Laboratory Certification Bulletin, March 2003

Office of Water (MLK 140) EPA 815-N-03-001 March 2003 www.epa.gov/safewater

TABLE OF CONTENTS

LabCert Bulletin

EPA 815-N-03-001
March 2003

Certification Officers Training

Chemistry - June 17-20, 2003
Microbiology - June 23-27, 2003
The Technical Support Center in Cooperation with the National Exposure Research Laboratory in Cincinnati provides two 5-day long courses designed to meet the need for training Federal and State personnel whose responsibilities include the evaluation of laboratories analyzing potable water for chemical and microbiological parameters. Persons who do not have this responsibility should not apply for these courses. Persons attending these courses from State facilities must go through their respective Regional Coordinator in order to secure their placement in this training.

In This Issue...

This issue of the Labcert Bulletin addresses issues which have been brought to our attention by laboratories, and Regional and State Certification Officers. You will find articles on the National Environmental Methods Index (NEMI), recent legislation, Stage1 Disinfectants and Disinfection Byproducts Rule, chlorite, cyanide, and other drinking water issues.
If there are certification topics you would like to see discussed, please call, write, fax or e-mail the editors.

Editors

Ed Glick 513 569-7939, glick.ed@epa.gov
Patricia Hurr 513 569-7678, hurr.pat@epa.gov
Caroline Madding 513 569-7402, madding.caroline@epa.gov

Mailing Address:
U.S. Environmental Protection Agency
Technical Support Center (MS-140)
26 W. Martin Luther King Drive
Cincinnati, OH 45268

Fax Number:
513 569-7191

Contact for USEPA Laboratory ID Numbers

Every laboratory wishing to be certified to analyze compliance monitoring drinking water samples must have a unique laboratory ID Number. Laboratories must include this number when reporting proficiency testing (PT) results.

Charles Feldmann, Office of Ground Water and Drinking Water, Technical Support Center, is the primary contact for assignment of new laboratory IDs. He may be reached at 513-569-7671 or FAX: 513-569-7191.

If the laboratory has ever participated in a USEPA-run PT study, the laboratory will already have a unique ID number. Please review any previous "study results" report to locate the ID number. If a laboratory cannot locate this information, the laboratory should contact Mr. Feldmann for assistance.

Reminder

It is no longer a Federal requirement to monitor for the unregulated VOCs or to analyze PT samples for these analytes. This requirement was removed when the UCMR was signed on September 17, 1999.

National Environmental Methods Index (NEMI)

by Herb Brass, OGWDW/Technical Support Center

NEMI is an Oracle database of environmental method summaries for use in regulatory and non-regulatory water quality analyses. The database may be searched from anywhere in the world, free of charge, using the Internet at www.nemi.gov.

With NEMI, you can compare methods at a glance and find the method that best meets your needs. NEMI also supports sharing of monitoring data among different agencies and projects, which may use different methods at different times. The Advisory Committee on Water Information (ACWI), the senior advisory committee in the federal government that deals with water information, has "endorsed the continued development and timely delivery of NEMI as a vital tool to enhance the generation of comparable data of known quality, across all entities that conduct water quality monitoring." A letter announcing the public release of NEMI was recently co-signed by Diane Regas, then EPA Deputy Assistant Administrator for Water, and Bob Hirsch, US Geological Survey Associate Director for Water. The letter can be accessed at: http://water.usgs.gov/wicp/whatsnew.html.

NEMI has been developed under the guidance of the Methods and Data Comparability Board (MDCB). EPA and USGS co-chair the MDCB, which includes representatives from the federal, state/tribal, and private sectors. The MDCB and its parent organization, the National Water Quality Monitoring Council are committees under ACWI. Currently, NEMI contains information on more than 600 chemical, microbiological, and radiological water methods that are used for compliance and other purposes. Regulatory information, that includes citations in the Federal

Register, are available for drinking water and wastewater methods. For each method, NEMI provides a summary of the procedure and performance data. Quick method comparisons are arranged in tables, with supporting details in text. Links are provided to full methods available on line or, when the methods are proprietary, a link is provided to the appropriate website, so that the method can be purchased or otherwise obtained.
The NEMI database was constructed using a state-of-the-art Oracle platform so that it could accommodate a broad range of method types that require different data fields and search parameters. The following classes of methods are currently being or will soon be added -- additional chemical, microbiological, and radiological methods; biological and field methods; methods related to water security; and methods used in matrices other than water. A strategic plan is being developed to accommodate the addition of these methods consistent with expressed priorities, anticipated resources, and time.

Rule to Update Drinking Water and Wastewater Methods

On October 23, 2002, a final "methods update" rule was published in the Federal Register (Vol. 67, No. 205, pp 65220-65253). This rule approves updated versions of chemical, microbiological, and radiological analytical methods developed by ASTM, Standard Methods, the US Geological Survey, and the Department of Energy. No EPA methods were approved. The methods apply to the Safe Drinking Water Act and the Clean Water Act compliance monitoring programs. A Fact Sheet and the Final Rule are available at http://www.epa.gov/ogwdw/regs.html and http://www.epa.gov/waterscience/methods/.

Additional Methods Approval

On October 29, 2002, a final rule was published in the Federal Register (Vol. 67, No. 209, pgs 65888-65902) that approves EPA Method 515.4 to support previously required NPDWR compliance monitoring for 2,4-D, 2,4,5-TP, dinoseb, pentachlorophenol, picloram and dalapon. In addition, EPA Method 531.2 is approved for carbofuran and oxamyl. Additional methods approved in this Federal Register include a method for the determination of atrazine, two methods for the determination of cyanide, two methods for the determination of total coliforms and E. coli, a method for the determination of heterotrophic bacteria, and a method for the determination of turbidity. More information can be found at http://www.epa.gov/ogwdw/regs.html.

Chlorite Monitoring Requirements under the Stage 1 DBPR

The Stage 1 Disinfectants/Disinfection Byproducts Rule requires two types of chlorite monitoring for systems that use chlorine dioxide in their treatment process: daily monitoring at the entry point to the distribution system and monthly monitoring at three points in the distribution system.

Daily chlorite monitoring:

The water entering the distribution system must be analyzed daily for chlorite using one of three approved analytical methods. Standard Method 4500-ClO2 E is an amperometric method for determining both chlorite and chlorine dioxide. EPA Method 300.0 and EPA Method 300.1 are both ion chromatographic methods. It is anticipated that most of the daily analyses will be performed by treatment plant personnel using SM 4500-ClO2 E. The rule states that the analyses must be performed by a party approved by the State. This is the same type of approval that is required to measure disinfectant residuals such as chlorine dioxide or chlorine.

Distribution system chlorite monitoring:

In order to demonstrate compliance with the chlorite maximum contaminant level (MCL), water systems using chlorine dioxide must collect a set of three samples in the distribution system on a monthly basis. One sample is collected near the first customer, one at a location representative of average residence time, and the third at a location reflecting maximum residence time in the distribution system. The samples must be analyzed using either EPA Method 300.0 or EPA Method 300.1 and the laboratory must be certified to perform the analysis.

Compliance with the chlorite MCL of 1.0 mg/L is based on the arithmetic average of each 3-sample set from the distribution system. If any daily sample at the entry point indicates a chlorite concentration greater than the MCL, then the water system must collect a set of distribution system samples on the following day. If none of the daily samples have chlorite concentrations greater than the MCL, then the distribution system sampling is only required once each month. A chlorite compliance determination is made for each 3-sample set.

Stage 1 DBP Rule

The Stage 1 Disinfection By-Product (DBP) Rule which was promulgated in December 1998 became effective for large surface water systems in January 2002. These utilities were required to begin monitoring for additional DBPs at that time. All large surface water systems must monitor for five haloacetic acids with the summation of their concentrations to be reported as HAA5 (similar to the concept used for total trihalomethanes). Utilities that use chlorine dioxide must monitor for chlorite and systems using ozone must monitor for bromate. This means that laboratories need to be certified to analyze for HAA5, chlorite and bromate.

The DBP Rule also requires that water systems monitor for TOC. The regulation requires the TOC analyses be performed by a party approved by the State. Please contact your states to ascertain they are approving laboratories for TOC.

Methods 300.0 and 300.1 Differences and Similarities

by Dan Hautman, OGWDW/Technical Support Center

In response to compliance inquiries about the appropriate use of EPA Method 300.0 and EPA Method 300.1, this article has been prepared to clarify the differences and similarities, as well as to relate the significance of these differences to both laboratory certification and the classification of these methods as approved for compliance monitoring. Both of these methods employ ion chromatography (IC) with suppressed conductivity detection, hence, when considering the determinative step, they are identical. The only real differences between these two procedures are the specified analytical columns, with their respective eluents, and for Part B, the "on column" injection volume.

Method 300.1 was written primarily to identify specific parameters (column, eluent and injection volume) which could be employed to allow the quantitation of lower concentrations of bromate in drinking water. While doing this primarily for bromate, it was decided that it would be best to include all the 300.0 analytes into 300.1. Additionally, we could simplify the method by specifying a single analytical column for both Parts A and B, and include some additional QC such as a surrogate analyte.

EPA Method 300.0 is the general purpose IC method approved for compliance monitoring of fluoride, nitrate, nitrite, chloride, sulfate, and o-phosphate as well as chlorite at water systems employing chlorine dioxide disinfection.

By closely examining Method 300.0, Section 2.4, regarding method modifications and Sections 6.2.2.1 and 6.2.2.2 regarding optional analytical columns, it becomes clear that Method 300.1 completely overlaps into Method 300.0. A laboratory can adopt the parameters, columns and specifications identified in 300.1, apply and pass all the required QC that is shown in Section 9 of 300.0, and legitimately claim for certification or approved method classification that they are using Method 300.0, modified as permitted in the above referenced sections. The reverse can not be said about applying the operating conditions found in Method 300.0 to Method 300.1. Comparable low level measurements of bromate are not possible using the Method 300.0 standard operating conditions.

Cyanide Clarification

We were recently asked for clarification about the cyanide methods, specifically, what methods are approved for analysis of cyanide in drinking water and whether or not distillation is required. The 1994 Technical Notes (EPA600/R-94/173, October 1994) emphasizes that spectrophotometric measurements for cyanide in water always require a manual distillation of the sample to prepare the sample for measurement. EPA felt the Technical Note was needed because some laboratories seemed to be unaware of the requirement to distill samples. Although free cyanide is regulated, the approved spectrophotometric methods are for total and amenable cyanide; therefore, distillation is required. The “total” cyanide methods are used to screen samples for cyanide. If the “total” cyanide level is greater than the MCL (0.2 mg/L), then analysis for “free” (amenable) cyanide must be performed to see if the MCL has been exceeded. The “total” cyanide analysis is still recommended because it is cheaper than the amenable test.

All approved methods for cyanide are listed at 40 CFR 141.23(k)(1). The mandatory manual distillation procedure is described in Standard Method SM-4500–CN-C and ASTM D2036-91.

The approved amenable, manual and automated spectrophotometric methods are shown in the table below.

Technology (use only after distillation)	EPA	ASTM	SM	USGS
Manual Spectrophotometric, Amenable		D2036-91B	4500-CN-G	
Manual Spectrophotometric, Total		D2026-91A	4500-CN-E	I-3300-85
Semi-automated Spectrophotometric, Total	335.4			

Free cyanide can also be determined by one method approved for drinking water compliance monitoring analysis that does not require distillation, the specific ion electrode method, SM-4500-CN-F. When using this method, it is mandatory to maintain a constant ionic strength background for the electrode measurement, that is, samples and standards must contain the same concentration of sodium hydroxide. More information concerning methods can be found in FRN Vol 57, No 138, Friday, July 1992, p 31800.

Sparging Chlorite Samples

The ion chromatographic methods for chlorite recommend that the sample be sparged in order to remove any residual chlorine dioxide that may be present in the sample. This is because chlorite is formed from chlorine dioxide. Thus, chlorine dioxide will cause a positive bias in the analytical result if it isn't removed at the time of sample collection. Most water systems do not use chlorine dioxide as a residual disinfectant, so usually the water leaving the treatment plant does not contain a significant chlorine dioxide residual. If this is the case, the water system does not need to worry about the sparging step. In fact, sparging chlorite compliance samples is only recommended when chlorine dioxide is present at a high enough concentration that if it completely converted to chlorite, it would result in a chlorite concentration near the maximum contaminant level (MCL) of 1.0 mg/L. Since the chlorine dioxide concentration is monitored daily at the entry point to the distribution system, water systems should know whether there is a potential for significant chlorine dioxide residuals at the chlorite sampling points.

If it is determined that chlorine dioxide poses a potential problem in chlorite compliance monitoring samples, then the sampler should sparge the samples at the time of collection. Since chlorine dioxide is volatile, it is not hard to remove it. The sample should be collected in a clean, wide-mouth container (such as a beaker or Erlenmeyer flask). The sparging gas can be obtained by using a lecture bottle of nitrogen or helium fitted with a regulator and connected to a disposable glass Pasteur pipette with PVC tubing. The gas flow should be adjusted to produce a steady flow of bubbles. After 10-15 minutes of sparging, all traces of chlorine dioxide should be removed from the sample. It can then be poured from the container into the sample bottle that contains the ethylenediamine (EDA) preservative.

In order to eliminate potential cross- contamination problems, it is recommended that a clean container and a new disposable pipette be used at each sampling point.

A blank should be prepared and analyzed for chlorite prior to the first field use of the sparging apparatus. Reagent water should be sparged for 15 minutes and then poured into a sample bottle that contains the EDA preservative. This blank sample should be analyzed for chlorite in order to ensure that contaminants are not introduced into the sample from the sparging gas or the PVC tubing which would interfere with the chlorite analysis. Periodic preparation and analysis of sparged blanks is recommended to demonstrate that the sparging procedure does not introduce interferences.

Micro PT Q & A

The following are some questions we have received concerning evaluation of Micro PTs. In the discussion:
Positive = Present
Negative = Absent

1. False Positives: Is it permissible to report a false positive result on both a total coliform analyte and a fecal coliform/E. coli analyte in the same or separate samples within the PT set and be considered "acceptable" for the study?

   Yes. One sample (vial) may be missed per analyte. However, a lab cannot report an “Absent” for a Total Coliform and a “Present” for Fecal/E. Coli for the same sample (vial) and have that false positive be considered "acceptable." If a lab reports “absent” for Total Coliform, the test ends.

2. False Negatives: Does one false negative reported value result in a "not acceptable" for the PT study, even though a lab could still pass nine out of ten samples within the set for one analyte but not the other?

   Yes. This means the lab missed a positive sample which is a public health concern.

3. Analyte Definition: It is my understanding that Total Coliform is considered one analyte and Fecal Coliform/E. Coli is considered one analyte.

   That is correct.

4. "Acceptable " analysis of a sample: Each PT study consists of ten samples. If a lab misses one analyte within the sample, is the sample considered "not acceptable"?

   Any false negative or more than one false positive per analyte would be considered "not acceptable". Otherwise same as answer No. 1.

Websites that you may find useful

www.epa.gov/safewater/regs.html lists drinking water regulations;

www.epa.gov/safewater/methods/index.html lists all promulgated methods and contains copies of some methods;

http://www.epa.gov/safewater/methods/laboratorycertification.html lists state certification contacts for every state and also gives links to lists of state laboratories certified for drinking water analyses. There are links for those states, which have electronic lists of their certified laboratories;

www.nelac-institute.org/ contains the NELAC Standards, lists NELAC Accrediting Authorities and accredited laboratories, and has information about past and future NELAC meetings;

http://ts.nist.gov/Standards/Accreditation/index.cfm lists NIST-accredited PT providers;

www.epa.gov/quality/ contains all EPA Quality Documents and requirements, as well as available QA training and information about the annual EPA QA meeting.

Interested in acquiring FR Notices?

They make it easier all the time. At http://www.gpoaccess.gov/fr/ you can subscribe to have the daily Federal Register delivered to your email box. And if your mailbox gets too full, you can unsubscribe at any time.