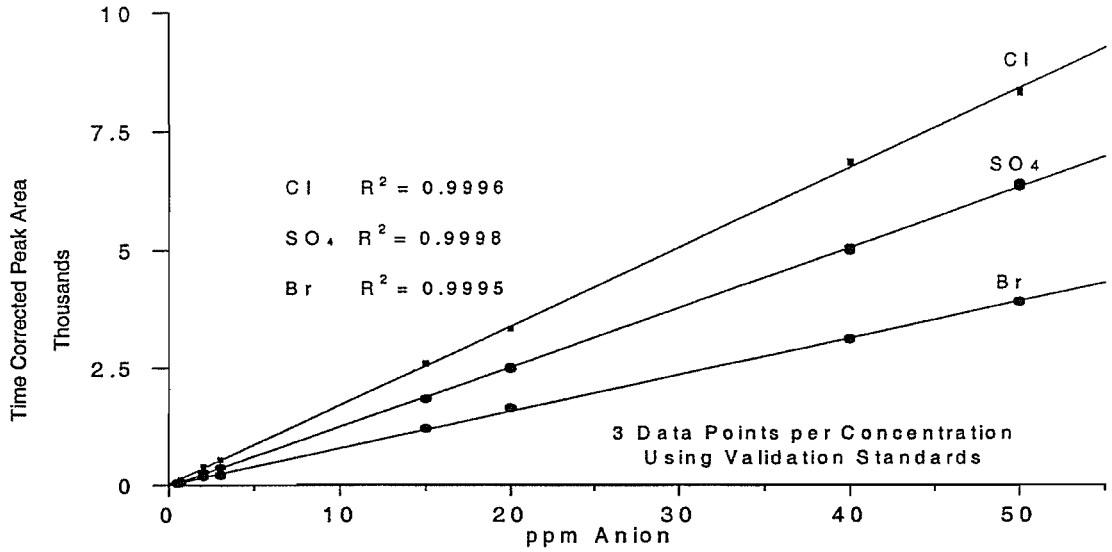
Method Validation:

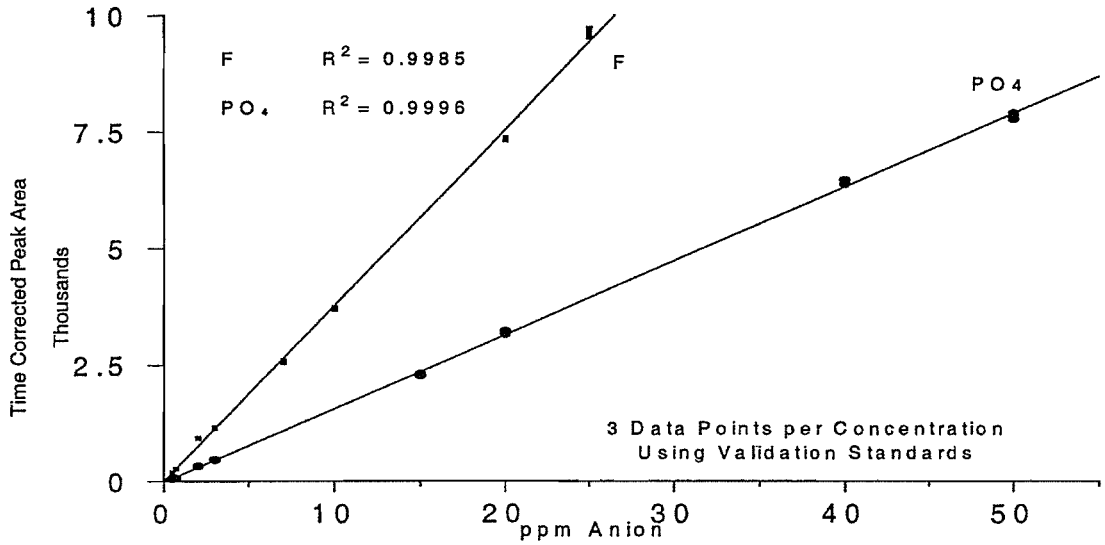
The single operator performance given below using the ASTM validation design is intended as a basis to evaluate Initial Demonstration of Performance.

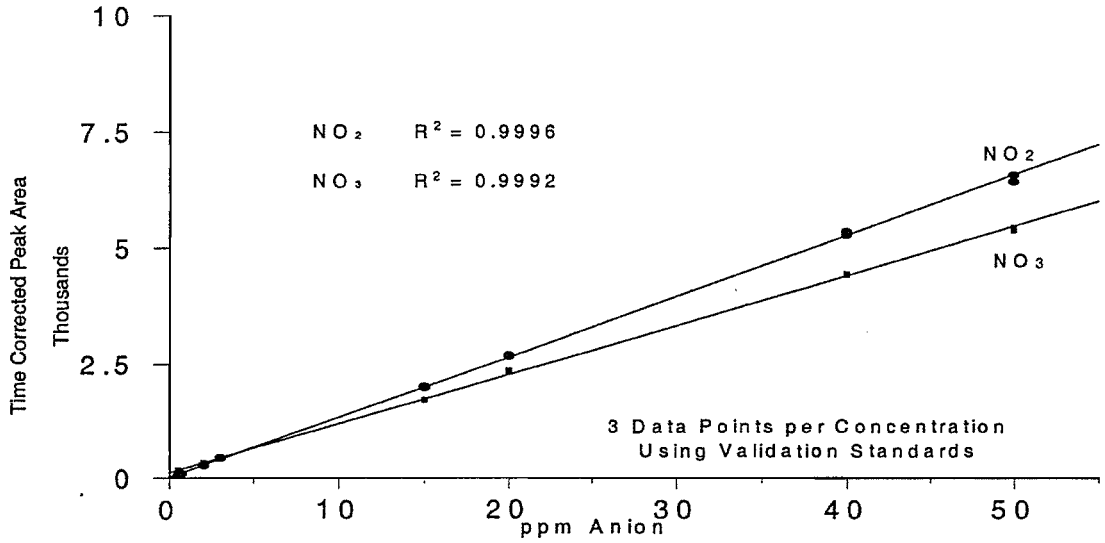
Individual Youden Pair Standard, in ppm

Analyte Anion	1	2	3	4	5	6	7	8
Cl	0.7	2.0	3.0	15.0	40.0	20.0	50.0	0.5
Br	2.0	3.0	15.0	40.0	20.0	50.0	0.7	0.5
NO_2	3.0	40.0	20.0	15.0	50.0	0.5	2.0	0.7
SO_4	40.0	50.0	0.5	0.7	2.0	3.0	15.0	20.0
NO_3	15.0	20.0	40.0	50.0	0.5	0.7	2.0	3.0
F	2.0	0.7	0.5	3.0	10.0	7.0	20.0	25.0
PO_4	50.0	40.0	20.0	0.5	3.0	2.0	0.7	15.0

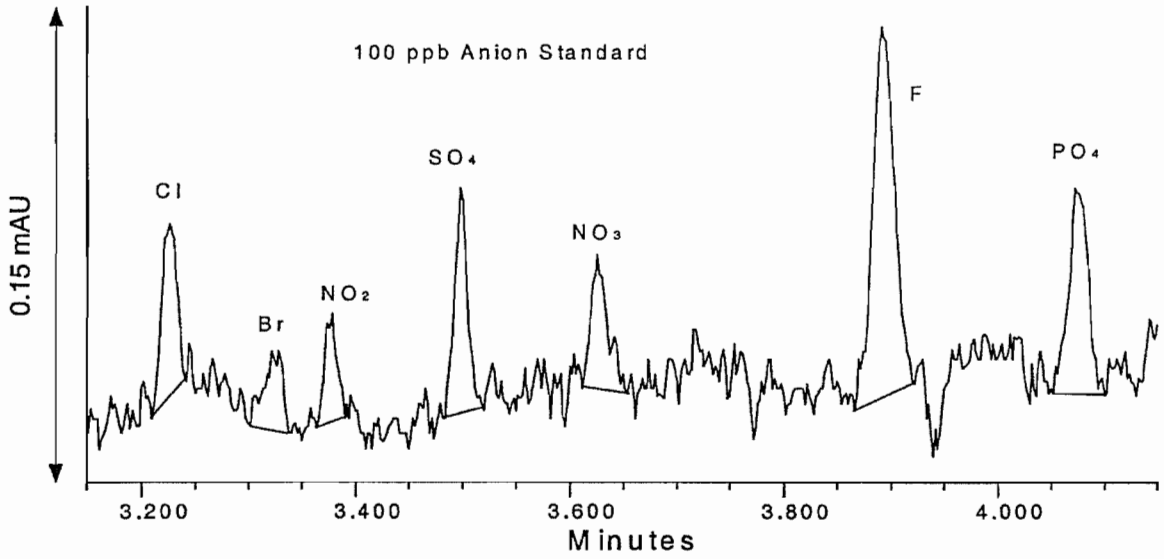
Method Linearity:







Method Detection Limits:



Seven replicates of the above 100 ppb anion standard were used to calculate time corrected peak area precision. Using EPA and Standard Methods protocols, the detection limits, as ppb, for these analytes are:

Chloride = 46	Bromide = 90	Nitrite = 72	Sulfate = 32
Nitrate = 84	Fluoride = 20	Phosphate = 41	

This method has been validated between 0.1 to 50 ppm. Quantitation below 0.1 ppm is not advised.

Migration Time Reproducibility:

Use mid-point of analyte peak width at the baseline as the analyte migration time determinant. Data given as average absolute migration time for each validation standard analyzed in triplicate.

Analyte		Cl	Br	NO_2	SO_4	NO_3	F	PO_4
Validation Standard	1	3.132	3.226	3.275	3.405	3.502	3.761	3.906
	2	3.147	3.239	3.298	3.431	3.517	3.779	3.931
	3	3.138	3.231	3.283	3.411	3.497	3.771	3.925
	4	3.158	3.244	3.307	3.434	3.510	3.781	3.963
	5	3.184	3.271	3.331	3.435	3.551	3.787	3.981
	6	3.171	3.260	3.312	3.418	3.537	3.776	3.964
	7	3.191	3.272	3.315	3.437	3.544	3.773	3.978
	8	3.152	3.248	3.294	3.418	3.526	3.739	3.954
Std Dev		0.021	0.015	0.018	0.012	0.20	0.015	0.027
%RSD		0.67%	0.46%	0.55%	0.36%	0.56%	0.40%	0.68%

Average Standard Deviation = 0.018 min = 1.1 sec
Average %RSD of Analyte Migration Time = 0.53%

Quantitation Precision:

Time Corrected Peak Area Precision, given as %RSD, based upon 3 samplings per concentration.

Analyte		Cl	Br	NO_2	SO_4	NO_3	F	PO_4
ppm concentration	0.1	12.36	18.89	16.19	13.25	23.13	9.82	14.00
	0.5	10.51	20.00	3.90	2.25	2.18	2.03	7.71
	0.7	1.23	13.36	2.01	2.95	0.37	2.72	4.41
	2	0.32	3.76	4.14	1.79	2.17	0.73	1.91
	3	0.63	1.80	1.72	1.70	0.58	0.98	2.70
	15	0.43	0.27	0.48	0.07	0.36	0.15	1.37
	20	0.45	0.66	0.17	0.13	0.88	0.16	0.81
	40	0.36	0.56	0.36	0.46	0.58		0.47
	50	0.45	0.51	0.48	0.16	0.46		0.46

Quantitation Accuracy:
Used a Certified Performance Evaluation Standard diluted 1:100 with DI water. Amounts based upon multi-point calibration curve prepared from certified standards.

	Analyte	Cl	NO_2	SO_4	NO_3	F	PO_4
Performance Evaluation Standard	True Value in ppm	43.00	1.77	37.20	15.37	2.69	6.29
Official Anion Methods Wet Chem & IC	Measured Mean	43.30	1.77	37.00	15.42	2.75	6.38
	Measured Std Dev	3.09	0.07	2.24	1.15	0.26	0.21
CIA Using Chromate Electrolyte	Ave CIA n=18	43.34	1.64	37.11	14.41	2.64	6.34
	CIA/Mean	1.003	0.927	1.003	0.935	0.959	0.993
	CIA/TrueValue	1.008	0.927	0.996	0.938	0.981	1.008

A CIA/True Value, or Mean = 1.000 indicates perfect agreement between CIA and official anion methods.

Method Recovery:
A Certified Performance Evaluation Standard (PES) was diluted 1:100 with Typical Drinking Water (DW). Amounts based upon multi-point calibration curve prepared from certified standards.

Analyte	Cl	NO_2	SO_4	NO_3	F	PO_4
Drinking Water n=3, as ppm	24.72 ± 0.18	Not Detected	7.99 ± 0.07	0.36 ± 0.05	Not Detected	Not Detected
Amount %RSD	0.73%		0.91%	13.3%		
Performance Evaluation Std	43.00	1.77	37.20	15.37	2.69	6.29
DW + PES n=3; as ppm	66.57 ± 0.34	1.74 ± 0.03	45.19 ± 0.17	15.42 ± 0.12	2.62 ± 0.07	5.55 ± 0.31
Amount %RSD	0.51%	1.85%	0.38%	0.79%	2.69%	5.52%
% Recovery	97.9%	98.3%	100.2%	98.1%	97.4%	88.2%

Fig. 1 Electropherogram of Mixed Anion Working Solution and Added Common Organic Acids

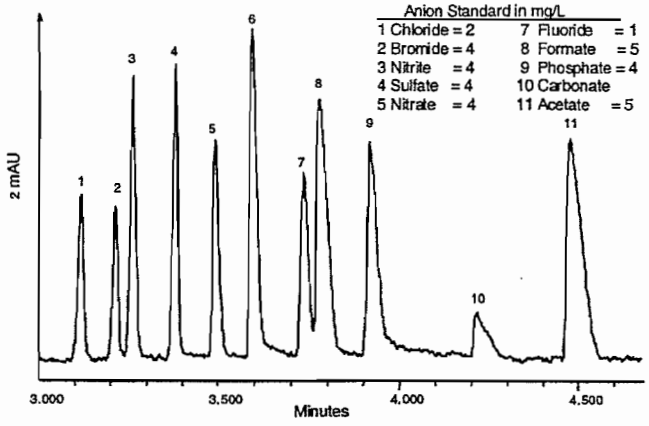


Fig. 2 Electropherogram of 0.2 mg/L Anions Used to Determine MDL

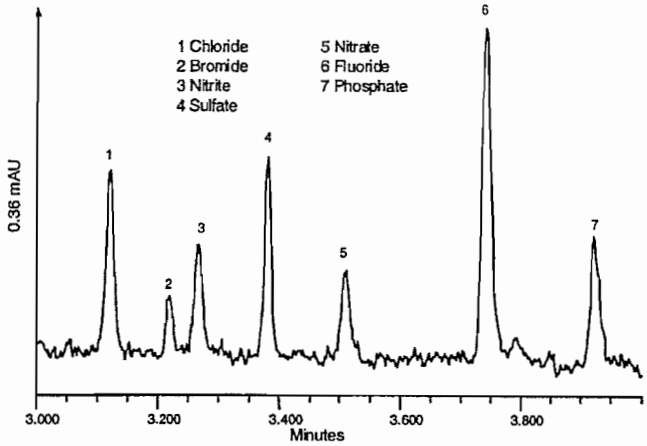


Fig. 3 Electropherogram of Substitute Wastewater

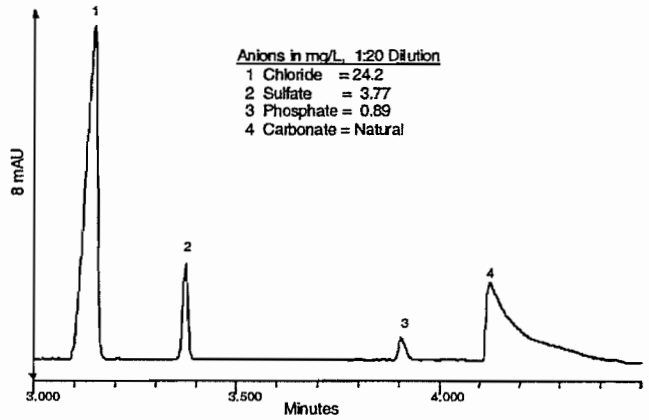


Fig. 4 Electropherogram of Drinking Water

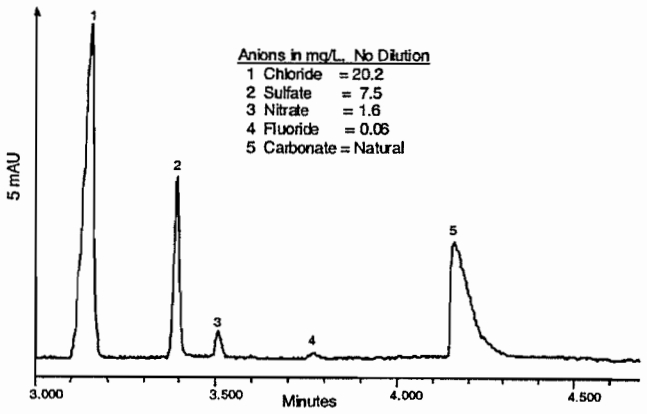


Fig. 5 Electropherogram of Municipal Wastewater Treatment Plant Discharge

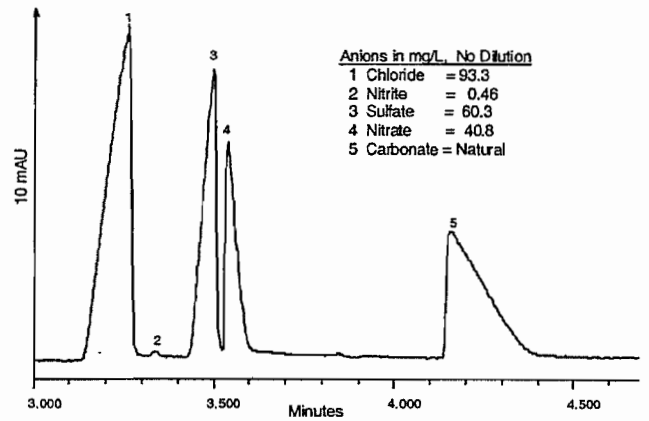


Fig. 6 Electropherogram of Industrial Wastewater

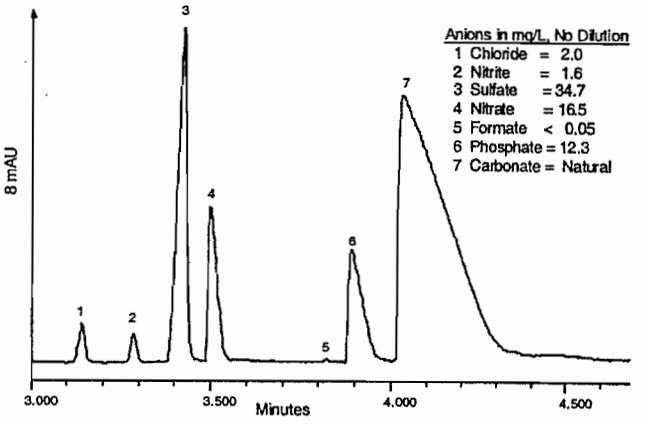


Fig. 7 Pictorial Diagram of Anion Mobility and ElectroOsomotic Flow Modifier

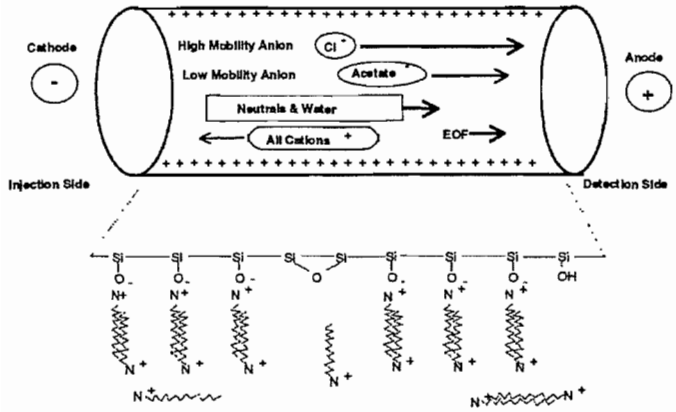


Fig. 8 Selectivity Diagram of Anion Mobility Using Capillary Ion Electrophoresis

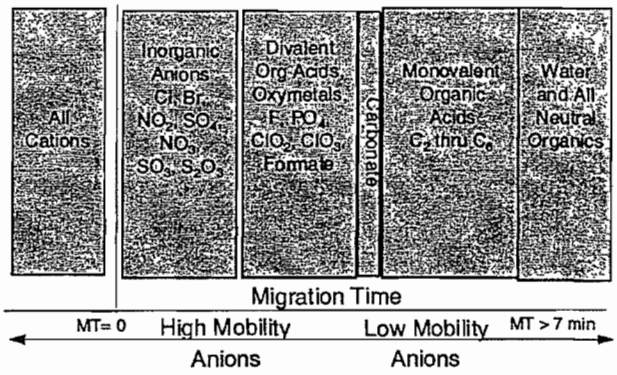


Fig. 9 Pictorial Diagram of Indirect UV Detection

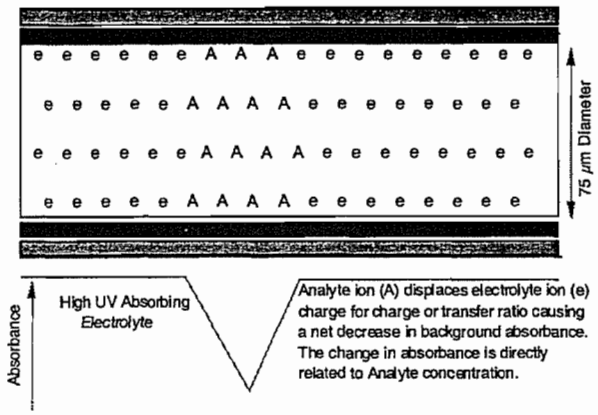


Fig. 10 General Hardware Schematic of a Capillary Ion Electrophoresis System