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# **DBP/ICR Analytical Methods Manual**

Technical Support Division  
Office of Ground Water and Drinking Water  
U.S. Environmental Protection Agency  
Cincinnati, OH 45268



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## **Foreword**

The Information Collection Rule (ICR) for Public Water Systems [Subpart M of the National Primary Drinking Water Regulations, §141.141(e)] requires public water systems that meet certain applicability criteria to collect specified information for a limited period of time. The ICR establishes data collection requirements and specifies the manner of collecting data and transmitting these data to the United States Environmental Protection Agency (EPA). Four technical manuals serve as supporting documents for implementing the rule requirements. They are:

- ICR Sampling Manual, EPA 814-B-96-001, NTIS # PB96-157508
- DBP/ICR Analytical Methods Manual, EPA 814-B-96-002, NTIS # PB96-157516
- ICR Manual for Bench- and Pilot-Scale Treatment Studies, EPA 814-B-96-003, NTIS # PB96-157524
- ICR Microbial Laboratory Manual, EPA/600/R-95/178, NTIS # PB96-157557

These technical manuals serve as "rule by reference" documents, and have two main objectives: (1) to complement the ICR by further specifying the details of the rule requirements; and (2) to provide guidance on how to comply with the ICR requirements. Copies of the manuals are available for a fee from the National Technical Information Service (NTIS), U.S. Department of Commerce, 5285 Port Royal Road, Springfield, VA 22161. The toll free number for NTIS is (800)-336-4700.

The purpose of the DBP/ICR Analytical Methods Manual is to provide detailed information to the laboratory community that will be analyzing the samples collected by the Public Water Systems to meet the ICR requirements. The manual is intended to:

- Describe the laboratory approval process
- Describe the procedures that EPA will use to assess a laboratory's ability to produce data of known accuracy and precision
- Describe laboratory data quality control requirements for ICR analyses
- Specify how ICR data are to be reported back to the utilities and to EPA
- Clarify specific analytical procedures that are not adequately described in some methods that are referenced in this manual or that are unique to the ICR

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## **Disclaimer**

**Mention of trade names or commercial products does not constitute endorsement or recommendation for use.**

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## **Section 1. Introduction**

### **Background on the Information Collection Rule (ICR)**

The U.S. Environmental Protection Agency (EPA) instituted a formal regulation negotiation process in 1992 to develop the Disinfectant/Disinfection Byproduct (D/DBP) Rule. The Advisory Committee that was established to negotiate the regulation included representatives from the water industry, State health agencies, environmental groups, consumer groups, and EPA. During negotiations, the Advisory Committee realized that setting strict limits on the levels of disinfectants and disinfection byproducts (D/DBPs) in drinking water could result in an increasing risk of waterborne disease from pathogens. To balance the risks between pathogens and chemicals, the Advisory Committee made several recommendations. These recommendations were developed into three new drinking water regulations.

- **Disinfectant/Disinfection Byproduct (D/DBP) Rule**
- **Enhanced Surface Water Treatment Rule (ESWTR)**
- **Information Collection Rule (ICR)**

The D/DBP Rule was the primary rule negotiated, with the Advisory Committee recommending a two stage approach to regulating D/DBPs. The first stage of the Rule introduces specific limits for certain disinfectants and disinfection byproducts in drinking water. As proposed, it:

- Sets limits on the amount of disinfectants allowed in drinking water.
- Reduces the limits on total trihalomethanes (TTHMs) from 0.10 mg/L to 0.080 mg/L.
- Sets limits on additional DBPs [sum of five haloacetic acids (HAA5), chlorite, and bromate].
- Requires the use of enhanced coagulation by utilities treating surface water containing total organic carbon (TOC) concentrations above a certain level.
- Applies to all community and nontransient noncommunity water systems.

In the second stage of this rule, the acceptability limits of disinfectants and disinfection byproducts in drinking water will be refined. Data collected in the Information Collection Rule (see below) and in concurrent health effects investigations will be used to justify any modifications to the stage one limits.

The second rule developed during the negotiation process is the Enhanced Surface Water Treatment Rule (ESWTR). This rule specifies levels of treatment to control pathogens in drinking water based on the microbial quality of the source water. This rule will be initially

introduced as an "interim" rule that will include a range of regulatory alternatives affecting only systems serving more than 10,000 people. The "interim" Enhanced Surface Water Treatment Rule will become effective at the same time as the Stage 1 D/DBP Rule.

The third rule that was recommended by the Advisory Committee is the Information Collection Rule (ICR). This rule addresses data needs in three areas, or elements. The most critical element involves the collection of data on the concentrations of specific microbes (including *Cryptosporidium*, *Giardia lamblia*, and total culturable viruses) in surface water that is treated to produce drinking water. (Monitoring for microbes in the drinking water may also be required, in certain situations, for very large water systems.) Information concerning treatment processes which are used to control pathogens will be collected in conjunction with the microbial monitoring data. The data from the ICR will be used in the development of the ESWTR.

The second data collection element of the ICR involves the monitoring of the source water and drinking water for general water quality characteristics, DBPs, surrogates for DBPs, surrogates for DBP precursors, and the collection of treatment plant operational data. Data from the DBP/ICR will be used to characterize the source water parameters that influence DBP formation, determine concentrations of DBPs in drinking water, refine models for predicting DBP formation, and establish cost-effective monitoring techniques. Successful development of the Stage 2 Disinfectant/Disinfection Byproduct Rule will be dependent on analyses of these data.

(Note that in the preceding paragraph, the term DBP/ICR was used. There are two basic types of analyses for the ICR, microbial analyses, and disinfectant/disinfection byproduct (D/DBP) analyses. In this manual, for clarity, D/DBP analyses for the ICR are identified as DBP/ICR, while microbial analyses, if referred to, will be identified as Micro/ICR. This distinction is necessary to separate D/DBP lab approval procedures from microbial lab approval procedures. **This manual only addresses the approval of laboratories to perform D/DBP analyses.**

The third element of the ICR involves a requirement for some systems to conduct bench or pilot scale studies to more completely investigate the use of granular activated carbon or membrane filtration in removing DBP precursors during water treatment operations. The systems must conduct TOC monitoring in order to determine whether they are subject to performing the precursor removal treatment studies. (This TOC monitoring is referred to as Treatment Study/ICR applicability monitoring in this manual.) The Treatment Study/ICR is intended to:

- Obtain more information regarding the cost effectiveness of using these technologies to reduce DBP levels
- Decrease the time water treatment facilities will need to install such technology should such technology be required under the Stage 2 Disinfectant/Disinfection Byproduct Rule

## **Ensuring Data Quality for the DBP/ICR**

One of the major issues discussed during development of the ICR concerned the quality of the data that are to be generated during the monitoring period. The Advisory Committee recognized that the data must meet specific accuracy and precision targets in order to meet the ICR objectives. Since the data are to be generated by many laboratories, strict data quality controls will be essential. Maintaining data comparability between laboratories will be necessary if the data are to be successfully used in sophisticated correlational analyses which will reliably predict DBP formation as a function of water quality conditions. The Advisory Committee felt that the only way to ensure useable data is to define and maintain strict controls on the collection and analysis of the data, and for EPA to assist the drinking water industry in identifying qualified laboratories which can accurately and reliably perform the analyses required by the DBP/ICR.

In August of 1993, EPA convened a panel of technical experts to assist in the development of guidelines and requirements for ensuring analytical data was of adequate quality. Representatives from utility, state, university, and commercial laboratories, and a nonprofit certification organization were present at the two-day meeting. Attendees were invited to this meeting based on their expertise in one or more of the following areas:

- Analyzing for DBPs
- Day-to-day management of laboratory operations
- Drinking water laboratory certification programs.

The technical experts made several general recommendations regarding approaches that could be used to ensure data quality. EPA used information from the panel as a basis for developing the first draft of a manual titled "DBP/ICR Analytical Methods Guidance Manual - Public Comment Draft," and it was made available to the public when the ICR was proposed on February 10, 1994. EPA received comments on the manual content during the public comment period following the ICR proposal. The comments were generally supportive of the procedures described in the manual, but issues were raised concerning some of the specific QC and PE acceptance criteria. Commenters also identified areas that needed clarification, and recommended that additional information, concerning certain methods, be added.

The panel of experts was reconvened on April 28-29, 1994 to assist EPA in evaluating the comments and recommendations that were received. This manual reflects EPA's finalization of the document after considering the panels comments and recommendations. This manual is intended to:

- Describe the laboratory approval process

- Describe the data that EPA will use to assess a laboratory's ability to produce data of known accuracy and precision for the DBP/ICR
- Describe laboratory data quality control requirements for ICR analyses for both the DBP/ICR and the Treatment Study/ICR
- Specify how ICR data are to be reported back to the utilities and to EPA for the DBP/ICR
- Clarify specific analytical procedures that are not adequately described in some methods that are referenced in this manual

Laboratories will be approved to perform analyses for the DBP/ICR and the TOC monitoring to determine applicability for treatment study requirements under the ICR according to the procedures outlined in this manual. To maintain approval, they are required to follow the procedures outlined herein.

## **Section 2. Laboratory Quality Assurance Plan and ICR Quality Assurance Manual**

### **Laboratory Quality Assurance Plan**

To ensure that analytical data generated for the ICR are scientifically valid and are of known and acceptable precision and accuracy, all laboratories analyzing samples for the ICR will be required to adhere to defined quality assurance procedures. To facilitate the accomplishment of these goals, each laboratory must have a written description of its quality assurance (QA) activities, a QA Plan, which describes the QA management of day to day routine operations. The plan must be available for review for ICR laboratory approval, and it must be kept current during the time the laboratory is performing ICR measurements. A copy of the Laboratory QA Plan table of contents must be submitted to EPA as part of the laboratory approval application for analyses not covered under state certification/approval processes.

The Laboratory QA Plan should be a separately prepared text. However, certain sections in the Plan can simply reference existing documented procedures, such as the laboratory's standard operating procedures (SOPs), EPA Methods, or other literature (e.g., *Standard Methods for the Examination of Water and Wastewater*). Since most drinking water laboratory certification programs require the preparation of a Laboratory QA Plan in order to obtain/maintain certification, EPA anticipates that many laboratories applying for ICR approval will already have a Laboratory QA Plan in place.

The following items should be addressed in each Laboratory QA Plan:

1. Laboratory organization and responsibility
  - include a chart showing the laboratory organization and line authority, including QA Managers
  - list the key individuals who are responsible for ensuring the production of valid measurements and the routine assessment of quality control (QC) measurements
  - specify who is responsible for internal audits and reviews of the implementation of the Laboratory QA plan and its requirements
  - describe training available to keep personnel up to date on regulations, methods, etc.
2. Field sampling procedures
  - who collects, how collected, preservation, containers, holding times, transport to laboratory
  - documentation of procedures

### 3. Laboratory sample handling procedures

- bench sheets used
- storage; temperature, how isolated from standards and highly contaminated samples
- tracking; specify procedures used to maintain integrity of all samples, i.e., logging, tracking samples from receipt by laboratory through analysis to disposal

### 4. Calibration procedures

- type used for each method
- frequency of calibration
- standards; source, age, storage, labeling
- comparability checks

### 5. Analytical procedures

- reference method used
- SOP availability

### 6. Data reduction, verification, validation and reporting

- data reduction; conversion of raw data to mg/L, coliforms/100 mL, etc.
- verification; includes ensuring accuracy of data transcription and calculations
- validation
- reporting; includes procedures and format for reporting data to clients

### 7. Types of quality control (QC) checks and frequency of their use

- laboratory performance check standard
- Method Detection Limit (MDL) generation; acceptable, frequency
- internal standards and surrogate standards
- blanks; field, method, frequency
- replicate analyses; frequency
- QC samples; source, frequency
- Performance Evaluation (PE) samples
- fortified sample analyses; frequency
- initial demonstration of precision and accuracy and control charts

### 8. Preventive maintenance procedures and schedules

- manuals available
- spare parts inventory

- schedule
- documentation

#### 9. Corrective action contingencies

- response to obtaining unacceptable results from analysis of PE samples and from internal QC checks
- who is responsible
- documentation of actions taken and effectiveness of actions

#### 10. Record Keeping

- how are records maintained (electronically?)
- how long are records kept
- where are records stored

The Laboratory QA Plan should be concise but responsive to the above-listed items. Minimizing paperwork while improving data dependability and quality are the intended goals.

### **ICR Quality Assurance Manual**

All laboratories seeking approval to perform chemical analyses for the ICR will also be required to prepare a Quality Assurance (QA) Manual, specific to the Information Collection Rule. The goals of the Laboratory QA Plan in general are different from the goals of the ICR QA Manual. The former describes QA management of day to day routine operations while the latter describes goals, interactions and procedures for a specific project, in this case, the ICR. The ICR QA Manual is intended to supplement the Laboratory QA Plan by documenting the specific changes in sample handling, analytical methods, QC, and data reporting that the laboratory makes to address ICR requirements. This Manual must be available for review, if requested.

*"Preparation Aids for the Development of Category I Quality Assurance Plans, EPA/600/8-91/003", is a document laboratories may find useful in preparing the ICR QA Manual. It can be obtained by calling the Center for Environmental Research Information at 513-569-7562.*



### **Section 3. Laboratory Registration for DBP/ICR Analyses**

Analyses for the ICR must be performed only by laboratories that are capable of producing data meeting the ICR accuracy and precision criteria. All laboratories wishing to perform analyses for the DBP/ICR or TOC analyses for Treatment Study/ICR applicability must register with EPA by requesting a Laboratory Registration Form (see Appendix A) from EPA at the address noted below:

ICR Laboratory Coordinator  
Technical Support Division/USEPA  
26 West Martin Luther King Jr. Drive  
Cincinnati, OH 45268

After receiving the official Laboratory Registration Form from EPA, the laboratory is to identify, on the form, the ICR parameters that the laboratory wishes to analyze. There are several reasons why EPA is requiring laboratory registration:

- To assist EPA in determining which analyses will be performed by each laboratory
- To allow EPA to send the correct application packages to a laboratory that requests approval
- To assist EPA in tracking the progress of the laboratory approval process
- To allow EPA to ensure that utilities are using only EPA approved laboratories for their DBP/ICR monitoring and their TOC monitoring to determine treatment study applicability requirements

Based on the information provided by a laboratory in its registration form, EPA will send the laboratory a "Verification of State Certification/Approval" form and/or application packages for specific methods for which the laboratory has requested approval. The process that EPA will use to approve laboratories for ICR analyses is outlined in Section 4.



## **Section 4. Laboratory Approval Process**

Laboratories that register with EPA to perform DBP/ICR analyses or TOC analyses for Treatment Study/ICR applicability will be approved to perform testing in one of two ways.

- Laboratories can be approved to perform certain analyses by submitting information to demonstrate that they have existing state certification/approval to perform these analyses using the methods specified in the ICR. Analyses that can be approved in this fashion are: alkalinity, ammonia, calcium hardness, disinfectant residuals, pH, temperature, total hardness, trihalomethanes, and turbidity.
- Laboratories requesting approval to perform analyses that are not currently required under other drinking water regulations (or not listed above) must complete a detailed evaluation process as outlined in the following pages.

### **Overview of the Laboratory Approval Process**

- Laboratories must notify EPA no later than six months after the ICR promulgation date of their intent to perform ICR chemical analyses by writing to the following address:  
  
ICR Laboratory Coordinator  
Technical Support Division/USEPA  
26 West Martin Luther King Jr. Drive  
Cincinnati, OH 45268
- EPA will forward an ICR Registration Form to the laboratory.
- The laboratory must complete the ICR Registration Form and return it to EPA at the above address.
- Based on the information in the registration form, EPA will forward appropriate application forms.
  - For analyses currently required under existing water regulations, laboratories can be approved by submitting information to demonstrate that they have state certification/approval to perform those analyses using ICR specified methods. See the paragraph "Approval via Existing State Certification/Approval," in the text that follows.
  - For analyses currently not required under other drinking water regulations, the approval process is more detailed. Laboratories, in general, are required to:

- Conduct precision, accuracy and method detection limit (MDL) studies for the analyses in question.
  - Demonstrate their capability by participating in, and passing, one or more PE studies.
  - Provide Personnel and Quality Assurance information (including the Table of Contents from their Quality Assurance Plan).
  - Provide information regarding analytical equipment, and sample handling procedures.
- EPA will acknowledge receipt of the completed application forms. All application forms must be received by EPA no later than nine months after the ICR promulgation date in order for the laboratory to be considered for ICR Laboratory Approval.
  - After reviewing the submitted application forms, EPA will notify the laboratory, in writing, of its approval, or identify the reasons why the laboratory is not approved and advise the laboratory of necessary action.
  - Laboratories are not authorized to analyze ICR compliance monitoring samples until the laboratory is formally approved by EPA.
  - Laboratories approved for ICR analyses are required to maintain their approval status by performing the various Performance Evaluation and Quality Control testing outlined in Sections 8 and 9 of this manual.

**NOTE: Approval of laboratories to perform ICR analyses will apply only during the ICR 18 month monitoring period. If similar analyses are required as a result of the promulgation of new drinking water regulations, laboratories will then be required to be certified through the certification process appropriate for their State and/or Region.**

**The ICR approval process is not related to the laboratory certification process for conducting compliance monitoring under other drinking water regulations. Approval, or failure to obtain ICR laboratory approval, will have no impact on a laboratory's certification to perform compliance monitoring under other drinking water regulations.**

## **Approval via Existing State Certification/Approval**

**General Water Quality Analyses.** Several of the analyses that are required for the ICR are currently required under other water regulations. As a result, mechanisms for reviewing laboratory qualifications are already in place for these measurements. Measurements for pH, alkalinity, turbidity, temperature, calcium hardness and disinfectant residuals are required in order to meet current drinking water regulations, while ammonia and total hardness are specified in other water regulations. If a laboratory documents that it is currently approved by a state to perform these analyses using one of the methods specified in the ICR, then it will be approved, by EPA, to perform the same analyses for the ICR. (See relevant Note that follows.)

To obtain approval for these general water quality analyses and THM analyses (for most methods) laboratories must complete the "Verification of State Certification/Approval" form (see Appendix B). The completed form will be reviewed by EPA to ensure that all requested data were provided. If the information is complete, the laboratory will be advised, in writing, of its approval to perform the requested analyses.

**NOTE:** In some circumstances, a laboratory may be performing some of these analyses and reporting data to a State Primacy Agency with only de facto, and not documented, State approval. In such situations (where the laboratory does not have a formal State document to forward to EPA), a letter explaining the State's de facto approval must be written by the laboratory manager and forwarded, along with the "Verification of State Certification/Approval" form, to EPA.

**Trihalomethane (THM) Analyses.** Trihalomethane (THM) analyses for compliance monitoring with the existing THM Rule must be conducted by laboratories that are certified by a State Primacy Agency for drinking water. To obtain certification, the laboratory must demonstrate the ability to generate accurate data by passing at least one Performance Evaluation (PE) study sample for THMs on an annual basis. (Many states also conduct periodic on-site audits of laboratories they certify.) If a laboratory can demonstrate that it is currently certified by a state for THM compliance monitoring (see "Verification of State Certification/Approval" form, Appendix B), then EPA will not need to evaluate the laboratory's capability to measure these analytes prior to allowing it to perform THM analyses for the ICR (as long as the laboratory uses the same method for which it is certified).

All laboratories approved to perform THM analyses for the ICR, however, are required to participate in the ICR Chemistry Performance Evaluation (PE) Studies (see Section 8) that will be conducted on a quarterly basis during the monitoring period. They are also required to follow the quality control requirements described in Section 9. Therefore, although laboratories are State certified to perform THM analyses, if they wish to perform analyses for the ICR, they are required to meet additional requirements during the ICR monitoring period. (These additional requirements will be separate from the certification process.) This "approval via state

certification" applies only for THM analyses using methods 502.2, 524.2, and 551. See text below regarding methods 551 and 551.1.

Again, the approval of a laboratory to perform ICR testing, or the failure of a laboratory to obtain ICR laboratory testing approval, has no impact on a laboratory's certification to perform compliance monitoring under other drinking water regulations.

### **Approval for Analyses not Covered under Current Drinking Water Regulations**

Laboratories that register with EPA to perform ICR analyses not listed in the above subsection, are required to pass a review process prior to being granted approval to perform those analyses for the ICR. EPA will also evaluate laboratories that do not have state approval/certification to perform ammonia or total hardness analyses or THM analyses by Method 551. EPA will request information from the laboratory for each method for which the laboratory wants approval. On a method by method basis, the laboratory must list the names and qualifications of all personnel involved in each method, the equipment used for each analysis, and its general sample handling protocols. Samples of the forms to be used in reporting the applicable information are included in Appendix C. (Note: The appendix does not contain forms for aldehyde and cyanogen chloride methods, because EPA is performing these measurements for the water utilities.)

Laboratories are required to meet specific precision, accuracy, and method detection limit (MDL) requirements for most methods for which they are seeking approval (as specifically shown in the ICR application forms). The procedures that must be used to demonstrate precision, accuracy, and MDLs are described in Section 6. Data from these analyses must be reported as part of the laboratory approval application. Laboratories are also required to pass at least one ICR Chemistry PE study, or to provide satisfactory historical PE study data, prior to being approved. (PE studies are discussed in Section 8 of this manual.)

All laboratories that are approved to perform analyses for the ICR will be assigned unique identification (ID) numbers or codes. The laboratory ID must be reported with the monitoring data to allow laboratory precision and accuracy data to be associated with specific monitoring data in the ICR Federal Database.

To maintain approval during the DBP/ICR monitoring period, laboratories are required to participate in quarterly PE studies and to submit, to EPA, selected QC data (see Section 11). Analyses exempted from these requirements are ammonia and total hardness.

## Approval for Special Analyses

**Additional Haloacetic Acids.** Approval to perform haloacetic acid (HAA) analyses for the ICR encompasses the six HAAs for which the water systems are required to monitor:

- monochloroacetic acid (MCAA)
- dichloroacetic acid (DCAA)
- trichloroacetic acid (TCAA)
- monobromoacetic acid (MBAA)
- dibromoacetic acid (DBAA)
- bromochloroacetic acid (BCAA).

Laboratories may analyze and report data for up to three additional HAAs:

- bromodichloroacetic acid (BDCAA)
- chlorodibromoacetic acid (CDBAA)
- tribromoacetic acid (TBAA)

if they are approved for the six HAAs. EPA will only accept monitoring data for these additional HAAs, if the QC criteria specified in Section 9 are met.

**Standard Method 4500-Cl B.** Water systems are permitted to use this method when determining free residual chlorine concentrations in hypochlorite stock solutions. This method is not approved for drinking water compliance monitoring, so it is unlikely that a water system has state approval/certification to perform this analysis. EPA will grant ICR laboratory approval to perform this analysis to laboratories that are approved for other free residual chlorine methods under the ICR.

**Simulated Distribution System Test.** This test involves storing a sample of disinfected water for a set period of time at a known temperature and pH and then analyzing the sample for: trihalomethanes (THMs), HAAs, haloacetonitriles (HANs), chloropicrin (CP), haloketones (HKs), chloral hydrate (CH), total organic halide (TOX), pH, alkalinity, turbidity, temperature, calcium and total hardness, and disinfectant residual. EPA *recommends* that the storage part of the test be conducted at the individual water treatment plants. There is no laboratory approval requirement for setting up and conducting the test. The specific analyses at the conclusion of the storage period must be conducted by laboratories approved to perform those analyses for the ICR.

**Chlorine Demand Test.** There is no laboratory approval requirement specific to the chlorine demand test. However, this test includes measurements of free residual chlorine, pH and temperature and these analyses must be conducted by laboratories approved to perform them for the ICR.

**Assimilable Organic Carbon (AOC) and Biodegradeable Organic Carbon (BDOC) Analyses.** There is no laboratory approval requirement for these analyses, but laboratories are required to obtain an ICR Laboratory Identification (ID) Number. Laboratories can obtain this ID number by writing to:

ICR Laboratory Coordinator  
Technical Support Division/ USEPA  
26 West Martin Luther King Jr. Drive  
Cincinnati, OH 45268.

Laboratories must indicate in their letter to the Coordinator whether they are under consideration for approval to perform other analyses for the ICR (either chemical or microbial).

The ID number must be provided to the water system when monitoring data for AOC or BDOC are reported. In addition, the laboratory must report specific quality control data to the water system (see Section 10). Water systems are required to report laboratory ID numbers and associated QC data to EPA when AOC or BDOC monitoring data are reported. This will provide the users of the ICR Federal Database the ability to assess the quality of the AOC/BDOC data when they analyze/use them.

## **Section 5. Approved Methods for ICR DBP Monitoring**

Laboratories must use the methods specified in §141.142 (b)(1) to perform DBP/ICR analyses during the 18-month monitoring period and during the treatment studies. (A list of methods, in effect as of July 1, 1996, is summarized in Table 5.1) They must also follow all analytical (see following text) and quality control procedures (see Section 9) outlined in this manual. With the exception of analyses for chlorine demand, assimilable organic carbon (AOC), and biodegradable organic carbon (BDOC), analyses shall be conducted only by laboratories that have been formally approved, by EPA, for ICR water sample analyses during the 18-month monitoring period. The TOC monitoring to determine whether a water system is subject to the treatment study requirements must also be performed by a laboratory approved for TOC analyses. It is recommended that the THM, HAA or TOX monitoring to determine treatment study applicability requirements be performed by a laboratory approved for those analyses; the laboratory must meet the performance evaluation requirements described in Section 8 and the quality control requirements in Section 9 of this manual. Water systems that are required to conduct treatment studies are encouraged (but not required) to have the samples from these studies analyzed by laboratories that were approved by EPA for the 18-month monitoring period.

The list of analytical methods promulgated in the ICR is not exactly the same as the list that was included in the February 14, 1994 proposal. A brief discussion of the changes and the rationale for making them is included in this section under the subsection titled "Proposed and Promulgated Methods for ICR Monitoring" (see page 26).

### **Special Analytical Procedures**

**Chlorine Residual Analyses.** The ICR requires water systems to monitor disinfectant residuals using the methods specified at §141.74(a)(2), and a summary of those methods is included in Table 5.1. Section 141.74(a)(2) also states: "If approved by the State, residual disinfectant concentrations for free chlorine and combined chlorine also may be measured by using DPD colorimetric test kits." Therefore, water systems that are using these test kits to perform drinking water compliance monitoring under approval from the State, may also use the test kits to perform analyses for the ICR.

**Haloacetic Acids.** The ICR requires water systems to monitor for six haloacetic acids (HAA6) (monochloroacetic, dichloroacetic, trichloroacetic, monobromoacetic, dibromoacetic, and bromochloroacetic acids) [§ 141.142(a)] and therefore the ICR laboratory approval process only pertains to these six compounds. Studies that were not available during negotiations for the ICR

indicate that some drinking waters could contain significant concentrations of additional HAAs.<sup>1,2</sup> As a result, EPA is encouraging, but not requiring, water systems to collect monitoring data for these additional compounds (bromodichloroacetic, chlorodibromoacetic, and tribromoacetic acids). [§ 141.142(a) Table 1b]

Only EPA Method 552.2 lists these three compounds as analytes and provides method performance data. The data presented in the above references were generated using an expanded version of SM 6251 B, but the precision, accuracy and sensitivity achievable using SM 6251 B was not documented. Laboratories that decide to provide analytical services for these additional compounds are encouraged to use EPA Method 552.2. However, data from the other HAA method will be accepted by EPA (i.e., entered into the ICR Federal Database) as long as the laboratory is able to meet the quality control requirements for the compounds as specified in Section 9. These QC requirements are based on criteria easily achievable using EPA Method 552.2 and may not be achievable using other methods.

**Standard Method 6251 B Errata/Clarification.** Two corrections to this method were brought to the attention of the Standard Methods Committee after the 19th edition was published. An errata/clarification sheet was issued to address the corrections. The text changes to the method and their explanations are described below:

The 19th edition version of this method implies that all extracts must be dried prior to the derivatization step. This step may not be necessary if the analyst is careful to not transfer any of the aqueous phase from the extraction vial. Therefore, section 5.d of the method is amended as shown below.

The procedure to be used for preparing the acidified sodium sulfate that is used in the drying step was inadvertently omitted from the method. Therefore section 4.b of the method is now divided into two subsections (4.b.1 and 4.b.2) and the original "4.b" is now 4.b.1.

*4.b.1. Sodium sulfate, granular reagent grade, ....*

*4.b.2. Acidified sodium sulfate (acidified  $\text{Na}_2\text{SO}_4$ )* After heating 100 g anhydrous sodium sulfate to 400°C and cooling to room temperature, prepare the acidified sodium sulfate by making a slurry in di-ethyl ether. The solid should be just covered. Add 0.1 mL concentrated sulfuric acid and thoroughly mix. Remove the ether under low vacuum. Mix

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<sup>1</sup>Pourmoghaddas, H. et. al. Effect of Bromide Ion on Formation of HAAs During Chlorination. *Jour. AWWA*, 85:1:82 (Jan. 1993)

<sup>2</sup>Cowman, G. & P.C. Singer. Effect of Pre-ozonation on Haloacetic Acid Speciation in Chlorinated Waters Containing Bromide. *AWWA Water Quality Technology Proceedings*, Nov 1994.

1 g of the acidified sodium sulfate with 5 mL of reagent water and measure the pH of the mix. The pH must be less than 4. Store at 130°C.

*5.d. Separation and concentration:* NOTE: Ensure that all items .... sulfuric acid.

The drying step included here may be used if excess diazomethane is required to maintain the persistent yellow color of the sample (5.e). It has been found not to be necessary in all cases and may be used at the discretion of the analyst. Plug a small disposable pipet ....

**EPA Method 551.1 Analyses.** This method can be used to determine the concentrations of trihalomethanes (THMs), haloacetonitriles (HANs), haloketones (HKs), chloropicrin (CP), and chloral hydrate (CH) in water. Sodium sulfite must be used to dechlorinate samples for CH analyses and ammonium chloride must be used when HAN, HK, or CP analyses are to be performed. The THMs can be determined in samples that have been treated with either sodium sulfite or ammonium chloride. In order to ensure that laboratories do not mistakenly analyze the same sample for CH and HANs, laboratories are required to extract and analyze CH and HAN samples in separate batches.

**Oxyhalides and Bromide.** EPA Method 300.0 is divided into two parts. Bromide is listed as an analyte in Part A and the oxyhalides (bromate, chlorite, and chlorate) are listed in Part B. One of the primary differences between the two parts is the analytical column. Part A specifies an AS4A column while Part B specifies an AS9 column. Some analysts have found that they can analyze for bromide ion using the AS9 column. This option is allowed according to Section 6.2.2.1 of the method which states that "An optional column may be used if comparable resolution of peaks is obtained, and the requirements of Section 9.2 can be met." Therefore, laboratories are permitted to use an AS9 column to perform bromide analyses for the ICR as long as the necessary performance criteria are met.

Chloride ion interferes with the measurement of bromate ion in some samples, because it is present in much higher concentrations than bromate and it elutes from the chromatography column close to the bromate peak. Analysts are allowed to pretreat the sample to remove the chloride ion, but this should only be done after it is demonstrated that optimizing the performance of the chromatographic system is not enough to resolve the chloride and bromate peaks. In some cases, the purchase of a new chromatographic column may provide the necessary resolution. Some laboratories may find it necessary to use a weaker eluent in order to achieve the necessary resolution between the bromate ion and chloride ion peaks. This is permitted (Sections 11.8-9 of the method) as long as the QC performance criteria are met. The strength of the carbonate eluent can be adjusted to provide additional resolution. A borate eluent has also been used successfully to improve resolution.<sup>3</sup>

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<sup>3</sup>Hautman, D.P. & M. Bolyard. Using Ion Chromatography to Analyze Inorganic Disinfection By-Products, *Jour. AWWA*. 84:11:88 (Nov 1992).

If chloride ion is still a problem after implementing the above measures, then pretreatment of the sample to remove the chloride ion should be considered. (Samples with chloride concentrations  $>30$  mg/L are likely to require pretreatment.) This can be accomplished by passing the sample through a silver cartridge or pretreatment guard column. If this procedure is used for samples, it must also be used on blanks, calibration standards and QC samples even though they do not contain significant concentrations of chloride ion. Analysts must be aware that some of the silver will leach into the sample and become deposited on the analytical column, if additional precautions are not taken. When this happens, the column CANNOT be used to determine bromide ion concentrations.

In order to prevent the deposition of silver onto the analytical column, the sample may be passed through a chelating cartridge or pretreatment guard column after the silver column but prior to the analytical column in order to remove the silver. If a guard column is used, it must be periodically regenerated according to the manufacturer's instructions to ensure continued performance. The analyst must monitor the instrument's sensitivity for bromide ion to verify that the chelating cartridge or guard column is removing the silver. A loss in sensitivity or a change in the bromide ion peak shape indicates silver may have been deposited in the analytical system. As stated above, if chelating cartridges or guard columns are used for samples, they must also be used on blanks, calibration standards and QC samples.

Analysis for bromide ion must not be performed on samples that have been pretreated to remove chloride ion, because the silver removes all halide ions, including bromide.

The method performance data listed in Method 300.0 were generated using a carbonate eluent and a  $50\text{ }\mu\text{L}$  sample injection volume. A larger sample volume (e.g.,  $200\text{ }\mu\text{L}$ ) may also be required in order to measure bromate ion concentrations as low as  $5\text{ }\mu\text{g/L}$ .

**Total Organic Halide.** The ICR requires water systems to monitor total organic halide (TOX) concentrations in untreated water and in the finished drinking water. Particulates may cause problems in the analysis of untreated water samples, because they clog the activated carbon columns during the adsorption step. For the ICR, analysts must not use traditional filtration techniques to remove gross particulates from the sample prior to the adsorption step, since that would cause volatiles, such as trihalomethanes, to be lost from the sample. If the sample is suspected to contain particulates which could prevent the free-flow of sample through the carbon column, a small amount of quartz wool can be used as a prefilter during the adsorption process. The quartz wool is inserted into a clean and empty glass column (or TOX-free holder) and placed in series ahead of the two carbon columns. (Note that insertion of a Cerafelt plug, at the bottom of the glass column, may be necessary to retain the quartz wool.) After sample adsorption, this column is nitrate washed, then pyrolyzed. Prior to the use of a quartz wool column, a system blank should be analyzed with the quartz wool column in place in order to ensure the column does not introduce contamination to the sample.

**Total Organic Carbon.** The ICR requires water systems to monitor total organic carbon (TOC) concentrations on a monthly basis at several sampling points. [§ 141.142 (a)(1)] The methods cited in the ICR are not clear concerning whether TOC includes the volatile fraction of organic carbon. Many studies published in the literature<sup>4,5,6</sup>, which support the use of organic carbon as a surrogate for disinfection byproduct (DBP) precursors, measured the non-purgeable fraction of organic carbon. This was done by acidifying the samples to a pH  $\leq 2$  to convert the inorganic carbon (e.g., carbonates and bicarbonates) to carbon dioxide and then sparging the samples to eliminate the carbon dioxide. The sparging process eliminated the volatile fraction of organic carbon. Therefore, for the ICR, the term TOC refers to the non-purgeable fraction of the organic carbon.

Several researchers have used dissolved organic carbon (DOC) instead of TOC as a surrogate for precursors. However, TOC was chosen by the negotiators as the parameter to be measured during the ICR. Therefore, samples must not be filtered prior to analyses for TOC. The methods specify that samples containing particulates may be homogenized or mixed and diluted prior to analysis. In some cases, the use of certain instruments may be precluded, if the sample introduction system cannot accommodate particulates.

**UV Absorbance at 254 nm.** The Standard Method (5910) provides some procedural options that are not applicable for the ICR. The absorbance must be measured at 254 nm for all ICR samples. All samples must be filtered to remove particulates. Filtration is the only pretreatment of the sample prior to measuring UV absorbance. There must not be any pH adjustment made to the samples; nor should a buffer be used in the spectrophotometer check standards. The UV absorbance reading must not be corrected for interferences. Samples should be analyzed as soon as possible after collection; samples must be analyzed within two days of sample collection. Absorbance must be reported on a  $\text{cm}^{-1}$  basis, which means that appropriate calculations must be performed if a 5 or 10-cm cell path length is used to perform the measurements; e.g., The absorbance reading should be divided by five when a 5-cm cell is used for the measurement. The method indicates that the sample pH should be recorded; however, the laboratory is not required to determine pH on UV samples for the ICR, because the pH is measured at the water treatment plant when the UV sample is collected.

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<sup>4</sup>Miller, R.E. et. al. Organic Carbon and THM Formation Potential in Kansas Groundwaters, *Jour. AWWA*. 82:3:49 (Mar 1990).

<sup>5</sup>Symons, J.M. et. al. National Organics Reconnaissance Survey for Halogenated Organics, *Jour. AWWA*. 67:11:634 (Nov 1975).

<sup>6</sup>Reckhow, D.A. & P.C. Singer. Chlorination by-products in drinking waters: from formation potentials to finished water concentrations, *Jour. AWWA*. 82:4:173 (Apr 1990).

**Simulated Distribution System (SDS) Test.** This test involves storing a sample of disinfected water for a set period of time at a known temperature and pH and then analyzing the sample for certain parameters. The ICR specifies Standard Method 5710 C for the SDS test. This method provides a general description of the test, but users are given many procedural options depending upon the purpose of conducting the test. For the ICR, the DBP concentrations in the SDS sample will be compared to the DBP concentrations measured in a sample from the distribution system. Therefore, the conditions under which the SDS test is conducted for the ICR are specific to each water treatment plant.

The SDS test conditions (i.e., storage time and temperature) are selected based on information about the distribution system equivalent (DSE) sample which is collected from the distribution system of each water treatment plant. The DSE sample's detention time (time the water has spent traveling from the water treatment plant to the sampling point in the distribution system) is used as the basis for establishing the SDS storage time. The SDS sample should be stored for a time period comparable in length to the DSE sample's detention time. The storage temperature should be comparable to the temperature of the water in the distribution system between the treatment plant and the DSE sampling point. In order to accomplish this, the SDS sample should be maintained at the temperature measured at either the SDS sampling point or the DSE sampling point. The goal should be to achieve a temperature within  $\pm 2^{\circ}\text{C}$  of one of these temperatures.

The contact time of the SDS test begins when the sample is collected. Therefore the storage part of the test is best conducted at the treatment plant where the sample is collected. If this is not possible, then the sample should be transported to a nearby site for the test. The SDS sample must not be iced or treated in any other manner and shipped to off-site laboratories until after the storage part of the test is completed and the sample is divided into aliquots with the appropriate dechlorinating agents for the individual analyses.

There are many techniques available to maintain the SDS sample at a constant temperature during the storage period. Some examples include (but are not limited to):

- using an incubator or constant temperature water bath set at the appropriate temperature
- placing the SDS sample container(s) in an insulated container (e.g., an ice chest) and allowing a constant flow of finished water to pass through the container to maintain the sample at the finished water temperature
- placing the SDS sample container(s) in a bucket in a sink and allowing a constant flow of finished water to pass around the sample to maintain it at the finished water temperature
- suspending the SDS sample container(s) in the treatment plant clearwell to maintain it at the finished water temperature

The goal should be to store the SDS sample for the same length of time as the detention time of the DSE sample. Since the DSE detention time is estimated, the SDS storage time should reasonably approximate (within  $\pm 25\%$ ) the DSE detention time.

At the conclusion of the storage time, the SDS sample must be analyzed for several parameters. The SDS sample must be divided by pouring it into sample bottles containing the appropriate dechlorinating agents/preservatives. (This may be done at the storage site or at a nearby laboratory, if the sample temperature is maintained during transport and the transport time is factored into the storage time.) Care must be taken to not aerate the sample during this transfer, in order to prevent the loss of volatile compounds such as THMs. (The samples for THM, HAN, TOX, and CH analyses should be transferred first, because they contain volatile analytes which can be easily lost during the pouring process.) The subsamples must be analyzed by ICR approved laboratories using the appropriate analytical methods. Three analyses must be conducted as soon as possible after the conclusion of the storage period: chlorine residual, pH and temperature. Holding times for the remainder of the analyses begin when the SDS sample is divided for individual analyses.

**Chlorine Demand Test.** The method cited in the ICR is Standard Method 2350 B. This method describes how to perform the test, but it leaves the choice of chlorine dose, temperature, pH and contact time up to the discretion of the person performing the test. In order to meet the objectives of determining the chlorine demand resulting from the presence of inorganics, specific guidelines are established which must be followed in order to comply with the ICR. The test is to be conducted under conditions specific to each water treatment plant.

**Chlorine Dose.** If the first disinfectant (or oxidant) used in the treatment process is chlorine and breakpoint chlorination is practiced, selection of an appropriate chlorine dose should be based on what is used at this point in the treatment process to achieve a desired free chlorine residual. Ideally, the same dose should be used, with the exception that the goal for this test is to obtain a final free residual chlorine concentration (as measured in this test) between 0.5 and 1.0 mg/L. In order to consider the test results valid, the residual must be no less than 0.2 mg/L and no greater than 1.5 mg/L.

If breakpoint chlorination is not practiced at the first point of chlorine application, then the dose used for the chlorine demand test must be based on a dosage that will result in a free residual chlorine between 0.2 and 1.5 mg/L (goal is between 0.5 and 1.0 mg/L, as described above). Selection of an appropriate dosage may require several iterations in the test. If the water contains ammonia-nitrogen as the major contributor to inorganic chlorine demand, then the chlorine dose necessary for this test can be estimated by multiplying the ammonia concentration (as mg nitrogen/L) by 7.6 and then adding an additional 1.0 mg/L. (This should provide a free residual chlorine concentration near 1 mg/L.)

If chlorine is not the first disinfectant (or oxidant) used in the treatment process, then the chlorine dose must be determined using the same guidelines as for when breakpoint chlorination is not practiced.

**Contact Time.** Free residual chlorine should be measured approximately 5 minutes after the chlorine is added to the sample. If the residual cannot be measured in the dosed sample within 10 minutes, then the test must be repeated with a fresh sample. This short time period was chosen because reactions with the inorganics are expected to occur quickly and it is physically feasible to make the free residual chlorine measurement within the 10 minute time frame.

The free residual chlorine measurement must be made using the same method as is used to make other free residual chlorine measurements for the ICR.

**Temperature.** The water sample must be at the same temperature as the process water. This means that the test should be conducted on a freshly collected aliquot of water. The temperature of the sample should be determined after the free residual chlorine measurement is completed.

**pH.** The pH of the water must not be adjusted for this test. It should reflect the pH of the water at the point of first disinfectant/oxidant addition in the treatment process. The pH of the sample should be determined after the free residual chlorine measurement is completed.

**Reporting Requirements.** The following data must be reported for this test:

- Chlorine dose (mg/L)
- Contact time (min)
- Analysis date
- Chlorine residual (mg/L)
- pH (after contact time)
- Temperature (°C) (after contact time)

EPA will calculate the chlorine demand by subtracting the chlorine residual from the chlorine dose.

**Analyses of Hypochlorite Stock Solutions.** Water systems that use hypochlorite solutions for disinfection are required to measure the pH, temperature, free residual chlorine, and chlorate ion concentrations in the feed stock solution. The chlorine and chlorate concentrations in hypochlorite stock solutions are expected to be hundreds to thousands times greater than the concentrations typically measured in drinking water samples. Therefore, the water systems are required to report the concentrations of these two parameters in g/L units for this sample type. All other analyses for free residual chlorine and chlorate ion must be reported as mg/L as  $\text{Cl}_2$  and  $\mu\text{g/L}$ , respectively. Laboratories are encouraged to report the results of these analyses in the same units as the water systems are required to report the data to EPA.

EPA recommends that the hypochlorite stock solution sample for chlorate determination be collected without a preservative in the sample bottle. The sample must be chilled upon collection in order to minimize the formation of additional chlorate from the decomposition of the hypochlorite solution. The sample will probably require significant dilution prior to analysis for chlorate ion concentration. Enough ethylenediamine (EDA) should be added to the diluted sample to eliminate the free residual chlorine before the sample is analyzed by ion chromatography.

Five methods for determining free residual chlorine are listed in Table 5.1 and are approved for use on the hypochlorite stock solution samples. These stock solution samples are expected to contain free residual chlorine concentrations that are orders of magnitude above the normal working range of approved methods, so users must exercise care in diluting the samples to concentrations that are appropriate for the method in use. In order to minimize the magnitude of the necessary dilution, EPA encourages the use of Standard Method 4500-Cl B with the following modifications (numbers refer to sections in the method as described in the 19th edition of *Standard Methods for the Examination of Water and Wastewater*):

- **2.d. Standard sodium thiosulfate titrant, 0.01N or 0.025N:** **Do not prepare this dilution.** Use the 0.1N  $\text{Na}_2\text{S}_2\text{O}_3$  standard solution prepared and standardized according to 2.c when performing the titration described in 3.c.
- **3.a. Volume of sample:** Prepare a dilution of the stock hypochlorite solution sample by pipetting 20 mL of it into a 1 liter volumetric flask. Dilute to the mark with chlorine-demand-free water (see 4500-Cl C.3.m.). Use an aliquot from this dilution when performing the titration described in 3.c. For hypochlorite stock solutions with concentrations in the range of 5 - 15% chlorine by weight, use a 10-mL aliquot of the diluted sample for the titration. (The goal is to select a sample volume that will require between 1 and 10 mL of the 0.1N  $\text{Na}_2\text{S}_2\text{O}_3$  titrant to reach the starch-iodide end point.)
- **3.b. Preparation for titration:** Place 5 mL acetic acid, .....Pour sample (aliquot from dilution made in 3.a.) in, add approximately 400 mL chlorine demand free water, and mix with a stirring rod.
- **3.c. Titration:** Titrate away from direct sunlight. Add 0.1N  $\text{Na}_2\text{S}_2\text{O}_3$  from a buret until.....
- **3.d. Blank titration:** Correct result of sample titration....  
Take a volume of chlorine demand free water corresponding to the volume of diluted sample used for the titration in 3.c and the volume of chlorine demand free water added in 3.c, add 5 mL acetic acid, ....Perform blank titration as in 1) or 2) below, whichever applies.

1) If a blue color develops, titrate with 0.1N  $\text{Na}_2\text{S}_2\text{O}_3$  to disappearance of blue color and record result. B (see ¶ 4, below) is negative.

2) If no blue color occurs, titrate with 0.0282N iodine solution until a blue color appears. Back-titrate with 0.1N  $\text{Na}_2\text{S}_2\text{O}_3$  and record the difference. B is positive.

Before calculating the chlorine concentration,.....

- 4. **Calculation:** For determining total available residual chlorine in a hypochlorite stock solution sample, use the following equation:

$$\text{g Cl as Cl}_2/\text{L} = \frac{(A \pm B) \times N \times 35.45 \times 1000}{C \times 20}$$

where:

A = mL titration for sample

B = mL titration for blank (positive or negative)

C = mL of diluted sample

N = normality of  $\text{Na}_2\text{S}_2\text{O}_3$  used as titrant (should be approximately 0.1N)

The above equation assumes:

20 mL of the hypochlorite stock solution sample is diluted to 1000 mL (hence the correction factor of 1000/20) and the titration is performed on an aliquot from the 1000 mL dilution.

(mL of diluted sample) is the volume of the diluted sample which is used in the titration. If the undiluted hypochlorite stock solution concentration is in the range of 5 - 15% chlorine by weight, and the sample is diluted according to 3.a., then this volume is 10 mL.

35.45 is the equivalent weight of chlorine and is used to convert the concentration from Normality to g/L as  $\text{Cl}_2$ .

Concentration of hypochlorite stock solution is reported as: g Cl as  $\text{Cl}_2$ /L.

## **Proposed and Promulgated Methods for ICR Monitoring**

The final ICR did not promulgate all the methods that were included in the February 1994 proposal. These method modifications to the ICR rule were made in response to public comments, revisions in related EPA regulations, updates to *Standard Methods* and incorporation of improved methodology.

In the interim between proposal and promulgation, EPA revised the list of methods approved for drinking water compliance monitoring. [See National Primary and Secondary Drinking Water Regulations: Analytical Methods for Regulated Drinking Water Contaminants; Final Rule, Federal

Register 59(232) pg. 62456-62471, December 5, 1994.] Approval for several methods was withdrawn effective July 1, 1996. Therefore, these methods are not listed in Table 5.1 and EPA will not approve laboratories to perform analyses for the ICR using the withdrawn methods.

The 19th edition of *Standard Methods for the Examination of Water and Wastewater* was published between proposal and promulgation. EPA proposed three draft methods from the 19th edition (HAAs, UV<sub>254</sub>, and Aldehydes). The final ICR promulgated two of these (SM 6251 B, formerly 6233 B, for HAAs and SM 5910 for UV<sub>254</sub>). The third method (SM 6252 B) is being used by EPA when aldehyde samples are analyzed for the water systems during the 18-month monitoring period.

EPA also cited only the 19th (not 18th) edition of *Standard Methods* in the ICR for analyses that were not previously required under other drinking water regulations. This necessitated dropping one method for ammonia (nesslerization - SM 4500-NH<sub>3</sub> D), because it was no longer supported by *Standard Methods* due to the use of mercury. The ammonia method numbers were also changed between the two editions, so the method numbers were changed between the ICR proposal and promulgated rule. SM 4500-NH<sub>3</sub> F in the proposal is listed as SM 4500-NH<sub>3</sub> D in the final rule.

EPA received public comments from the proposal requesting the addition of automated methods for ammonia analyses. EPA deemed three automated methods to be equivalent to the manual methods included in the proposal. Therefore, EPA Method 350.1, SM 4500-NH<sub>3</sub> G, and Industrial Method 379-75 WE were added in the final rule.

EPA received many comments concerning the proposed methods for TOC analyses. EPA evaluated the data that were submitted indicating that some combustion instruments based on SM 5310 B are sensitive and precise enough to meet ICR requirements and EPA concurred with the commenters. Therefore, EPA added SM 5310 B to the list of methods approved for TOC monitoring under the ICR.

The preamble to the proposed ICR rule discussed difficulties in the preservation of samples for the determination of haloacetonitriles, halo ketones, chloropicrin, and chloral hydrate concentrations in drinking water. In the interim between proposal and promulgation, EPA was able to develop a preservation technique for these samples and a revised method was published. Because the new version of the method (EPA Method 551.1) addresses a problem that was of concern both to EPA and many commenters, EPA promulgated 551.1 instead of EPA Method 551 for the compounds listed above.

EPA was also able to develop a new method for measuring HAA concentrations in drinking water during the period between proposal and promulgation. EPA Method 552.2 combines the positive aspects of the two methods that were included in the proposal and eliminates some of the concerns expressed by the laboratory community regarding the proposed methods. Therefore,

EPA decided to list Method 552.2 as an additional approved method for performing HAA analyses.

## Low Bromate

EPA Method 300.0 is not sensitive enough to meet all the ICR objectives. The routine method can be used to determine whether a utility would be able to comply with the proposed 10  $\mu\text{g/L}$  Maximum Contaminant Level (MCL) proposed in the Stage 1 D/DBP Rule. However, the variability in the data below 10  $\mu\text{g/L}$  prevents using the data to determine how changes in treatment processes affect the formation of bromate. In order to obtain that type of information, samples must be analyzed using methodology that can quantitate bromate at concentrations < 1  $\mu\text{g/L}$ . EPA's laboratory has the capability to measure down to approximately 0.2  $\mu\text{g}$  bromate/L using a technique that involves selectively concentrating the bromate prior to the ion chromatographic analysis.<sup>7</sup> EPA will be performing this analysis for the utilities during the 18-month monitoring period. EPA's analyses will be in addition to the analyses that are performed using Method 300.0 by laboratories commissioned by the water utilities. Many of the tables in this manual refer to a "low  $\text{BrO}_3^-$ " analysis. It is included, in order to document the criteria that EPA will follow when performing this analysis.

## Aldehyde and Cyanogen Chloride Analyses

EPA will perform all the required aldehyde and cyanogen chloride analyses for the water utilities during the 18-month monitoring period. EPA will use Standard Method 6252 B<sup>8</sup> to perform the aldehyde analyses. A modified version of EPA Method 524.2<sup>9</sup> will be used for the cyanogen chloride analyses. Many of the tables in this manual refer to the aldehyde and cyanogen chloride analyses. They are included, in order to document the criteria that EPA will follow when performing these analyses.

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<sup>7</sup>Hautman, D.P. Analysis of Trace Bromate in Drinking Water Using Selective Anion Concentration and Ion Chromatography. *AWWA Water Quality Technology Proceedings*, Nov. 1992.

<sup>8</sup>Standard Methods for the Examination of Water and Wastewater, 19th edition, 1995, American Public Health Association, 1015 Fifteenth Street NW, Washington, D.C. 20005.

<sup>9</sup>Flesch, J.J. and P.S. Fair. The Analysis of Cyanogen Chloride in Drinking Water. *AWWA Water Quality Technology Proceedings*, Nov 1988.

**Table 5.1. Analytical Methods Approved for DBP Monitoring**

Analyte	Methodology		
	EPA Method	Standard Method <sup>1</sup>	Other
pH	150.1 <sup>2</sup> , 150.2 <sup>2</sup>	4500-H <sup>+</sup> B	ASTM D1293-84 <sup>3</sup>
Alkalinity		2320 B	ASTM D1067-92B <sup>3</sup> , I-1030-85 <sup>4</sup>
Calcium hardness	200.7 <sup>5,6</sup>	3111 B <sup>6</sup> , 3120 B <sup>6</sup> , 3500-Ca D	ASTM D511-93A <sup>3</sup> , ASTM D511-93B <sup>3,6</sup>
Turbidity	180.1 <sup>6,7</sup>	2130 B <sup>6</sup>	GLI Method 2 <sup>6,8</sup>
Temperature		2550 B	
Free Residual Chlorine		4500-Cl B <sup>9</sup> , 4500-Cl D, 4500-Cl F, 4500-Cl G, 4500-Cl H	
Total Residual Chlorine		4500-Cl D, 4500-Cl E <sup>6</sup> , 4500-Cl F, 4500-Cl G <sup>6</sup> , 4500-Cl I	
Chlorine Dioxide Residual		4500-ClO <sub>2</sub> C, 4500-ClO <sub>2</sub> D, 4500-ClO <sub>2</sub> E	
Ozone Residual		4500-O <sub>3</sub> B	
Trihalomethanes (THMs): Chloroform (CHCl <sub>3</sub> ) Bromodichloromethane (BDCM) Dibromochloromethane (DBCM) Bromoform (CHBr <sub>3</sub> )	502.2 <sup>6,10</sup> , 524.2 <sup>6,11</sup> , 551 <sup>6,12</sup> , 551.1 <sup>13</sup>		

Analyte	Methodology		
	EPA Method	Standard Method <sup>1</sup>	Other
Haloacetic acids (HAAs): Monochloroacetic Acid (MCAA) Dichloroacetic Acid (DCAA) Trichloroacetic Acid (TCAA) Monobromoacetic acid (MBAA) Dibromoacetic acid (DBAA) Bromochloroacetic acid (BCAA) Optional analytes: Bromodichloroacetic acid (BDCAA) Chlorodibromoacetic acid (CDBAA) Tribromoacetic acid (TBAA)	552.1 <sup>11</sup> , 552.2 <sup>13</sup>	6251 B <sup>14</sup>	
Chloral Hydrate (CH)	551.1 <sup>13</sup>		
Haloacetonitriles (HANs): Trichloroacetonitrile (TCAN) Dichloroacetonitrile (DCAN) Bromochloroacetonitrile (BCAN) Dibromoacetonitrile (DBAN)	551.1 <sup>13</sup>		
Haloketones (HKs): 1,1-Dichloropropanone (DCP) 1,1,1-Trichloropropanone (TCP)	551.1 <sup>13</sup>		
Chloropicrin (CP)	551.1 <sup>13</sup>		
Chlorite (ClO <sub>2</sub> <sup>-</sup> )	300.0 <sup>7</sup>		
Chlorate (ClO <sub>3</sub> <sup>-</sup> )	300.0 <sup>7</sup>		
Bromide (Br <sup>-</sup> )	300.0 <sup>7</sup>		
Bromate (BrO <sub>3</sub> <sup>-</sup> )	300.0 <sup>7</sup>		
Total Organic Halide (TOX)		5320 B	
Total Organic Carbon (TOC)		5310 B, 5310 C, 5310 D	
UV absorbance at 254 nm (UV-254)		5910 <sup>14</sup>	

Analyte	Methodology		
	EPA Method	Standard Method <sup>1</sup>	Other
Simulated Distribution System Test (SDS)		5710 C	
Total Hardness		2340 B <sup>15</sup> , 2340 C	
Ammonia	350.1	4500-NH <sub>3</sub> D <sup>14</sup> , 4500-NH <sub>3</sub> G <sup>14</sup>	379-75 WE <sup>16</sup>
Chlorine Demand Test		2350 B	
Assimilable Organic Carbon (AOC) (Optional analysis)		9217 B	
Biodegradeable Organic Carbon (BDOC) (Optional analysis)			See Footnote <sup>17</sup>

- <sup>1</sup> Except where noted, the 18th and 19th editions of Standard Methods for the Examination of Water and Wastewater, 1992 and 1995, respectively, American Public Health Association, 1015 Fifteenth Street NW, Washington, D.C. 20005 are equivalent for the methods cited. Therefore, either edition may be used.
- <sup>2</sup> Methods 150.1 and 150.2 are available from US EPA, NERL, Cincinnati, Ohio 45268. The identical methods are also in "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020, March 1983, available from the National Technical Information Service (NTIS), U.S. Department of Commerce, 5285 Port Royal Road, Springfield, Virginia 22161, PB84-128677. (Note: the NTIS toll-free number is 800-553-6847.)
- <sup>3</sup> Annual Book of ASTM Standards, 1994, Volumes 11.01 and 11.02, American Society for Testing and Materials, 1916 Race Street, Philadelphia, PA 19103.
- <sup>4</sup> Available from Books and Open-File Reports Section, US Geological Survey, Federal Center, Box 25425, Denver CO 80225-0425.
- <sup>5</sup> "Methods for the Determination of Metals in Environmental Samples - Supplement I," EPA-600/R-94-111, May 1994. Available at NTIS, PB 94-184942.
- <sup>6</sup> Mandatory and recommended modifications to this approved procedure are identified in "Technical Notes on Drinking Water," EPA-600/R-94-173, October 1994. Available at NTIS, PB95-104766.

- 7 "Methods for the Determination of Inorganic Substances in Environmental Samples," EPA-600/R-93-100, August 1993. Available at NTIS, PB94-121811.
- 8 GLI Method 2, "Turbidity," November 2, 1992, Great Lakes Instruments, Inc., 8855 North 55th Street, Milwaukee, Wisconsin 53223.
- 9 This method is only applicable for determining free residual chlorine in samples of hypochlorite stock solutions. It is not approved for other types of samples required under the ICR.
- 10 "Methods for the Determination of Organic Compounds in Drinking Water," EPA-600/4-88-039, December 1988, Revised, July 1991. Available at NTIS, PB91-231480.
- 11 "Methods for the Determination of Organic Compounds in Drinking Water - Supplement II," EPA-600/R-92-129, August 1992. Available at NTIS, PB92-207703.
- 12 "Methods for the Determination of Organic Compounds in Drinking Water - Supplement I," EPA/600/4-90-020, July 1990. Available at NTIS, PB91-146027.
- 13 "Methods for the Determination of Organic Compounds in Drinking Water - Supplement III," EPA-600/R-95-131, August 1995. Available at NTIS, PB95-261616.
- 14 This method is only found in the 19th edition of Standard Methods for the Examination of Water and Wastewater.
- 15 The following methods can be used to determine both calcium and magnesium concentrations for use in conjunction with Standard Method 2340 B: EPA Method 200.7, Standard Method 3111 B, Standard Method 3120 B, or ASTM method D511-93 B.
- 16 Ammonia, Automated Electrode Method, Industrial Method Number 379-75 WE, February 19, 1976, is available from Bran & Luebbe Analyzing Technologies, Inc., Elmsford, N.Y. 10523.
- 17 When Public Water Systems request laboratories to perform optional Biodegradable Organic Carbon (BDOC) analyses, the laboratory must use one of the following methods to conduct the analysis:
  - (i) Biodegradable Organic Carbon (BDOC). Servais, P., Billen, G., and Hascoët, M. Determination of the Biodegradable Fraction of Dissolved Organic Matter in Waters, Water Research 21(4), pp 445-450, 1987.
  - (ii) Biodegradable Organic Carbon (BDOC). Joret, J.C., Lévi, Y., Dupin, T., Gibert, M. and Recherche, A. Rapid Method for Estimating Bioeliminable Organic Carbon in Water, Proceedings of AWWA Annual Conference, Orlando, FL, June, 1988.

(iii) Biodegradeable Organic Carbon (BDOC). Summers, R.S. Biocharacterization of Natural Organic Matter, Natural Organic Matter in Drinking Water, Origin, Characterization, and Removal, Workshop Proceedings, Chamonix, France, Sponsored by AWWA Research Foundation and Lyonnaise des Eaux-Dumez, September 19-22, 1993.

(iv) Biodegradeable Organic Carbon (BDOC). Mogren, E.M., Scarpino, P., and Summers, R.S., Measurement of Biodegradable Dissolved Organic Carbon in Drinking Water, Proc. of AWWA Annual Conference, Cincinnati, OH, June, 1990.

(v) Biodegradeable Organic Carbon (BDOC). Friar, J., Ribas, F., and Lucena, F., A Method for the Measurement of Biodegradable Organic Carbon in Waters, Water Research 26(2), pp255-258, 1992.



## **Section 6. Initial Demonstration of a Laboratory's Ability to Perform DBP/ICR Analyses Not Covered Under Current Drinking Water Regulations**

An Initial Demonstration of a Laboratory's Ability to Perform the Method must be completed by each laboratory desiring to be approved for analytes/methods not currently included in States' certification or approval programs. EPA recognizes that a laboratory may use multiple instruments and analysts (or groups of analysts) to perform analyses. If more than one analyst is to perform ICR analyses, EPA recommends that each analyst perform each of the determinations described in this section (Section 6) before they are allowed to perform ICR analyses. (Prior to performing these determinations, the analyst must be thoroughly familiar with the method.) Similar testing of each instrument that will be used in ICR analyses should also be conducted. This will ensure that each operator and each instrument will be able to maintain minimum quality standards. Data from each of these tests should be maintained in the laboratory for review, should such review become necessary during the ICR monitoring and data analysis period.

Data from a representative set of the following determinations are to be reported to EPA as part of the laboratory approval application package. This representative data is to be just one set of data for each type of analysis, and it can represent any combination of operators/instruments. The application form for each method (or set of analytes) provides the format for reporting these data. (See Appendix C for examples of appropriate application forms.)

1. **Initial Demonstration of Low System Background** - Analyze a Laboratory Method Blank to verify that no contamination exists above  $\frac{1}{2}$  the minimum reporting levels for the analytes of interest (see Table 7.1).
2. **Initial Demonstration of Precision** - Analyze a total of five samples of reagent water fortified at the "Precision Demonstration" concentration listed in Table 6.1, for each analyte of interest, on five separate days (e.g., one per day for five days). The five days need not be consecutive. Samples must not be batched with each other for extraction or analysis. The relative standard deviation must be no greater than 20%.
3. **Initial Demonstration of Accuracy** - Calibrate the instrument as directed in the method.
  - a. Analyze a quality control sample obtained from either a commercial source, or one made from chemicals not used in the preparation of the calibration standards. Recovery must be within  $\pm 20\%$  of the true value.
  - b. Calculate the average recovery of the replicates in the Initial Demonstration of Precision (see preceding paragraph). The average recovery must also be within  $\pm 20\%$  of the expected amount.

**4. Method Detection Limit (MDL) Determination** - Laboratories must calculate their Method Detection Limits for each analysis (using the primary column) according to the procedure in CFR §136 Appendix B, with the following additional requirements. (A copy of the CFR procedure is included in Appendix D.)

- a. All sample processing steps must be included in the determination. Extractions and analyses must be conducted over at least three days.
- b. Select a fortifying concentration which provides an instrument signal 2 to 5 times above the noise level, but which does not exceed the concentration limits of Table 6.1. Analyze a total of seven replicates of reagent water fortified to a concentration in the range of the estimated detection limit but no more than the maximum MDL fortifying concentrations listed in Table 6.1.

**NOTE:** EPA recognizes that the bromate MDL fortifying level in Table 6.1. may be below the estimated detection limit for some laboratories. For this reason, bromate results are exempted from the 50% measurement accuracy requirement in paragraph 4.d. below. However, this MDL fortifying concentration is the maximum level which can be used by participants applying for ICR testing approval.

- c. Calculate the MDL for each analyte according to the formula listed in CFR §136 Appendix B. Do not subtract the blank value as suggested in the procedure.
- d. From the data collected in 4.b, calculate measurement accuracy. Each data point must be within  $\pm 50\%$  of the value of the fortified solution concentration. (See NOTE in paragraph 4.b. for bromate accuracy requirements.)

**Table 6.1. Laboratory Performance Assessment Requirements**

Method/Analyte(s)	Concentration of each Analyte for Demonstrating Precision	Maximum MDL Fortifying Conc.
551, 551.1/CHCl <sub>3</sub> , BDCM, CDBM, CHBr <sub>3</sub>	20. µg/L ± 1.0 µg/L	0.50 µg/L
551.1/TCAN, DCAN, BCAN, DBAN, DCP, TCP, CP	5.0 µg/L ± 0.5 µg/L	0.25 µg/L
551.1/CH	10. µg/L ± 0.5 µg/L	0.25 µg/L
552.1, 552.2, 6251 B/DCAA, TCAA, MBAA, DBAA, BCAA	20. µg/L ± 1.0 µg/L	0.50 µg/L
552.1, 552.2, 6251 B/MCAA	20. µg/L ± 1.0 µg/L	1.0 µg/L
300.0/ClO <sub>2</sub> <sup>-</sup> , ClO <sub>3</sub> <sup>-</sup>	250 µg/L ± 10. µg/L	10. µg/L
300.0/BrO <sub>3</sub> <sup>-</sup>	10. µg/L ± 0.50 µg/L	5.0 µg/L
300.0/Br <sup>-</sup>	0.10 mg/L ± 0.010 mg/L	0.010 mg/L
5310 B, 5310 C, 5310 D/TOC	4.0 mg/L ± 0.50 mg/L	0.50 mg/L
5910 B/UV <sub>254</sub>	6.5 mg/L* ± 0.50 mg/L (This DOC concentration produces an absorbance reading of 0.10 cm <sup>-1</sup> .)	0.50 mg/L* (This DOC concentration produces an absorbance reading of 0.009 cm <sup>-1</sup> .)
5320 B/TOX	250 µg Cl <sup>-</sup> /L ± 10 µg Cl <sup>-</sup> /L	25. µg Cl <sup>-</sup> /L
6252 B/Formaldehyde**	20. µg/L ± 1.0 µg/L	1.0 µg/L
6252 B/Acetaldehyde, Butanal, Glyoxal, Methyl Glyoxal, Pentanal, Propanal (Optional: Benzaldehyde, Decanal, Hexanal, Heptanal, Nonanal, Octanal)	20. µg/L ± 1.0 µg/L	0.50 µg/L
Low BrO <sub>3</sub> <sup>-</sup> **	1.0 µg/L ± 0.1 µg/L	0.20 µg/L
modified 524.2/CNCl**	5.0 µg/L ± 0.5 µg/L	0.50 µg/L
350.1, 4500-NH <sub>3</sub> D, 4500-NH <sub>3</sub> G, 379-75 WE/Ammonia	1.0 mg/L ± 0.1 mg/L	Not Applicable ***

\* Concentration as dissolved organic carbon (DOC) in potassium hydrogen phthalate (KHP) standards.

\*\* The minimum reporting level (MRL) for this analyte must be as low as possible. Therefore, the concentrations listed here are based on an estimate of the laboratory's capability to report quantitative results at the MRL listed in Table 7.1. The final concentrations may change slightly based on the laboratory's capabilities at the time DBP/ICR monitoring begins.

\*\*\* Laboratory is not required to perform an MDL study for this analyte.



## Section 7. Minimum Reporting Levels

The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. Usually, measurements at the MDL concentration are considered qualitative, because they are not precise enough to meet the needs of the data user(s). If accurate and precise data are required, concentrations are not reported below the level at which the necessary precision and accuracy are achieved.

Based on recommendations from the panel of technical experts, minimum reporting levels (MRLs) were established for the ICR. A list of MRLs is presented in Table 7.1. All laboratories performing analyses for the ICR must be able to measure the analyte concentrations at these levels with specified accuracy and precision. (A discussion of the accuracy and precision requirements is included in Section 9.)

The MRLs were established based on two factors:

- meeting the precision and accuracy criteria at the MRL concentrations was technically feasible without placing undue burden on the laboratories.
- based on current information concerning DBP occurrence, most of the samples analyzed during the ICR are expected to contain concentrations greater than the respective MRL.

Laboratories must demonstrate that they can achieve reliable data at the minimum reporting level (MRL) for each analyte. Therefore, the calibration curve must encompass the MRL concentration. The laboratory must verify the accuracy of the curve at the MRL by analyzing a calibration check standard at the MRL concentration (see Section 9).

EPA recognizes that some laboratories are able to provide reliable data at concentrations lower than those shown in Table 7.1. However, in order to achieve consistency in the ICR Federal Database, laboratories are only required to report quantitative results for concentrations equal to or greater than the MRLs. The laboratory may report lower concentrations to the water utility, but only concentrations equal to or greater than the MRLs will be entered into the ICR Federal Database.

When performing analyses during the treatment studies, laboratories are required to achieve the specified accuracy and precision at lower concentrations for two analyses: TOC and TOX. This is because determining precursor removal efficiencies depends on the capability to obtain quantitative data for samples collected after application of the precursor removal technology. The lower MRL reporting requirements for the treatment studies are listed in Table 7.1 and subsequent tables in this manual.

**Table 7.1. Minimum Reporting Levels (MRLs)**

Method/Analyte(s)	MRL
502.2, 524.2, & 551, 551.1/CHCl <sub>3</sub> , BDCM, CDBM, CHBr <sub>3</sub>	1.0 µg/L for each analyte
551.1/TCAN, DCAN, BCAN, DBAN, DCP, TCP, CP, CH	0.50 µg/L for each analyte
552.1, 552.2, 6251 B/DCAA, TCAA, MBAA, DBAA, BCAA	1.0 µg/L for each analyte
552.1, 552.2, 6251 B/MCAA	2.0 µg/L
552.2/BDCAA (Optional)	1.0 µg/L
552.2/CDBAA (Optional)	2.0 µg/L
552.2/TBAA (Optional)	4.0 µg/L
300.0/Br <sup>-</sup>	0.020 mg/L
300.0/ClO <sub>2</sub> <sup>-</sup> , ClO <sub>3</sub> <sup>-</sup>	20. µg/L for each analyte
300.0/BrO <sub>3</sub> <sup>-</sup>	5.0 µg/L
5310 B, 5310 C, 5310 D/TOC	0.70 mg/L (0.50 mg/L during treatment studies)
5910 B/UV <sub>254</sub>	0.009 cm <sup>-1</sup>
5320 B/TOX	50. µg Cl <sup>-</sup> /L (25. µg Cl <sup>-</sup> /L during treatment studies)
6252 B/Formaldehyde*	2.0 µg/L
6252 B/Acetaldehyde, Butanal, Glyoxal, Methyl Glyoxal, Pentanal, Propanal Optional: Benzaldehyde, Decanal, Hexanal, Heptanal, Nonanal, Octanal	1.0
Low BrO <sub>3</sub> <sup>-</sup> *	0.20 µg/L
modified 524.2/CNCl*	0.50 µg/L

\* The minimum reporting level (MRL) for this analyte must be as low as possible. Therefore, the concentration listed here is based on an estimate of the laboratory's capability to report quantitative results at the MRL. The final concentrations may change slightly based on the laboratory's capabilities at the time DBP/ICR monitoring begins.

## **Section 8. Performance Evaluation (PE) Studies**

### **Requirements for Initial Approval via Existing State Certification/Approval**

Laboratories that apply for approval to perform ICR analyses based on current state certification or approval status (see Section 4) are not required to participate in special PE studies prior to receiving ICR Laboratory Approval for those analyses.

### **Requirements for Initial Approval - Analyses Not Covered by State Certification/Approval**

Laboratories that apply for approval to perform one of the ICR analyses not covered by state certification or approval programs (see Section 4) are required to demonstrate their capabilities to perform the analysis through successful participation in Performance Evaluation (PE) Studies. This must be demonstrated in one of two ways for laboratories that submit completed application packages no later than three months following the ICR promulgation date:

- Successful analysis of an ICR Chemistry PE Study sample using the method for which approval is desired. (If the laboratory participated in more than one of these studies prior to applying for approval, then successful performance must be demonstrated in the most recent study in which the laboratory participated.) EPA conducted two ICR Chemistry PE Studies prior to promulgation of the ICR. Study 1 was completed in August of 1994 and Study 2 was completed in March of 1995. Two additional ICR Chemistry PE Studies (3 & 4) will be conducted prior to the start of the 18-month monitoring period and laboratories can participate in one or more of these four studies to demonstrate capability to successfully perform analyses for the ICR.

**OR**

- Provide data from the three most recent Water Supply (WS) or Water Pollution (WP) PE studies in which the laboratory participated using the method for which approval is desired. All PE data must be from studies conducted after June 1993 with at least one set of data from a study conducted after June 1994. (This ensures that at least some of the data were generated in the same time frame as when the first two ICR Chemistry PE Studies were conducted.) The laboratory must have successfully analyzed two samples, including the most recent one, in these studies. (If a laboratory only participated in two WS or WP studies and both were successfully completed, then the laboratory has also met the PE requirements for approval.)

Laboratories that submit applications for approval more than three months after the ICR promulgation date must successfully participate in an ICR Chemistry PE Study prior to receiving approval. (Approval to perform ammonia analyses will be granted based on WP PE study data, because this parameter is not included in the ICR Chemistry PE Studies.)

Successful performance in the above-mentioned PE studies (ICR, WS, or WP) is defined as meeting the acceptance criteria listed in Table 8.1. (Note that these criteria are different from the acceptance criteria normally applied to data in WS or WP PE studies.)

Two analytical methods approved for use during the ICR were not available to laboratories when ICR Chemistry PE Studies 1 and 2 were conducted. Because EPA Method 551.1 is very similar to EPA Method 551, EPA will accept PE Study 1 and 2 data generated using 551 as the basis for meeting the PE acceptance criteria for approval to perform Method 551.1. However, laboratories must use 551.1 (not 551) in ICR Chemistry PE Studies conducted after the ICR promulgation date and during the 18-month monitoring period.

EPA Method 552.2 was also not available during ICR Chemistry PE Studies 1 and 2. Laboratories are required to successfully analyze a PE sample using Method 552.2 in order to meet the PE acceptance criteria for laboratory approval, if they propose to use Method 552.2 to analyze samples for the ICR.

### **ICR Chemistry PE Studies During Monitoring**

EPA will conduct ICR Chemistry PE Studies on approximately a quarterly basis beginning shortly prior to the 18-month monitoring period. All laboratories approved for the analyses listed in Table 8.1 are required to participate in these studies in order to maintain ICR Laboratory Approval. The first of these "required" studies (ICR Chemistry PE Study 4) will be conducted close to the start of monitoring, in order to verify that previously approved laboratories are still capable of acceptable performance. The acceptance criteria described in Table 8.1 will apply for all ICR Chemistry PE Studies.

ICR Chemistry PE Studies 5 through 9 will be conducted during the 18-month monitoring period. Further details on how these studies will be used to monitor laboratory performance are given in Section 11.

Laboratories that perform general water quality analyses (pH, alkalinity, turbidity, calcium hardness, total hardness, ammonia, and disinfectant residuals) are strongly encouraged to analyze and pass a PE sample annually. Acceptance criteria for these analyses are listed in Table 8.2. PE samples for these analytes can be obtained as part of the routine EPA Water Supply (WS) or Water Pollution (WP) Series PE Studies. There is no requirement to report these WS or WP PE studies to the ICR Laboratory Coordinator, but the results should be kept on file.

**Table 8.1. Acceptance Criteria for ICR Chemistry PE Studies**

ICR Parameter (# of cpds)	Pass Criteria (% of True Value)	Minimum # of cpds passing
Bromide	$\pm 35\%$ <sup>(1)</sup>	
Chloral Hydrate	$\pm 40\%$ <sup>(2)</sup>	
Haloacetic Acids (6)	$\pm 40\%$ for each cpd <sup>(2)</sup>	4 of 5 cpds (excluding MCAA)
Haloacetonitriles (4) and Haloketones (2)	$\pm 40\%$ for each cpd <sup>(2)</sup>	4 of 5 cpds (excluding TCAN)
Inorganic DBPs (3)	$\pm 40\%$ for each ion <sup>(2)</sup>	3 of 3 ions
Trihalomethanes (4)	$\pm 20\%$ for each cpd <sup>(3)</sup>	3 of 4 cpds
TOC	$\pm 25\%$ <sup>(1)</sup>	
TOX	$\pm 25\%$ <sup>(1)</sup>	
UV Absorbance at 254nm	$\pm 25\%$ <sup>(4)</sup>	

<sup>(1)</sup> The listed value was derived from laboratory performance data given in the method, ASTM laboratory studies and/or EPA PE studies

<sup>(2)</sup> These values were established by recommendation of the expert panel.

<sup>(3)</sup> EPA criterion for TTHM drinking water laboratory certification.

<sup>(4)</sup> Determined from interlaboratory data given in SM 5910 B. The value given represents twice the maximum percent relative standard deviation for absorbances  $\geq 0.014 \text{ cm}^{-1}$  at 254nm for potassium acid phthalate concentrations from 0.93 to 100 mg/L (as Dissolved Organic Carbon).

**Table 8.2. PE Acceptance Criteria for ICR General Water Quality Parameters**

ICR Parameter (# of cpds)	Pass Criteria (% of True Value)
Alkalinity	$\pm 15\%$ <sup>(1)</sup>
Ammonia	$\pm 30\%$ <sup>(2)</sup>
Chlorine - Free	$\pm 30\%$ <sup>(1)</sup>
Chlorine - Total	$\pm 30\%$ <sup>(1)</sup>
Hardness - Calcium	$\pm 10\%$ <sup>(1)</sup>
Hardness - Total	$\pm 20\%$ <sup>(1)</sup>
pH	$\pm 5\%$ <sup>(1)</sup>
Turbidity	$\pm 20\%$ <sup>(1)</sup>

- <sup>(1)</sup> This criterion was determined based on the results from at least four EPA WS/WP PE studies. The relative percent deviation was calculated for each study by dividing the concentration represented by two standard deviations, around the study true value, by the true value, and multiplying by 100%. The maximum relative percent deviation from the studies was used as the basis for this criterion.
- <sup>(2)</sup> The listed value was derived from laboratory performance data given in the method, ASTM laboratory studies and/or EPA PE studies.

## Section 9. Quality Control Requirements

Laboratories that perform analyses for the DBP/ICR and Treatment Study/ICR are required to use only the analytical methods specified in the ICR. (See Section 5 for a listing of the methods.) These methods specify quality control (QC) procedures which must be followed to ensure accurate and precise data.

QC procedures and the frequency of QC testing vary among the methods. In an effort to standardize these requirements and to obtain consistent application of QC protocols, a frequency for performing QC analyses has been established for many of the methods specified in the ICR. This standardization was necessary because much of the QC data for these analyses is being reported to EPA and the water utilities in order to document the quality of the monitoring data.

Many of the methods specified in the ICR provide criteria to be used in evaluating and accepting laboratory performance based on related QC data. These criteria were compared to what EPA and technical experts believe are necessary to meet the objectives of the ICR. This comparison indicated that some of the QC procedures required by the ICR are not specifically addressed in some methods, and in other methods the QC acceptance criteria are different from those identified as necessary for the ICR.

This section describes the various QC procedures required as part of the ICR and the rationale for the ICR acceptance criteria. The general water quality parameters (alkalinity, ammonia, calcium hardness, disinfectant residuals, pH, temperature, total hardness, and turbidity) are not addressed in this section, because there are no QC reporting requirements for them included in the ICR Laboratory Quality Control (QC) Database System. Laboratories performing analyses for the general water quality parameters must adhere to the QC protocols specified in the methods and they are encouraged to take additional measures as appropriate.

Aldehydes, cyanogen chloride, and low-level  $\text{BrO}_3^-$  are discussed in this section even though these ICR analyses are being conducted by EPA. They are included simply to document the QC criteria that are applicable.

It is imperative that laboratories adhere to the QC described in this section, because monitoring data will be deleted from the ICR Federal Database if the applicable ICR QC requirements are not met. Loss of monitoring data due to failures in QC could result in loss of ICR laboratory approval (see Section 11). The following will cause monitoring data to be invalidated and not included in the database:

- failure to use the correct calibration check standard concentration
- failure to verify the calibration curve at the specified frequency

- failure to meet the acceptance criteria for verifying calibration
- analytes detected in the laboratory reagent (method) blank at concentrations equal to or more than one-half the minimum reporting level
- for aldehydes, analytes detected at concentrations equal to or more than one-half the minimum reporting level in the field reagent (shipping or travel) blank
- for TOC and UV<sub>254</sub>, failure to meet the precision acceptance criteria for duplicate analyses
- when applicable, failure to meet the acceptance criteria for the internal standard
- when applicable, failure to meet the acceptance criteria for the surrogate standard.
- when applicable, failure to measure and report the pH of samples prior to analysis.
- failure to analyze samples and/or extracts within the specified holding times.
- for TOX, TOC, and UV<sub>254</sub>, failure to analyze ICR samples in duplicate

Laboratories must also report the following QC data in order to maintain ICR laboratory approval. Since these data are being collected to evaluate the quality of the monitoring data, there are no acceptance criteria for them and the data will not impact laboratory approval:

- duplicate analyses, except for TOC and UV<sub>254</sub>
- laboratory fortified matrix (spiked) sample recoveries.

## Calibration

Each method describes calibration procedures that are used to determine the concentrations of the method analytes. Some methods allow several options:

- a calibration curve based on either external standards or detector responses to the analyte relative to an internal standard
- an average response factor for each analyte
- a single point calibration.

The laboratory must select and follow one of the calibration procedures outlined in the approved method in order to meet the requirements of the ICR. In addition, the mass spectrometer method has specific tuning criteria that must be met prior to performing the calibration procedure.

All methods specified in the ICR require that calibration span the expected concentration range of the samples being analyzed. The number of calibration standards necessary to do this varies from one to five, depending upon the method. The ICR does not require laboratories to change method calibration procedures, nor does it specify the concentrations of the standards to be used in the calibration process. (Note: There is no calibration process for the UV<sub>254</sub> analysis. The method only requires that the spectrophotometer performance be checked using a standard.)

One of the techniques that EPA will use to assure that data generated in many laboratories are consistent is to provide stock solutions of the method analytes to each laboratory that is approved to perform the analysis. The laboratories are required to use these stock solutions in the preparation of the standards that are used for calibration.

## **Verify Calibration**

The analyst must periodically verify calibration during the analysis of samples in order to ensure accuracy of the analytical results. The methods vary in the frequency at which calibration must be checked. In order to meet the accuracy requirements of the ICR, EPA is defining specific frequencies at which the instrument calibration must be verified. These frequencies are listed in Table 9.1.

Most of the methods recommend checking the instrument calibration using a mid-level calibration check standard. The method acceptance criteria for verifying calibration are based on this standard. However, in order to meet the objectives of the ICR, calibration must be verified across the range of analyte concentrations that are being measured. Based on the recommendations from technical experts experienced with these methods, EPA is specifying three concentrations at which the calibration must be verified for each method. These concentrations were chosen based on the concentrations that are expected to be found in samples collected for the ICR. Laboratories are required to prepare and use aqueous calibration check standards with concentrations that are within  $\pm 20\%$  of the concentrations listed in Tables 9.2-9.4 when they verify their calibration curves. The check standards must be processed through each step of the sample preparation procedure prior to analysis.

The frequency of verifying calibration for ICR samples is based on the number of samples being analyzed together in an analysis batch. For the ICR, an analysis batch is defined as samples analyzed using the same instrument within a 24 hour period AND the maximum number of ICR samples that can be included in one analysis batch is 30. The 24-hour period begins with the analysis of the low-level calibration check standard and it ends with the analysis of the final calibration check standard. The 24-hour period does not necessarily include the analysis time used to generate the calibration curve. However, if a new curve is prepared each time samples are analyzed, the 24-hour period still begins with the analysis of the low level calibration check standard.

Method blanks, shipping blanks, calibration check standards, duplicate samples, fortified samples, and any independent QC samples [see Quality Control (QC) Sample Subsection] that are analyzed with the ICR samples are not counted in determining the 30 sample maximum.

Analysis of the low-level calibration check standard must be completed prior to analysis of any samples and each analyte must meet the acceptance criteria given in Table 9.2. If the criteria cannot be met, the source of the problem must be identified and eliminated. Then a new instrument calibration must be performed according to the method calibration procedures.

After analyses of no more than ten ICR samples for all methods except TOX (no more than seven TOX samples analyzed in duplicate), the calibration curve must be verified using either a mid- or high-level calibration check standard and each analyte must meet the acceptance criteria listed in Table 9.3 or 9.4. If the criteria are not met, then all samples or extracts that were analyzed between this standard and the last one meeting the acceptance criteria must be reanalyzed for the problem analyte(s) after the calibration problem is resolved. If the samples or extracts cannot be reanalyzed, then the data for the problem analyte(s) are considered invalid for those samples and the monitoring data should be flagged as not meeting QC criteria. If reported, these monitoring data will be deleted from the ICR Federal Database.

After each additional ten ICR samples (or seven TOX samples analyzed in duplicate), the curve must be verified by alternating between the mid- and high-level check standards. The final analysis in an analysis batch MUST be a calibration check standard and all the analytes must meet the acceptance criteria.

The interval between calibration check standards is smaller for TOX than the other analyses, because each ICR TOX field sample must be analyzed in duplicate. Seven is approximately the number of field samples that can be realistically analyzed in duplicate by an analyst during a routine work shift.

The TOX, TOC and  $UV_{254}$  methods specify that each analysis should be performed in duplicate. EPA will not require laboratories to analyze TOX calibration check standards in duplicate. However, TOC and  $UV_{254}$  analyses of calibration check standards must be performed in duplicate and the analyses must meet the precision acceptance criteria listed in Table 9.2, 9.3, or 9.4 in addition to the accuracy requirements. The relative percent differences (RPDs) listed in Tables 9.2, 9.3 and 9.4 are calculated using the following formula:

$$RPD = [|r_1 - r_2| / ((r_1 + r_2)/2)] \times 100, \text{ where}$$

RPD = Relative Percent Difference

$r_1$  = First analytical result

$r_2$  = Duplicate analytical result

**Table 9.1. Frequency Requirements for Verifying Calibration**

Method	Method Specifications	ICR Specifications
502.2 (THMs)	Daily	Use low-level calibration check standard to verify calibration before analysis of first sample. Verify calibration after every tenth sample and after last sample in analysis batch by alternating between mid- and high-level calibration check standards.
524.2 (THMs)	Beginning each 8-hr work shift	
551 (THMs)	<u>External Standard Calibration</u> : Check at beginning and end of analysis day <u>Internal Standard Calibration</u> : Check at beginning of day plus monitor IS response in all samples	
551.1 (THMs, HANs, HKs, CP, & CH)	Preceding each analysis set, after every tenth sample analysis and after the final sample analysis	
552.1 (HAAs)	Daily	
552.2 (HAAs)	Preceding each analysis set, after every tenth sample analysis and after the final sample analysis	
6251 B (HAAs)	With each sample batch	
300.0 (Br <sup>-</sup> , BrO <sub>3</sub> <sup>-</sup> , ClO <sub>2</sub> <sup>-</sup> , ClO <sub>3</sub> <sup>-</sup> )	After every tenth sample plus at the beginning of each 8 hour period and as the last analysis run on the instrument	
5310 B, 5310 C, 5310 D (TOC)	Daily	
5910 B (UV <sub>254</sub> )	Daily	
5320 B (TOX)	Perform several microcoulometer/titration cell checks with NaCl std soln at start of each day; Analyze several nonvolatile TOX calibration stds daily	Perform 3 microcoulometer/titration cell checks with NaCl std soln at beginning of each 8-10 hr work shift; Use low-level calibration check standard to verify calibration before analysis of first sample. Verify calibration after every seventh sample (analyzed in duplicate) and after last sample in analysis batch by alternating between mid- and high-level calibration check standards
6252 B Aldehydes	Daily	Use low-level calibration check standard to verify calibration before analysis of first sample. Verify calibration after every tenth sample and after last sample in analysis batch by alternating between mid- and high-level calibration check standards.
Low BrO <sub>3</sub> <sup>-</sup>	Not specified	
modified 524.2 (CNCI)	Beginning each 8-hr work shift	

**Table 9.2. Low-Level Calibration Check Standard Concentrations & Acceptance Criteria**

Method/Analyte(s)	Low-Level Standard	Acceptance Criteria
502.2, 524.2, 551, 551.1/CHCl <sub>3</sub> , BDCM, CDBM, CHBr <sub>3</sub>	1.0 µg/L	50 - 150%
551.1/TCAN, DCAN, BCAN, DBAN, DCP, TCP, CP, CH	0.50 µg/L	50 - 150%
552.1, 552.2, 6251 B/DCAA, TCAA, MBAA, DBAA, BCAA	1.0 µg/L	50 - 150%
552.1, 552.2, 6251 B/MCAA	2.0 µg/L	50 - 150%
552.2/BDCAA (Optional)	1.0 µg/L	50 - 150%
552.2/CDBAA (Optional)	2.0 µg/L	50 - 150%
552.2/TBAA (Optional)	4.0 µg/L	50 - 150%
300.0/Br <sup>-</sup>	0.020 mg/L	50 - 150%
300.0/ClO <sub>2</sub> <sup>-</sup> , ClO <sub>3</sub> <sup>-</sup>	20. µg/L	75 - 125%
300.0/BrO <sub>3</sub> <sup>-</sup>	5.0 µg/L	50 - 150%
5310 B, 5310 C, 5310 D/TOC	0.70 mg/L (0.50 mg/L during treatment studies)	50 - 150% (≤20% RPD)
5910 B/UV <sub>254</sub>	.009 cm <sup>-1</sup> (prepared using 0.50 mg/L as DOC*)	75 - 125% (≤20% RPD)
5320 B/TOX	50. µg Cl <sup>-</sup> /L (25. µg Cl <sup>-</sup> /L during treatment studies)	75 - 125%
6252 B/Formaldehyde**	2.0 µg/L	50 - 150%
6252 B/Acetaldehyde, Butanal, Glyoxal, Methyl Glyoxal, Pentanal, Propanal Optional: Benzaldehyde, Decanal, Hexanal, Heptanal, Nonanal, Octanal	1.0 µg/L	50 - 150%
Low BrO <sub>3</sub> <sup>-</sup> **	0.20 µg/L	75 - 125%
modified 524.2/CNCl **	0.50 µg/L	50 - 150%

\* Concentration as dissolved organic carbon (DOC) in potassium hydrogen phthalate (KHP) standards.

\*\* The minimum reporting level (MRL) for this analyte must be as low as possible. Therefore, the concentrations listed here are based on an estimate of the laboratory's capability to report quantitative results at the MRL listed in Table 7.1. The final concentrations may change slightly based on the laboratory's capabilities at the time DBP/ICR monitoring begins.

**Table 9.3. Mid-Level Calibration Check Standard Concentrations & Acceptance Criteria**

Method/Analyte(s)	Mid-Level Standard	Acceptance Criteria
502.2, 524.2, 551, 551.1/CHCl <sub>3</sub> , BDCM, CDBM, CHBr <sub>3</sub>	20. µg/L	80 - 120%
551.1/TCAN, DCAN, BCAN, DBAN, DCP, TCP, CP	5.0 µg/L	80 - 120%
551.1/CH	10. µg/L	80 - 120%
552.1, 552.2, 6251 B/MCAA, DCAA, TCAA, MBAA, DBAA, BCAA	20. µg/L	80 - 120%
552.2/BDCAA, CDBAA, TBAA (Optional)	20. µg/L	80 - 120%
300.0/Br <sup>-</sup>	0.10 mg/L	90 - 110%
300.0/ClO <sub>2</sub> <sup>-</sup> , ClO <sub>3</sub> <sup>-</sup>	250 µg/L	90 - 110%
300.0/BrO <sub>3</sub> <sup>-</sup>	10. µg/L	80 - 120%
5310 B, 5310 C, 5310 D/TOC	4.0 mg/L	90 - 110% (≤10% RPD)
5910 B/UV <sub>254</sub>	.088 cm <sup>-1</sup> (prepared using 6.0 mg/L as DOC*)	85 - 115% (≤10% RPD)
5320 B/TOX	200 µg Cl <sup>-</sup> /L	85 - 115%
6252 B/Formaldehyde, Acetaldehyde, Butanal, Glyoxal, Methyl Glyoxal, Pentanal, Propanal Optional: Benzaldehyde, Decanal, Hexanal, Heptanal, Nonanal, Octanal	10. µg/L	80 - 120%
Low BrO <sub>3</sub> <sup>-</sup>	1.0 µg/L	80 - 120%
modified 524.2/CNCl	5.0 µg/L	80 - 120%

\* Concentration as dissolved organic carbon (DOC) in potassium hydrogen phthalate (KHP) standards.

**Table 9.4. High-Level Calibration Check Standard Concentrations & Acceptance Criteria**

Method/Analyte(s)	High-Level Standard	Acceptance Criteria
502.2, 524.2, 551, 551.1/CHCl <sub>3</sub> , BDCM, CDBM, CHBr <sub>3</sub>	40. µg/L	80 - 120%
551.1/TCAN, DCAN, BCAN, DBAN, DCP, TCP, CP	15. µg/L	80 - 120%
551.1/CH	25. µg/L	80 - 120%
552.1, 552.2, 6251 B/MCAA, DCAA, TCAA, MBAA, DBAA, BCAA	40. µg/L	80 - 120%
552.2/BDCAA, CDBAA, TBAA (Optional)	40. µg/L	80 - 120%
300.0/Br <sup>-</sup>	0.30 mg/L	90 - 110%
300.0/ClO <sub>2</sub> <sup>-</sup> , ClO <sub>3</sub> <sup>-</sup>	750 µg/L	90 - 110%
300.0/BrO <sub>3</sub> <sup>-</sup>	30. µg/L	90 - 110%
5310 B, 5310 C, 5310 D/TOC	10. mg/L	90 - 110% (≤10% RPD)
5910 B/UV <sub>254</sub>	.87 cm <sup>-1</sup> (prepared using 60. mg/L as DOC*)	85 - 115% (≤10% RPD)
5320 B/TOX	500 µg Cl <sup>-</sup> /L	85 - 115%
6252 B/Formaldehyde, Acetaldehyde, Butanal, Glyoxal, Methyl Glyoxal, Pentanal, Propanal Optional: Benzaldehyde, Decanal, Hexanal, Heptanal, Nonanal, Octanal	40. µg/L	80 - 120%
Low BrO <sub>3</sub> <sup>-</sup>	5.0 µg/L	80 - 120%
modified 524.2/CNCl	20. µg/L	80 - 120%

\* Concentration as dissolved organic carbon (DOC) in potassium hydrogen phthalate (KHP) standards.

## Laboratory Reagent (Method) Blank

All of the methods approved for DBP/ICR monitoring require periodic analysis of a laboratory reagent (method) blank. For all the methods except TOX, this is defined as an aliquot of reagent water that is treated exactly as a sample, including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. This blank is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

The frequency of the laboratory reagent (method) blank analysis depends upon the type of sample manipulation required prior to the instrumental analysis. Methods that involve extraction of the sample usually stipulate analysis of a laboratory reagent blank with each set of samples that are extracted together. When the samples are analyzed directly, a blank is analyzed on a daily basis, with the exception of UV<sub>254</sub> and TOX analyses for which a blank is analyzed after the analysis of every ten and seven samples, respectively.

The required frequencies for analyzing laboratory reagent (method) blanks for the ICR are listed in Table 9.5. In order to meet the objectives of the ICR, the laboratory reagent (method) blank must be analyzed as the first sample on the instrument (prior to the calibration check standard). For methods that involve extractions, the laboratory reagent (method) blank must be carried through the extraction process. Each extraction batch of samples must include a laboratory reagent (method) blank. An extraction batch is defined as all samples prepared/extracted together by the same person(s) during a work day (normally an 8-10 hour period for routine working schedules). The same lot of extracting solvent, internal standard fortifying solution, and surrogate standard fortifying solution must be used for all samples included in a batch. When applicable, all samples in an extraction batch must be derivatized with the same batch of derivatizing agent. A maximum of 20 ICR samples can be included in an extraction batch. Method blanks, shipping blanks, calibration check standards, any independent QC samples [see Quality Control (QC) Sample Subsection], duplicate samples, and fortified samples that are extracted with the ICR samples are not counted as samples in determining the 20 sample maximum.

In the TOX method, several types of blanks are specified, and two of them will be required for the DBP/ICR:

- the laboratory reagent (method) blank - the analysis of 40 mg of nitrate-washed carbon, which is used to correct for TOX found in the carbon.
- the system blank - the analysis of a reagent water blank, which is used to assess background TOX contributions from the equipment, reagents, and procedure.

The laboratory must analyze two laboratory reagent (method) blanks (nitrate-washed activated carbon cartridges) at the beginning of each day and they must meet the acceptance criteria listed in Table 9.6. Analyses must not begin until this criterion is met. The system blank (reagent

water) is analyzed after the method blanks and this blank must meet the criteria listed in Table 9.6. After the TOX analysis of seven ICR samples (analyzed in duplicate), the laboratory is required to analyze another laboratory reagent (method) blank which is also subject to the acceptance criteria listed in Table 9.6. If the acceptance criteria are not met for this method blank, then no further TOX sample analyses should be performed until the source of carbon contamination is eliminated. All samples that were analyzed between this blank and the last one meeting the acceptance criteria must be reanalyzed after the contamination is eliminated. If the samples cannot be reanalyzed, then the TOX data are considered invalid for those samples and the monitoring data should be flagged as not meeting QC criteria. If reported, these TOX monitoring data will be deleted from the ICR Federal Database.

While some methods state that background interferences should be below the minimum detection limit, the general goal for all methods within the ICR is to ensure that the background levels are low enough so that they do not interfere with an accurate measurement. If any of the method analytes are detected at a concentration equal to or greater than half the minimum reporting levels (see Table 9.6), then no further analyses should be performed until the source of the problem is identified and eliminated. If the source is traced to any material that was used in the preparation of the set of samples to be analyzed, then all these prepared samples (or extracts) must be discarded and the preparation procedure repeated using another aliquot of each sample. If the samples cannot be re-extracted, then all data for the problem analyte(s) are considered invalid for all samples in the extraction or analysis batch, as appropriate and the monitoring data should be flagged as not meeting QC criteria. If reported, these monitoring data will be deleted from the ICR Federal Database.

Contamination problems in the extraction process cannot be detected until the analysis step. If a problem is discovered, then the data for one or more analytes in all the samples in the extraction batch are lost unless the laboratory has a back-up aliquot of each sample which can be extracted. EPA limited the extraction batch to 20 ICR samples in order to minimize the number of samples that could be potentially lost due to a contamination problem. More than one batch of samples may be extracted within a day.

Laboratories should be aware of the potential for carryover between samples when highly contaminated samples are analyzed. In order to avoid this, laboratories may find that additional blanks are needed to "rinse" the system after high concentration samples are analyzed. If blanks are analyzed for this purpose, the laboratory is not required to report data from these analyses.

**Table 9.5. Frequency Requirements for Analyzing Laboratory Reagent (Method) Blanks**

Method	Method Specifications	ICR Specifications
502.2 (THMs)	1/batch of samples processed as a group within a work shift	1 per analysis batch
524.2 (THMs)	Daily-shipping blank can be substituted for method blank	
551 (THMs)	1/set of samples	1 per analysis batch (1 per extraction batch)
551.1 (THMs, HANs, HKs, CP, & CH)	1 each time a set of samples is extracted or reagents are changed	
552.1 (HAAs)	1/set of samples	
552.2 (HAAs)	1 each time a set of samples is extracted or reagents are changed	
6251 B (HAAs)	1/set of samples	
300.0 (Br <sup>-</sup> , BrO <sub>3</sub> <sup>-</sup> , ClO <sub>2</sub> <sup>-</sup> , ClO <sub>3</sub> <sup>-</sup> )	1/batch of samples	1 per analysis batch
5310 B, 5310 C, 5310 D (TOC)	Daily	
5910 B (UV <sub>254</sub> )	Initial zero; Check after each 10 samples	Initial zero; Check after each 10 samples
5320 B (TOX)	1/set of 8 samples - minimum of 2/day (nitrate-washed activated carbon)	2 nitrate-washed activated carbon analyses at beginning of each analysis batch, then 1 after every 7 samples (analyzed in duplicate) (minimum of 3/day); Analyze 1 system blank per analysis batch
6252 B (Aldehydes)	1/set of samples	1 per analysis batch (1 per extraction batch)
Low BrO <sub>3</sub> <sup>-</sup>	Not Specified	1 per analysis batch
modified 524.2 (CNCl)	Daily	1 per analysis batch

**Table 9.6. Acceptance Criteria for Laboratory Reagent (Method) Blanks**

Method/Analyte(s)	Maximum Allowable Background Concentration
502.2, 524.2, 551, 551.1/CHCl <sub>3</sub> , BDCM, CDBM, CHBr <sub>3</sub>	< 0.50 µg/L
551.1/TCAN, DCAN, BCAN, DBAN, DCP, TCP, CP, CH	< 0.25 µg/L
552.1, 552.2, 6251 B/DCAA, TCAA, MBAA, DBAA, BCAA	< 0.50 µg/L
552.1, 552.2, 6251 B/MCAA	< 1.0 µg/L
552.2/BDCAA (Optional)	< 0.50 µg/L
552.2/CDBAA (Optional)	< 1.0 µg/L
552.2/TBAA (Optional)	< 2.0 µg/L
300.0/Br <sup>-</sup>	< 0.010 mg/L
300.0/ClO <sub>2</sub> <sup>-</sup> , ClO <sub>3</sub> <sup>-</sup>	< 10. µg/L
300.0/BrO <sub>3</sub> <sup>-</sup>	< 2.5 µg/L
5310 B, 5310 C, 5310 D/TOC	< 0.35 mg/L (< 0.25 mg/L during treatment studies)
5910 B/UV <sub>254</sub>	< 0.0045 cm <sup>-1</sup>
5320 B/TOX	< 0.80 µg Cl <sup>-</sup> /40 mg of activated carbon for method blank < 25. µg Cl <sup>-</sup> /L for system blank (< 12.5 µg Cl <sup>-</sup> /L during treatment studies)
6252 B/Formaldehyde*	< 1.0 µg/L
6252 B/Acetaldehyde, Butanal, Glyoxal, Methyl Glyoxal, Pentanal, Propanal Optional: Benzaldehyde, Decanal, Hexanal, Heptanal, Nonanal, Octanal	< 0.50 µg/L
Low BrO <sub>3</sub> <sup>-</sup> *	< 0.10 µg/L
modified 524.2/CNCl *	< 0.25 µg/L

- \* The minimum reporting level (MRL) for this analyte must be as low as possible. Therefore, the concentrations listed here are based on an estimate of the laboratory's capability to report quantitative results at the MRL listed in Table 7.1. The final concentrations may change slightly based on the laboratory's capabilities at the time DBP/ICR monitoring begins. The value in this table will be set at less than one-half the MRL.

## **Field Reagent Blank (Shipping Blank or Travel Blank)**

Five of the DBP/ICR methods require the preparation and analysis of a field reagent blank with each group of samples collected from the same general sample site at approximately the same time. This blank is an aliquot of reagent water or other blank matrix that is placed in a sample container in the laboratory and treated as a sample in all respects, including shipment to the sampling site, storage, preservation, and all analytical procedures. The purpose of this blank is to determine if method analytes or other interferences are present in the field or shipping environment.

If analyses using EPA Methods 502.2 or 524.2 are being performed only for the ICR, then field reagent blanks will not be required. It is rare to find trihalomethane (THM) contamination as a result of the shipping or storage conditions. (Field reagent blanks in Methods 502.2 and 524.2 are primarily focused on the volatile organic compounds that are measured by these methods.) However, laboratories may be required to include field reagent blanks in their sample's sets, if the analyses are being conducted for compliance with non-ICR Rules.

Field reagent blanks are required for aldehyde analyses. Formaldehyde contamination can result from improper sample containers or shipping material, or as a result of atmospheric contamination. A field reagent blank should be prepared in the laboratory using the same type of sample bottle and dechlorinating agent used in the collection of the aldehyde samples. This blank should accompany the sample bottles to the utility and it should be carried to each aldehyde sampling point. The blank should NOT be opened during this process. At the conclusion of sampling, the field reagent blank should be sent back to the laboratory with the group of samples collected at the utility (defined as a shipping batch) and it should be stored with the samples until processing. This blank should then be processed and analyzed with the samples from that utility. If any of the analytes are detected at concentrations equal to or greater than half the minimum reporting level, then all data for the problem analyte(s) are considered invalid for all samples in the shipping batch and the monitoring data should be flagged as not meeting QC criteria. If reported, these monitoring data will be deleted from the ICR Federal Database.

The requirements for field reagent blanks are listed in Table 9.7.

**Table 9.7. Requirements for Analyzing Field Reagent Blanks (Shipping Blanks)**

Method	Method Specifications	ICR Specifications	ICR Acceptance Criteria
502.2, 524.2 (THMs)	1/set of field samples	There will not be an ICR requirement to perform these analyses.	Methods do not set acceptance criteria for these analyses & no criteria are necessary for the ICR
6252 B (Aldehydes)	1/sampling location	1/shipping batch	< 1.0 $\mu\text{g/L}$ for formaldehyde, < 0.50 $\mu\text{g/L}$ for all other aldehydes

### Quality Control (QC) Sample

Most of the DBP/ICR analytical methods recommend that the laboratory analyze a quality control (QC) sample at least quarterly. A QC sample is a solution of method analytes of known concentration which is used to fortify an aliquot of reagent water or sample matrix. The QC sample is obtained from a source external to the laboratory, and different from the source of calibration standards. It is used to check laboratory performance.

One of the major reasons for analyzing a QC sample is to check the accuracy of the standards being used to calibrate the analytical instrumentation. Since EPA is providing the primary analytical standards for the DBP/ICR methods discussed in this section, all DBP/ICR laboratories will be using comparable standards of known quality. In addition, all of the DBP/ICR methods require the use of aqueous standards that are processed in the same way as the samples. This further minimizes the possibility of analytical errors.

Since EPA is providing the stock solutions for the preparation of calibration standards, laboratories are not required to analyze and report results from QC samples as part of the ICR. However, the use of QC samples is encouraged. Laboratories may wish to check their performance using QC samples containing concentrations that are known to them. Laboratories can prepare their own QC samples or purchase QC samples from one of several commercial suppliers. Splitting samples with another laboratory is another mechanism for evaluating performance. Use of either or both of these procedures is encouraged, especially when laboratories (or analysts) are developing capabilities to perform new methods.

## Laboratory Duplicates

One technique that is useful in evaluating a laboratory's precision for a method is to determine the precision of replicate analyses. The sample is divided into two or more aliquots in the laboratory and the aliquots are processed and analyzed as separate samples. This technique is only useful when the original sample contains background concentrations of the method analytes. Most samples that are analyzed using the DBP/ICR methods discussed in this section are expected to contain measurable concentrations of the majority of the analytes. Therefore, replicate analyses will be a valuable tool for determining the precision of the DBP/ICR monitoring data.

The DBP/ICR approved methods vary in their requirements pertaining to duplicates. There are generally two types of duplicate samples:

**Field Duplicates** - two separate samples collected at the same time and place under identical circumstances and treated exactly the same throughout field and laboratory procedures

**Laboratory Duplicates** - one sample divided into two aliquots in the lab and analyzed as two separate samples

Some methods specify the analysis of field duplicates, while other methods require laboratory duplicate analyses for all samples, and field duplicate analyses for a percentage of the samples. Several methods do not discuss any duplicate analyses. For the ICR, all duplicates will be laboratory duplicates, with the exception of samples which are analyzed using EPA Methods 502.2, 551.1 and 524.2. These methods require the use of field duplicates, because the sample is analyzed directly from the sample bottle. (The extraction is performed in the sample bottle in 551.1. Samples for 502.2 and 524.2 are usually collected in vials that contain only enough sample for one analysis and the vials are loaded directly onto an autosampler.)

The required frequencies for analyzing duplicates for the ICR are listed in Table 9.8. With the exception of TOX, TOC and UV<sub>254</sub> analyses, laboratories are required to perform duplicate analyses on a minimum of 5% of the ICR samples that are processed together. For methods that involve extractions, this means that at least one sample from each extraction batch must be divided into two aliquots prior to extraction. Both aliquots must be carried through the entire extraction and analysis process. For methods that do not involve extractions, this means that for analysis batches of 20 or less, one of the ICR samples in the batch must be analyzed in duplicate. If the analysis batch contains more than 20 ICR samples, then two samples must be analyzed in duplicate.

**Note:** As described earlier in this section under "Laboratory Reagent Blank," an extraction batch is defined as all samples prepared/extracted together by the same person(s) during a work day. The same lot of extracting solvent, internal standard fortifying solution, and surrogate standard fortifying solution must be used for all samples included in a batch. When applicable, all samples in a batch must be derivatized with the same batch of derivatizing agent. A maximum of 20 ICR

samples can be included in an extraction batch in order to minimize the potential for loss of data. As described earlier in this section under "Verify Calibration," an analysis batch is defined as samples analyzed within a 24-hour period AND the maximum number of samples that can be included in one analysis batch is 30.

Since duplicate measurements are only required on 5% of the samples in a batch, the precision data may not reflect the laboratory's performance on samples from a specific utility unless the laboratory is analyzing samples from only one utility. The laboratory will randomly select one of the samples being processed in the batch, unless it has an agreement with a specific utility to provide duplicate analyses.

EPA plans to use the data from duplicate analyses to provide an estimate of the precision of measurements made by individual laboratories. Subsets of the ICR monitoring data may be selected for specific modeling or correlational analyses, based on laboratory precision for the analytes of interest. The precision data from Methods 502.2, 551.1 and 524.2 will also provide an estimate of the overall precision of the ICR data for those three analyses, because they are generated using field duplicates.

With the exception of TOC and  $UV_{254}$ , laboratories will not be required to meet specific precision requirements for the duplicate analyses. TOC and  $UV_{254}$  duplicates must meet the requirements listed in Table 9.8 in order to be considered valid. Failure to meet the precision requirements indicates the instrument is not operating properly and the sample(s) should be reanalyzed. If this cannot be done, the monitoring data should be flagged as not meeting QC criteria. These data will not be entered into the ICR database.

**Table 9.8. Requirements for Performing Laboratory Duplicate Analyses**

Method	Method Specifications	ICR Specifications
502.2 (THMs)	No Requirement	At least 5% of the samples in each analysis batch (field duplicates)
524.2 (THMs)	No Requirement	At least 5% of the samples in each analysis batch (field duplicates)
551 (THMs)	No Requirement	1 laboratory duplicate per extraction batch
551.1 (THMs, HANs, HKs, CP, & CH)	(Field dups) 10% or 1 per sample set, whichever is greater	1 field duplicate per extraction batch
552.1 (HAAs)	No Requirement	1 laboratory duplicate per extraction batch
552.2 (HAAs)	No Requirement	
6251 B (HAAs)	10% of Samples	
300.0 (Br <sup>-</sup> , ClO <sub>2</sub> <sup>-</sup> , ClO <sub>3</sub> <sup>-</sup> , & BrO <sub>3</sub> <sup>-</sup> )	No Requirement	At least 5% of the samples in each analysis batch (laboratory duplicates)
5310 B, 5310 C, 5310 D (TOC)	No Requirement	All samples analyzed in duplicate (laboratory duplicates) (RPD ≤ 20% for TOC concn ≤ 2.0 mg/L; RPD ≤ 10% for TOC concn > 2.0 mg/L)
5910 B (UV <sub>254</sub> )	All samples (plus 10% field duplicates)	All samples analyzed in duplicate (laboratory duplicates) (RPD ≤ 20% for UV <sub>254</sub> ≤ 0.045; RPD ≤ 10% for UV <sub>254</sub> > 0.045)
5320 B (TOX)	All Samples Analyzed in Duplicate, with replicate of a different dilution, so that the concn. ratio is <0.7 or >1.4	All samples analyzed in duplicate (laboratory duplicates)
6252 B (Aldehydes)	10% of Samples	1 laboratory duplicate per extraction batch
Low BrO <sub>3</sub> <sup>-</sup>	Not Specified	At least 5% of the samples in each analysis batch (laboratory duplicates)
modified 524.2 (CNCI)	No Requirement	

## Laboratory Fortified Matrix Sample (Spiked Sample)

A laboratory fortified matrix sample is an aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. This fortified sample is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The concentrations of the analytes in the unfortified sample matrix must be determined in a separate aliquot.

Laboratories are required to fortify samples at the frequencies listed in Table 9.9. The stock solutions of the analytical standards provided by EPA must be used as the basis for preparing the fortified samples. With the exception of analyses for UV<sub>254</sub>, TOX and HAAs by EPA Method 552.1, laboratories are required to perform fortified sample analyses on a minimum of 5% of the ICR samples that are processed together. For methods that involve extractions, this means that one sample from each extraction batch must be fortified with a known concentration of the analytes prior to extraction. Both the fortified and unfortified sample must be carried through the entire extraction and analysis process. For methods that do not involve extractions, this means that for analysis batches of 20 or less, one of the ICR samples in the batch must be fortified and analyzed. If the analysis batch contains more than 20 ICR samples, then two samples must be fortified and analyzed.

**Note:** As described earlier, an extraction batch is defined as all samples prepared/extracted together by the same person(s) during a work day. The same lot of extracting solvent, internal standard fortifying solution, and surrogate standard fortifying solution must be used for all samples included in a batch. When applicable, all samples in a batch must be derivatized with the same batch of derivatizing agent. A maximum of 20 ICR samples can be included in an extraction batch. An analysis batch is defined as samples analyzed within a 24-hour period with 30 as the maximum number of samples that can be included in one analysis batch.

Laboratories will not be required to fortify samples for UV<sub>254</sub> analyses.

A minimum of 5% of all TOX field samples analyzed each quarter (three month period) must be fortified, instead of a minimum of 5% of the field samples that are processed together. This means at least one sample out of every 20 samples (excluding duplicates) must be fortified. This requirement for TOX is less stringent than for the other ICR analyses due to the relative labor intensity of the method. The fortified TOX sample must be analyzed in duplicate.

EPA Method 552.1 is subject to matrix interferences (see Section 4 of the method), so laboratories must demonstrate that use of this method is appropriate for the samples they are analyzing. At least one sample from each set of quarterly samples received from a water utility must be fortified. This requirement may mean that laboratories analyzing samples from many water utilities must fortify more than 5% of the samples that are processed together.

The laboratory must choose a fortifying concentration from one of the three concentrations listed in Table 9.10. The fortifying concentration should be within  $\pm 20\%$  of one of the levels given in the table. In order to obtain reliable data from laboratory fortified samples, the fortifying concentration should be equal to or greater than the background concentration of each analyte present in the sample. If EPA required laboratories to meet this criterion on all fortified samples, laboratories would have to analyze each sample prior to fortifying it. EPA does not consider this a reasonable requirement for meeting the ICR objectives. When possible, EPA recommends that the laboratory select a fortifying concentration based on information provided by the utility. If the utility has information concerning the levels of the various analytes found in samples collected at a previous time, then the laboratory should use these "historical" data to select appropriate fortifying concentrations. If there are no data available to predict the levels of individual analytes, then the laboratory should base the fortification level on the utility's "historical" total trihalomethane (TTHM) levels. (If the utility's TTHMs are normally  $\leq 20 \mu\text{g/L}$ , then the lowest level concentration should be chosen; for TTHMs between 20 and  $50 \mu\text{g/L}$ , the mid-level concentration should be chosen; and for TTHMs  $> 50 \mu\text{g/L}$ , the highest level concentration should be used.) EPA realizes that this system will result in analyses of some fortified samples that are not fortified at appropriate concentrations for all the analytes. However, over the course of the ICR monitoring period, EPA believes that enough data will be obtained to assess the bias of the measurements for all analytes over the range of concentrations found in drinking water samples.

EPA recognizes that for some laboratories, especially commercial laboratories, it may not be feasible to fortify samples using historical information from water utilities. In those cases, the laboratory should rotate the fortification concentrations (low, mid, and high) without regard to the background concentration in the sample matrix.

Laboratories must report all fortified sample recovery data and all data from the batch of samples processed/analyzed with the fortified sample. Data from samples fortified at appropriate concentrations (fortified at concentrations  $\geq$  background concentrations), will be used by EPA to evaluate the quality of the monitoring data. A comparison of recoveries in fortified samples and fortified reagent water (calibration check standards) will indicate whether there is a bias in the ICR monitoring data. Water systems and laboratories may also use these data to determine the appropriateness of the methodology used to analyze the ICR samples.

**Note:** Laboratories do not report the calculated recoveries for fortified samples to EPA. (See Table 10.2.) EPA will calculate recoveries using the data that are submitted by the laboratory and the water system.

Monitoring data will not be rejected from the ICR Federal Database based on fortified sample recovery data.

**Table 9.9. Requirements for Performing Fortified Sample Analyses**

Method	Method Specifications	ICR Specifications
502.2 (THMs)	No Requirement	At least 5% of the ICR samples in each analysis batch
524.2 (THMs)	No Requirement	
551 (THMs)	10% of samples or 1/set (whichever is larger)	At least 1 sample in each extraction batch
551.1 (THMs, HANs, HKs, CP, & CH)	10% of samples or 1/set (whichever is larger)	
552.1 (HAAs)	10% of samples or 1/set	At least 1 sample in each set of quarterly samples from a water utility
552.2 (HAAs)	10% of samples or 1/set (whichever is larger)	At least 1 sample in each extraction batch
6251 B (HAAs)	10% of samples or 1/set	
300.0 (Br <sup>-</sup> , ClO <sub>2</sub> <sup>-</sup> , ClO <sub>3</sub> <sup>-</sup> , BrO <sub>3</sub> <sup>-</sup> )	10% of samples	At least 5% of the ICR samples in each analysis batch
5310 B, 5310 C, 5310 D (TOC)	None Specified	At least 5% of the ICR samples in each analysis batch. (Fortified samples must be analyzed in duplicate.)
5910 (UV <sub>254</sub> )	None Specified	No requirement
5320 B (TOX)	10% of samples	At least 5% of all ICR samples analyzed each quarterly period. (Fortified samples must be analyzed in duplicate.)
6252 B (Aldehydes)	10% of samples or 1/set	At least 1 sample in each extraction batch
Low BrO <sub>3</sub> <sup>-</sup>	Not Specified	At least 5% of the ICR samples in each analysis batch
modified 524.2 (CNCl)	No Requirement	

**Table 9.10. Concentrations for Fortifying Samples**

Method	Low- Level	Mid-Level	High-Level
502.2, 524.2, 551, 551.1/CHCl <sub>3</sub> , BDCM, CDBM, CHBr <sub>3</sub>	1.0 µg/L	20. µg/L	40. µg/L
551.1/TCAN, DCAN, BCAN, DBAN, DCP, TCP, CP	0.50 µg/L	5.0 µg/L	15. µg/L
551.1/CH	0.50 µg/L	10. µg/L	25. µg/L
552.1, 552.2, 6251 B/DCAA, TCAA, MBAA, DBAA, BCAA	1.0 µg/L	20. µg/L	40. µg/L
552.1, 552.2, 6251 B/MCAA	2.0 µg/L	20. µg/L	40. µg/L
552.2/BDCAA (Optional)	1.0 µg/L	20. µg/L	40. µg/L
552.2/CDBAA (Optional)	2.0 µg/L	20. µg/L	40. µg/L
552.2/TBAA (Optional)	4.0 µg/L	20. µg/L	40. µg/L
300.0/Br <sup>-</sup>	0.020 mg/L	0.10 mg/L	0.30 mg/L
300.0/ClO <sub>2</sub> <sup>-</sup> , ClO <sub>3</sub> <sup>-</sup>	20. µg/L	250 µg/L	750 µg/L
300.0/BrO <sub>3</sub> <sup>-</sup>	5.0 µg/L	10. µg/L	30. µg/L
5310 B, 5310 C, 5310 D/TOC	0.70 mg/L (0.50 mg/L during treatment studies)	4.0 mg/L	10. mg/L
5320 B/TOX	50. µg Cl <sup>-</sup> /L (25. µg Cl <sup>-</sup> /L during treatment studies)	200 µg Cl <sup>-</sup> /L	500 µg Cl <sup>-</sup> /L
6252 B/Formaldehyde *	2.0 µg/L	10. µg/L	40. µg/L
6252 B/Acetaldehyde, Butanal, Glyoxal, Methyl Glyoxal, Pentanal, Propanal Optional: Benzaldehyde, Decanal, Hexanal, Heptanal, Nonanal, Octanal	1.0 µg/L	10. µg/L	40. µg/L
Low BrO <sub>3</sub> <sup>-</sup> *	0.20 µg/L	1.0 µg/L	5.0 µg/L
modified 524.2/CNCl *	0.50 µg/L	5.0 µg/L	20. µg/L

\* The minimum reporting level (MRL) for this analyte must be as low as possible. Therefore, the concentrations listed here are based on an estimate of the laboratory's capability to report quantitative results at the MRL listed in Table 7.1. The final concentrations may change slightly based on the laboratory's capabilities at the time DBP/ICR monitoring begins. The low-level fortifying concentration in this table will be set at the MRL.

## Internal Standard

Several of the DBP methods require or recommend the use of an internal standard (IS) for calibration and quantitation purposes. An internal standard is a pure analyte that is added to a sample or sample extract in a known amount. It is used to measure the relative responses of other method analytes and surrogates that are components of the same solution. The IS must be an analyte that is not a sample component. When used, the IS is added to all samples, standards, and QC samples or their extracts.

The methods usually recommend specific compounds and concentrations for use as internal standards. When the method provides flexibility in the selection of the IS or IS concentration, EPA allows the same flexibility during analyses of ICR samples.

The methods vary in their specifications of when the IS is added during the sample processing steps. Some methods require the addition of the IS to the sample prior to any processing, while other methods stipulate the addition to the sample extract immediately prior to instrumental analysis. Laboratories are required to follow the method directions when performing analyses for the ICR.

The methods also vary in the criteria used to evaluate the IS recovery. In general, the detector response to the IS should be monitored in each sample, and it should be relatively constant during the period in which a batch of samples is analyzed. Specific criteria for evaluating the IS for ICR analyses are presented in Table 9.11. Each sample's IS detector response should be compared to the average IS detector response obtained for the calibration curve. The acceptance criteria are given as % Recovery which is determined using the following formula:

$$\text{IS \% Recovery} = \frac{\text{Sample IS detector response}}{\text{Calibration Curve Average IS detector response}} \times 100$$

If the IS in a specific sample does not meet the acceptance criteria, then data from that sample analysis will not be considered valid. If possible, the laboratory should reanalyze the sample. If this cannot be done, then the data for that sample are considered invalid for the analysis and the monitoring data should be flagged as not meeting QC criteria. If reported, these monitoring data will be deleted from the ICR Federal Database.

**Table 9.11. Requirements for Internal Standard Analyses**

Method	Method Specifications	ICR Specifications	ICR Acceptance Criteria
502.2 (THMs)	2-Bromo-1-chloropropane	IS use is optional - depends upon the calibration procedure	70 - 130% Recovery
524.2 (THMs)	Fluorobenzene in each sample	Follow method & add to each sample as directed.	
551 (THMs)	Method doesn't specify compound, but recommends use of appropriate IS in each sample prior to processing (EPA has successfully used 1,2,3-Trichloropropane as IS for this method)	IS use is optional - depends upon the calibration procedure	
551.1 (THMs, HANs, HKs, CP, & CH)	Bromofluorobenzene in each extract (required when pentane is extracting solvent; IS use is optional for MTBE)	Follow method & add to each extract as directed. IS use is optional if MTBE is the extracting solvent.	
552.1 (HAAs)	1,2,3-Trichloropropane in each extract	Follow method & add to each extract as directed.	
552.2 (HAAs)	1,2,3-Trichloropropane in each extract		
6251 B (HAAs)	1,2-Dibromopropane OR 1,2,3-Trichloropropane in each extract		
6252 B (Aldehydes)	1,2-Dibromopropane OR Decafluorobiphenyl in each extract		
modified 524.2 (CNCl)	Fluorobenzene in each sample	Follow method & add to each sample as directed.	

## Surrogate Standard

Several of the DBP methods require the use of surrogate analytes. A surrogate is a pure analyte which is extremely unlikely to be found in any sample. It is added to a sample aliquot in a known amount before the sample is processed, and is measured with the same procedures used to measure other sample components. The purpose of a surrogate analyte is to monitor method performance with each sample. When used, the surrogate is added to all samples, standards, and QC samples.

The methods usually recommend specific compounds and concentrations for use as surrogate standards. When the method provides flexibility in the selection of the surrogate standard or its concentration, EPA allows the same flexibility during analyses of ICR samples.

A list of the methods that require surrogates, and the recommended surrogate(s) for each method, is included in Table 9.12. The criteria for evaluating surrogate recoveries are also listed in Table 9.12. Surrogate recovery must be monitored for each sample, standard and QC sample.

There are two techniques for monitoring the surrogate standard. If the method specifies that the same concentration of surrogate standard must be added to all samples, standards and QC samples, then the surrogate detector response in each analysis must be compared to the average surrogate detector response obtained for the calibration curve. The acceptance criteria are given as % Recovery which is determined using the following formula:

$$\text{Surrogate \% Recovery} = \frac{\text{Sample Surrogate detector response}}{\text{Calibration Curve Average Surrogate Detector Response}} \times 100$$

Some methods recommend preparing a calibration curve for the surrogate standard similar to the preparation of a curve for each of the method analytes. In those cases, the acceptance criteria are given as % Recovery which is determined using the following formula:

$$\text{Surrogate \% Recovery} = \frac{\text{Measured Surrogate Concentration}}{\text{Expected Surrogate Concentration}} \times 100$$

If the surrogate in a specific sample does not meet the acceptance criteria, then if possible, the laboratory should reanalyze the sample. If this cannot be done, then the data for that sample are considered suspect for the analysis in question and the monitoring data should be flagged as not meeting QC criteria. If reported, these monitoring data will be deleted from the ICR Federal Database.

EPA recognizes that failure to meet the surrogate standard recovery criteria could be the result of matrix interferences in a small number of instances. Even if this is the reason for failure, the data are suspect for all the analytes in the analysis and entry of the monitoring data into the ICR Federal Database would dilute the quality of the database.

**Table 9.12. Requirements for Surrogate Standard Analyses**

Method	Method Specifications	ICR Specifications	ICR Acceptance Criteria
524.2 (THMs)	Bromofluorobenzene in each sample	Add to each sample according to the method specifications	70 - 130% Recovery
551.1 (THMs, HANs, HKs, CP, & CH)	Decafluorobiphenyl in each sample		
552.1 (HAAs)	2-bromopropionic acid in each sample		
552.2 (HAAs)	2,3-dibromopropionic acid in each sample		
6251 B (HAAs)	2,3-dibromopropionic acid OR 2,3,5,6-tetrafluorobenzoic acid in each sample		
6252 B (Aldehydes)	2,3,5,6-tetrafluorobenzaldehyde in each sample		

### Additional QC

The laboratory has the responsibility to examine the samples when they arrive in the laboratory to determine if the proper shipping conditions were used. Samples for which the methods specify storage at 4°C should arrive at the laboratory packed in ice or frozen gel packs. If there is no visible ice or the gel packs are completely thawed, the laboratory should report the conditions to the utility. Samples should not be analyzed if they were not shipped properly. If resampling cannot be performed, then the utility should indicate in the report to EPA that the samples were invalidated due to a shipment problem and no data should be reported.

The laboratory also has the responsibility to invalidate samples that were collected in improper sampling containers (e.g., plastic bottles instead of glass) or that were improperly filled (e.g., half-filled bottles for samples that are required to be head-space-free). If resampling cannot be performed, then the utility should indicate in the report to EPA that the samples were invalidated due to a sampling error and no data should be reported.

The stability of some samples is dependent upon proper preservation techniques. The laboratory is required to check the pH of samples that are to be analyzed for haloacetonitriles, chloropicrin, haloketones, chloral hydrate, TOC, or TOX in order to determine that the samples were properly

preserved. The pH can be determined immediately prior to the analysis using narrow range pH paper. If the pH is not within the required ranges (see Table 9.13), the samples should not be analyzed. If resampling cannot be performed, then the utility should indicate in the report to EPA that the samples were invalidated due to a sampling error and no data should be reported.

**Table 9.13. ICR Sample pH Acceptance Criteria**

Method	ICR Specification
551.1 (THMs, HANs, HKs, CP, & CH)	pH $\geq$ 4.5 and pH $\leq$ 5.5
5310 B, 5310 C, 5310 D (TOC)	pH $\leq$ 2.0
5320 B (TOX)	pH $\leq$ 2.0

Finally, the laboratory has the responsibility to ensure each sample is analyzed within the required holding time. A list of applicable holding times is presented in Table 9.14. When appropriate, EPA standardized the holding times across analytical methods for the same analyte group. For example, each HAA method specifies a different holding time for the samples prior to the extraction procedure. Since all the HAA methods specify the same sample collection and storage conditions, EPA believes it is reasonable to assume these samples have the same shelf life. EPA has specified a 14 day holding time for HAA samples, because under standard storage conditions, all nine HAAs are stable for this period of time. However, the extract holding times (Table 9.14) cannot be standardized across the various HAA methods, because the extracts are not chemically equivalent.

EPA also shortened the holding time for a few ICR analyses. Method 300.0 indicates that bromate and chlorate samples may be stored up to 28 days, but chlorite samples must be analyzed within 14 days. The computer programs, that EPA is using to validate the QC data in the ICR Federal Database, check holding times based on the method/analyte group, not the analyte. Therefore, EPA had to set the maximum holding time at the shortest time applicable for the three inorganic DBPs covered by Method 300.0.

If an ICR sample is not extracted or analyzed within the times specified in Table 9.14, then the data for the sample should not be reported. The laboratory should indicate to the utility that the sample was invalidated due to a holding time problem. This information would then be reported to EPA when the utility submits its report for that monthly sampling period.

The ICR Sampling Manual provides additional information concerning recommended sample collection and holding procedures for ICR samples.

**Table 9.14. Maximum Holding Times (in Days) for Samples and Extracts**

Method	Sample	Extract
502.2, 524.2 (THMs)	14	Not Applicable
551 (THMs)	14	7
551.1 (THMs, HANs, HKs, CP & CH)	14	14
552.1 (HAAs)	14	2
552.2 (HAAs)	14	7
6251 B (HAAs)	14	7
300.0 (Br <sup>-</sup> )	28	Not Applicable
300.0 (ClO <sub>2</sub> <sup>-</sup> , ClO <sub>3</sub> <sup>-</sup> , & BrO <sub>3</sub> <sup>-</sup> )	14	Not Applicable
5310 B, 5310 C, 5310 D (TOC)	28	Not Applicable
5910 B	ASAP* Not to exceed 2 days	Not Applicable
5320 B	14	Not Applicable
6252 B (Aldehydes)	ASAP* Not to exceed 2 days	7
Low BrO <sub>3</sub> <sup>-</sup>	28	Not Applicable
modified 524.2 (CNCl)	ASAP* Not to exceed 2 days	Not Applicable

- \* This analysis should be performed "as soon as practical" after the sample is collected. The sample is not considered valid if the analysis is not done within 2 days from sample collection. (Note: Aldehyde samples must be extracted within 2 days.)



## Section 10. Reporting Quality Control Data

Laboratories that perform analyses for the DBP/ICR are required to comply with the quality control requirements described in Section 9 of this manual. Laboratories must report a subset of these data to the ICR Federal Database (see Tables 10.1 and 10.2.) to verify that the ICR monitoring data are of sufficient accuracy and precision to meet ICR data objectives. [The ICR Chemistry Performance Evaluation (PE) Studies are not included in these tables, because they are not directly associated with the routine ICR samples. These PE data must also be reported, but not through the same mechanisms that are used for the other ICR QC data. See Section 8 for a discussion of ICR Chemistry PE Studies.]

EPA has developed two data entry software packages that are to be used in reporting ICR data. The ICR Water Utility Database System is to be used by the utilities primarily to report treatment plant design information, treatment plant operational data, and the analytical results from the monthly sample collection. However, some of the ICR QC data will be reported to EPA using this system, because the data are associated with specific samples rather than batches of samples. QC data that must be reported by the water systems are listed in Table 10.1. Laboratories must provide the client water systems with this QC information when they report their analytical results for the ICR samples, because monitoring data that are reported to EPA without the appropriate QC data will be deleted from the ICR Federal Database.

The majority of the ICR QC data must be reported to EPA by the laboratory using the ICR Laboratory Quality Control (QC) Database System. This software, along with a user's guide, will be provided to each laboratory that is approved to perform analyses for the ICR. The data that will be collected using this software are summarized in Table 10.2.

The ICR Laboratory QC Database System is designed to be used after sample analyses are completed, instead of as a sample tracking system. The data entry screens collect the data on a method and batch basis, so laboratories that organize their QC data in this manner will be more efficient in their data entry activities.

The QC data listed in Table 10.2 must be reported to EPA on a monthly basis by the laboratories. The QC data from all batches that were completed during the month are included in the monthly report and laboratories have up to two months from the month in question to submit their QC data to EPA (e.g., QC data from all batches completed in January must be received by EPA no later than the last day of the following March). It is imperative that laboratories submit their QC data to EPA in a timely manner, because the monitoring data will be deleted from the ICR Federal Database when the appropriate QC data are not present. Lack of QC data will cause monitoring data to be invalidated. Water systems must submit their data reports, which include the monitoring data, to EPA no later than the fourth month following sampling [§141.142(c)(1)]. All associated QC data from the laboratories must be entered into the ICR Federal Database before these monitoring data are entered.

The QC data are to be reported on a computer disk in accordance with the requirements of the ICR data collection software. (Laboratories will not report internal standard responses and surrogate recoveries to EPA, but will rather report these data directly to the utility, because these data are associated with individual samples. These data are then to be reported, by the utility, to EPA when the utility submits its verified and validated monitoring data. Similarly, duplicate data for TOX, UV<sub>254</sub>, and TOC analyses will also be reported through the utility, because each sample is analyzed in duplicate.)

Mail the QC data disks to:

USEPA (ICR4600)  
ICR Data Center  
Room 111 East Tower  
401 M Street, SW  
Washington, DC 20460

Laboratories should provide a copy of the QC data to the utility when the monitoring data are reported, but the utility will not report, to EPA, QC data already reported by the laboratories. Exceptions to this, however, are the internal standard responses, the surrogate recoveries, and the TOX, UV<sub>254</sub>, and TOC analyses which were not previously reported to EPA.

The water systems will report to EPA, the EPA assigned laboratory ICR identification number to identify the laboratory that performed each analysis.

It is the utility's responsibility to report all ICR monitoring data, other than the QC data discussed above, to the EPA ICR database in accordance with the requirements for reporting ICR data. Laboratories can assist the water utilities by providing the results of their analyses in a format that is similar to the data entry screens used by the ICR Water Utility Database System.

**Table 10.1. QC Data to be Submitted to the ICR Federal Database by the Water System**

Data	Comments
Internal Standard Recovery	One data point for each ICR sample analyzed using the applicable methods.
Surrogate Standard Recovery	One data point for each ICR sample analyzed using the applicable methods.
ICR Sample pH	pH of each preserved ICR sample for the applicable methods.
Laboratory Duplicates	All TOC, UV <sub>254</sub> , and TOX samples are analyzed in duplicate and the results from both analyses are reported.
AOC QC Data	Semiannual report on AOC yield factors. Data are reported for P17 and NOX growth controls, P17 and NOX yield controls, and P17 and NOX blank controls.
BDOC QC Data	Quarterly report indicating average TOC blank concentration, estimated TOC detection limit, and results from analysis of a fortified reagent water sample.
Lab ID Code	ICR Laboratory Code for each laboratory performing analyses of ICR samples

**Table 10.2. QC Data to be Submitted to the ICR Federal Database by the Laboratory**

Data	Comments
Identification of Shipping Batches	Laboratory will report shipping batch ID number (laboratory generated) along with the sample ID numbers for the ICR samples and the shipping blank associated with the shipping batch. This requirement only applies to aldehyde analyses.
Identification of Extraction Batches	Laboratory will report the extraction batch ID number (laboratory generated) and date of extraction along with a list of sample ID numbers for the ICR samples, duplicate samples, fortified samples, the method blank, calibration check standards, and shipping blanks (aldehydes only) extracted in the batch.
Identification of Analysis Batches	Laboratory will report the analysis batch ID number (laboratory generated) and the beginning and ending date and time of analysis along with a list of sample ID numbers for the ICR samples, duplicate samples, fortified samples, the method blank, calibration check standards, and shipping blanks (aldehydes only) analyzed in the batch.
Method Blank	If the method blank met all the ICR QC acceptance criteria ( $< \frac{1}{2}$ MRL for each analyte, and the surrogate and internal standard recoveries are within the acceptance range, if applicable), then the laboratory is only required to indicate that the method blank was analyzed and met the QC criteria. If the criteria were not met for one or more parameters, then the laboratory is required to report the concentrations of those analytes which failed QC criteria and recovery data for the surrogate and internal standards, if applicable.
Verification of Calibration	At least two calibration standards will be associated with each analysis batch. Laboratory will report expected and measured concentrations of each analyte in the standards. Internal standard and surrogate standard recoveries will also be reported, if applicable.
Laboratory Duplicates	At least one duplicate analyses will be associated with each extraction or analysis batch of samples except for TOC, UV <sub>254</sub> , and TOX which require duplicates of ALL samples. Laboratory will report measured concentrations of each analyte in the duplicate sample analysis except for TOC, UV <sub>254</sub> , and TOX which will be reported by the water system.
Laboratory Fortified Samples	At least one fortified sample will be associated with each extraction or analysis batch of samples for most of the DBP methods. Laboratory will report the concentration of each analyte used to fortify the sample, the concentration of each analyte measured in the fortified sample without correcting for original concentration, and internal and surrogate standard recoveries, if applicable.
Lab ID Code	Each laboratory will be assigned a unique code for ICR reporting purposes.

## **Section 11. Laboratory Evaluation During DBP/ICR Monitoring**

Laboratories must be approved on a method by method basis prior to performing any chemical analyses for the ICR. Approval is based on the criteria specified in Sections 4, 6, and 8. EPA recognizes that demonstrating capability to perform a specific analysis does not necessarily guarantee that a laboratory will operate at the required level of performance on a day to day basis during the 18-month monitoring period. Therefore, EPA will also monitor laboratory performance during the period in which the laboratory is generating data for the ICR Federal Database. In order to maintain approval to perform analyses for trihalomethanes, the haloacetonitriles, haloketones, and chloropicrin, chloral hydrate, haloacetic acids, oxyhalides, bromide ion, total organic halide, total organic carbon and ultraviolet absorbance at 254 nm, the laboratory must meet the following criteria during the time of approval:

- Successful performance on periodic Performance Evaluation (PE) Studies
- Timely and accurate submission of Quality Control (QC) data
- Successfully meet the QC criteria for at least 80% of the ICR samples analyzed

EPA may also require submission of additional documentation and/or perform on-site audits during the time of approval.

### **Performance Evaluation (PE) Studies**

EPA will conduct ICR Chemistry PE Studies on approximately a quarterly basis during the 18-month monitoring period and all approved laboratories will be required to participate in these studies in order to maintain ICR Laboratory Approval. The first of these "required" studies (ICR Chemistry PE Study 4) will be conducted close to the start of monitoring, in order to verify that previously approved laboratories are still capable of acceptable performance. The acceptance criteria described in Section 8 will apply for all ICR Chemistry PE Studies.

ICR Chemistry PE Studies 5 through 9 will be conducted during the 18-month monitoring period.

EPA recognizes that even good laboratories can occasionally fail a PE study for a particular method. Therefore, laboratories that fail to meet the necessary criteria on one or more methods in a specific PE study will be provided an additional PE sample for each method that was failed. The PE sample(s) will be sent to the laboratory in the same time frame as the report of the PE study results and the laboratory will have three weeks to analyze the sample(s) and report the data back to EPA. A laboratory that fails the second sample (i.e., two consecutive PE samples for the same method) will not be allowed to continue performing that analysis for ICR samples. No further ICR samples should be analyzed by that method, because data from ICR samples analyzed using the same method as the failed PE sample after the date that the second PE sample was analyzed

will be deleted from the ICR Federal Database. The laboratory must meet the criteria specified in Section 12 in order to have ICR Laboratory Approval reinstated for the method in question.

## **Submission of QC Data**

EPA has developed computer programs to examine the QC data associated with the ICR samples. The programs will automatically match each analytical result from an ICR sample reported by a water system with the associated QC data for the extraction and analysis batch reported by a laboratory. The QC data must meet the acceptance criteria in order for the monitoring data for that analyte to be maintained in the ICR Federal Database.

Because the QC data must be available before the monitoring data from ICR samples can be evaluated and in order to identify problems at the laboratory as quickly as possible, EPA will use timeliness of data submission as one of the ongoing laboratory approval criteria. The QC data must be reported to EPA within the time frame specified in Section 10. EPA will notify laboratories when they have failed to submit data by the required date.

Laboratories also have the responsibility to fully review their data for accuracy prior to submitting the monthly QC reports to EPA. The water systems are required to report their monitoring data to EPA within four months from the sampling date. The water systems expect EPA to process the data quickly and report back to them concerning the results of EPA's QC verification process. Since laboratories are given almost three months to report the QC data, there is a limited time between laboratory submission of QC data and water system submission of monitoring data. There is not enough time for laboratories to submit "corrected" QC reports on a routine basis. Therefore, EPA will consider resubmissions on a case-by-case basis. The ICR Chemistry Laboratory Coordinator must authorize resubmissions and each resubmission will be considered the same as failing the timeliness criteria, even if the resubmission occurs within the time frame specified in Section 10. Laboratories must request approval to resubmit QC data by writing (or faxing) to the ICR Chemistry Laboratory Coordinator.

Because it is critical that the QC data be received by EPA in a timely manner, laboratories that fail to meet the timeliness criteria for three reporting periods over the course of the 18-month monitoring period will not be allowed to continue performing any analyses of ICR samples. No further ICR samples should be analyzed, because data from ICR samples analyzed after the date on which the laboratory is notified of loss of laboratory approval will be deleted from the ICR Federal Database. The laboratory must meet the criteria specified in Section 12 in order to have ICR Laboratory Approval reinstated for the remainder of the ICR.

## **Completeness of Data**

Because the data in the ICR Federal Database will be used as the basis for future regulations, EPA has established QC criteria that must be met for much of the monitoring data. Analytical results

from samples that do not meet the QC criteria will be deleted from the ICR Federal Database. This means that some monitoring data will be lost due to failures in the laboratories' QC. (There will also be losses outside the control of the laboratories for reasons such as sampling errors, sample breakage during shipment, etc.) EPA has estimated that the data set must be 80% complete in order to achieve all of the ICR objectives.

In order to ensure that enough monitoring data is maintained in the ICR Federal Database, EPA will determine the percentage of each laboratory's ICR sample analyses that meet all the QC requirements and are therefore kept in the ICR Federal Database (i.e., completeness rate). A laboratory must maintain an 80% or greater data completeness rate for each analytical method that is performed for the ICR during each reporting period in order to maintain laboratory approval for each method.

Multi-analyte methods are also subject to completeness criteria for each analyte in order to guard against bias in the data through the consistent loss of one analyte in a method. A laboratory must maintain a 60% or greater data completeness rate for each analyte in a method. As an example, analyses of ten trihalomethane samples will generate forty analytical results (4 analytes/sample X 10 samples). Of the forty results, thirty-two must be valid (meet all the QC requirements) in order to meet the 80% completeness rate for the method. In addition at least six of the ten results for each analyte (e.g., bromoform) must be valid in order to meet the 60% completeness criteria for each analyte. Without the latter criteria, it would be possible to meet the 80% completeness rate for the method and lose eight out of ten results for a single analyte.

Completeness will be determined for each reporting period that contains a minimum of ten ICR sample analyses and EPA will notify a laboratory when it has failed to meet this criterion.

A laboratory that fails the completeness criteria three times during the 18-monitoring period for the same method will not be allowed to continue performing that analysis for ICR samples. Data from ICR samples analyzed using the problem method after the date on which the laboratory is notified of loss of laboratory approval will be deleted from the ICR Federal Database, so no further ICR samples should be analyzed by that method. The laboratory must meet the criteria specified in Section 12 in order to have ICR Laboratory Approval reinstated for the method in question.



## **Section 12. Reinstatement of Laboratory Approval**

Should review of laboratory QC or PE data indicate that a laboratory is not meeting the ICR data requirements, EPA will notify the laboratory of the problem. EPA will identify those analyses which seem to be suspect, and summarize the reasons why the data are suspect. If the problem(s) cannot be resolved and the laboratory loses approval for one or more methods (see Section 11), the laboratory can apply for reinstatement of laboratory approval subject to the following requirements:

- Loss of approval was not the result of fraud.
- There are at least six months of DBP/ICR monitoring to be conducted after the month in which EPA issues a letter of disapproval.

In order to have EPA consider reinstating ICR Laboratory Approval, the laboratory must submit a new application package within two months of loss of approval for each method under consideration. All data in the application must be generated after loss of laboratory approval. EPA will provide the laboratory with the appropriate application forms to be used in applying for reinstatement.

In addition to the application, the laboratory must pass the first available ICR Chemistry PE study for each method under consideration. EPA may also require a laboratory audit or on-site inspection prior to reinstating laboratory approval.



## Appendix A



## ICR REGISTRATION FORM

Instructions: Please complete the following form. For your convenience, the return address is affixed to the back of this form.

Laboratory Type: ☐ Utility ☐ Commercial ☐ State ☐ Other \_\_\_\_\_

Lab Name: \_\_\_\_\_

Address: \_\_\_\_\_

\_\_\_\_\_  
\_\_\_\_\_

Contact Person: \_\_\_\_\_

Telephone: \_\_\_\_\_ - \_\_\_\_\_ - \_\_\_\_\_

Please check the following groups of ICR parameters that will be analyzed by the lab listed above.

Analyses which require EPA evaluation prior to ICR Approval:

☐ Ammonia ☐ Bromide ☐ Chloral Hydrate ☐ Haloacetic Acids ☐ Total Organic Carbon

☐ Total Organic Halide ☐ UV Absorbance ☐ Oxyhalides (bromate, chlorate, chlorite)

☐ Total Hardness ☐ Haloacetonitriles, Haloketones and Chloropicrin ☐ THMs  
(via 551/551.1)

The parameters listed below do not require EPA evaluation prior ICR Approval if state approval or certification can be demonstrated:

☐ Alkalinity ☐ Calcium Hardness ☐ pH ☐ Temperature ☐ THMs ☐ Turbidity  
(via 502.2/524.2/551)

Disinfectant Residuals:

☐ free-chlorine ☐ total-chlorine ☐ chlorine dioxide ☐ combined chlorine ☐ ozone

If any of the unchecked analytes are to be analyzed by another lab (contracted by you), please provide the name and address of the contracted laboratory in the space below. Also list the parameter for which they are analyzing.

Laboratory

Address

Analyte

(fold here first)

ICR Laboratory Approval (Chemistry)  
Technical Support Division / USEPA  
26 W. Martin Luther King Jr. Drive  
Cincinnati, OH 45268

## Appendix B



**VERIFICATION OF STATE  
CERTIFICATION / APPROVAL**

Laboratory Type: ☐ Utility ☐ Commercial ☐ State ☐ Other \_\_\_\_\_

**Lab Name:** \_\_\_\_\_

**Address:** \_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_

**Contact Person:** \_\_\_\_\_

**Telephone:** \_\_\_\_\_ - \_\_\_\_\_ - \_\_\_\_\_

**Certification**

The information requested in this section is necessary to demonstrate certification/approval of the ICR parameters listed below. Please fill out completely, and supply all requested documentation.

Does your laboratory intend to measure THMs for the ICR? ☐ Yes ☐ No  
(If "No", proceed to the State Approval section.)

Please check the EPA method used in your lab for the determination of THMs.

☐ 501.1 ☐ 501.2 ☐ 502.2 ☐ 524.2 ☐ 551 ☐ Other \_\_\_\_\_

Using the method you indicated above, is your laboratory currently certified to measure THMs in drinking water? ☐ Yes, ☐ No

If "yes", please list: 1) the states in which the lab is certified and the certification #s, 2) indicate if the certification was achieved via on-site inspection, reciprocity, or a paper evaluation, and 3) if the certification is full or provisional. (e.g. NY, 11383 onsite full )

(1)

(2)

(3)

\_\_\_\_\_  
\_\_\_\_\_

\_\_\_\_\_  
\_\_\_\_\_

\_\_\_\_\_  
\_\_\_\_\_

Please attach a copy of your certificate(s)

Within the last three years, has your laboratory ever lost certification for THMs? ☐ Yes, ☐ No  
(If yes, attach an explanation of when and why.)

## State Approvals

If your laboratory intends to measure any of the parameters listed in the table below and is approved by a State to perform analyses of water samples using one of the methods specified in the ICR, then complete this section of the form. Please check the appropriate analyte, list one State in which your lab is approved, and indicate the manner of approval (on-site inspection, reciprocity, via a paper evaluation, or de facto), the method used for the analysis, and the type(s) of samples for which you are approved (drinking water, ground water, wastewater, etc.). Please also attach a copy of your letter(s) or Certificate(s) of approval for conducting the analyses

ICR Parameter (Indicate with a ✓)	State in Which Approved, and Manner of Approval (e.g. De Facto, etc.)	Method Used for the Analysis (e.g. SM2320 B)	Type of Sample (e.g. Wastewater)
<input type="checkbox"/> Alkalinity			
<input type="checkbox"/> Ammonia			
<input type="checkbox"/> Calcium hardness			
<input type="checkbox"/> pH			
<input type="checkbox"/> Temperature			
<input type="checkbox"/> Total Hardness			
<input type="checkbox"/> Turbidity			
<input type="checkbox"/> Free-chlorine			
<input type="checkbox"/> Chlorine dioxide			
<input type="checkbox"/> Total-chlorine			
<input type="checkbox"/> Combined-chlorine			
<input type="checkbox"/> Ozone			

**NOTE:** In some circumstances, a laboratory may be performing some of these analyses and reporting data to a State Primacy Agency with only de facto, and not documented, State approval. In such situations (where the laboratory does not have a formal State document to forward to EPA), a letter explaining the State's de facto approval is to be written by the laboratory manager and forwarded to EPA along with the completed Verification of State Certification/Approval Form. This letter should indicate the nature of the data that are being submitted, the name of the State Primacy Agency, the types of samples, method(s) of analysis, and frequency of reporting.

Within the past three years, has your lab lost approval for the analysis of any parameter for which you are applying for approval?      ☐ Yes   ☐ No      (If yes, attach an explanation of when and why.)

Lab Manager Signature: \_\_\_\_\_ Date: \_\_\_\_\_

This signature affirms that the information in the completed package is correct.

## Appendix C



**ICR LABORATORY APPROVAL FORM**  
**(For Analyses Not Covered Under Existing Drinking Water Regulations)**

**INSTRUCTIONS:** Please fill-in these forms as completely as possible. The cover letter sent with this packet should address most of the questions you may have concerning the completion of these forms. It also provides a telephone number that can be called to obtain additional information.

**Lab Name:** \_\_\_\_\_

**Address:** \_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_

**Contact Person:** \_\_\_\_\_

**Telephone:** \_\_\_\_\_ - \_\_\_\_\_

What is your laboratory's EMSL RE Code #: \_\_\_\_\_

**Please check the following ICR required analyses for which your laboratory is seeking approval.**

☐ Chloral Hydrate (EPA 551.1)    ☐ Haloacetic Acids (EPA 552.1; EPA 552.2; SM6251 B)    ☐ Total Organic Carbon (SM 5310 B,C,D)    ☐ Total Organic Halide (SM 5320 B)

☐ UV Absorbance (SM 5910)    ☐ Total Hardness (SM 2340 B,C)    ☐ Ammonia (SM 4500-NH<sub>3</sub> D,G; EPA 350.1, 379-75 WE)    ☐ Bromide (EPA 300.0)

☐ Haloacetonitriles, Haloketones and Chloropicrin (EPA 551.1)    ☐ Oxyhalides - bromate, chlorate & chlorite (EPA 300.0)

☐ THMs (EPA 551, 551.1)

**Lab Manager**

**Signature:** \_\_\_\_\_ **Date:** \_\_\_\_\_

This signature affirms that the information in the completed package is correct.

## QUALITY ASSURANCE

Please provide the following quality assurance (QA) information:

- 1) QA Officer's name and telephone number
- 2) Her/his QA experience
- 3) An organizational chart (Be certain to show the position of the QA officer.)
- 4) The Table of Contents from your Laboratory QA Plan (After you receive ICR approval, you must have an ICR QA Manual available for review.)
- 5) The date of the last revision of your Laboratory QA Plan

## CERTIFICATION

Is your laboratory currently certified to perform drinking water analyses? ☐ Yes ☐ No

If Yes, please list in the table below, the following information:

- Methods for which your laboratory is certified (If lab is certified for many methods, limit submission to methods that are similar to the ones for which the lab is seeking ICR approval.)

- States in which your laboratory is certified, and the certification numbers (If certified by multiple states, list should include home state, if applicable, and specify how many additional states are applicable.)

- Indicate if the certification was achieved via on-site inspection, reciprocity, or a paper evaluation (Focus on home state, if applicable.)

- Identify whether the certification is full or provisional (as of the date of this application)

Methods for Which Lab is Certified	States in Which Certified - and Certification Numbers	Manner of Certification (on-site, reciprocity, paper)	Type of Certification (full or provisional)

Please attach a copy of your certificate(s) for conducting these analyses.

**Laboratory Name:**

**ICR Lab No.:**

## Personnel Qualifications

### Instructions:

Please complete a personnel qualification form for each employee who will be associated with the ICR analyses which require EPA approval (see list on page 1 of this Laboratory Approval form). Include those involved with ICR sample handling, analysis, data review and lab management. Note that professional biographies may be substituted for this part of the ICR application if they contain all the personnel information requested by this form.

NAME (Last, First, Middle)		<input type="checkbox"/> Full-Time	<input type="checkbox"/> Part-Time
POSITION CURRENTLY HELD/ ICR ASSOCIATION			
EDUCATION		<input type="checkbox"/> Yes	<input type="checkbox"/> No
a. High School Graduate or Equivalent			
b. Colleges & Universities			
Name and address of Institution	MAJOR	Degree, Diploma, Certificate. Inc. MO/YR Conferred	
c. Special Schools, Short Courses and Programs of Instruction			
Name and address of Institution	PROGRAM TITLE	Degree, Diploma, Certificate. Inc. MO/YR Conferred	
(Verification of Degree, Diploma, Certificate and/or Transcript of grades may be requested.)			

**PERSONNEL QUALIFICATIONS**

Last Name: \_\_\_\_\_

**LICENSE, CERTIFICATION, OR REGISTRATION**

Name of Granting Agency	License, Certification or Registration Title	Granted MO/YR	License, Certification or Registration #

Verification may be requested.

**LABORATORY EXPERIENCE**

Name and Address of Laboratory or Institution. Begin with earliest employment and continue THROUGH PRESENT EMPLOYMENT. Any gaps in employment will be assumed to be non-laboratory work periods.	PERIOD EMPLOYED <u>FROM</u> <u>TO</u> MO/YR MO/YR	POSITION(S) HELD	EXPERIENCE e.g. Micro, Chem, etc. (also include experience with specific analyses and methods)

**REMARKS** (Add information pertinent to education, training, employment, etc., not included above.)


Laboratory Name:

ICR Lab No.:

## ICR Method Approval: Chloral Hydrate, Haloacetonitriles, Haloketones, Chloropicrin, and Trihalomethanes

**DESCRIPTION:** This analysis determines the concentration of chloral hydrate (CH), 4 haloacetonitriles (HANs), 2 haloketones (HKs), chloropicrin (CP) and the 4 trihalomethanes in water. The HANs include bromochloroacetonitrile (BCAN), dibromoacetonitrile (DBAN), dichloroacetonitrile (DCAN), and trichloroacetonitrile (TCAN). The HKs include 1,1-dichloropropanone (DCP) and 1,1,1-trichloropropanone (TCP). The trihalomethanes include chloroform ( $\text{CHCl}_3$ ), bromodichloromethane (BDCM), dibromochloromethane (DBCM), and bromoform ( $\text{CHBr}_3$ ).

For which analytes are you seeking approval?

☐ CH    ☐ HANs, HKs, CP    ☐ THMs

Which method is used in your laboratory?

☐ EPA 551    ☐ EPA 551.1    ☐ Other

If "Other", please give the name, number or description of the method used.

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Does your lab have a written SOP for this analysis? ☐ Yes ☐ No

Is your lab currently certified for 501.2 or 504 or similar methods? ☐ Yes ☐ No

## EQUIPMENT

Please list the equipment used in the method for which you are seeking approval.

	Manufacturer	Model & Serial #
Gas Chromatograph		
Detector(s)		
Injector(s)		Type:
Analytical Column		Type:
Confirmation Column		Type:
Sample Storage Unit		
Extract Storage Unit		
Standard Storage Unit		

**NOTE:** In the following tables in this form, please provide information only for those analytes for which you are seeking approval.

### SAMPLE HANDLING INFORMATION

ANALYTE	SAMPLE STORAGE TEMP (°C)	MAX. HOLDING TIME (days)	PRESERVATIVE USED		DECHLORINATING AGENT	
			Name	Conc. in Sample (mg/mL)	Name	Conc. in Sample (mg/mL)
CH						
HANs, HKs, CP						
THMs						

What is the sample container made from?

\_\_\_\_\_ bottles \_\_\_\_\_ septa, liner, or cap (whichever contacts sample)

Sample bottle volume? \_\_\_\_\_

### EXTRACT HANDLING INFORMATION

ANALYTE	SOLVENT USED	EXTRACT STORAGE TEMP (°C)	MAX HOLDING TIME
CH			
HANs, HKs, CP			
THMs			

Laboratory Name:

ICR Lab No.:

### QC INFORMATION

**Initial Demonstration of Capability:** Using the procedure outlined in the DBP/ICR Analytical Methods Manual, Section 6, paragraphs 2 and 3, enter in the table below, the data, and resultant calculated values, for your initial determination of precision and accuracy

	Spike Conc. ( $\mu\text{g/L}$ )	Concentration Determined in Replicate Samples ( $\mu\text{g/L}$ )					Mean % Recovery (accuracy)	% RSD (precision)
		1	2	3	4	5		
CHCl <sub>3</sub>								
TCAN								
DCAN								
BDCM								
CH								
DCP								
CP								
DBCM								
BCAN								
TCP								
CHBr <sub>3</sub>								
DBAN								
Date of Analysis of Replicate Sample								

**NOTE:** Please attach an example chromatogram from one of these determinations. Be sure to label each analyte, giving its retention time, concentration, and detector attenuation.

## Internal Standard and Surrogate

If you used an internal standard and/or surrogate in the determination of precision and accuracy (see preceding paragraph) please identify in the table below, the name of the chemical, the amount used, and average recovery.

	Internal Standard	Surrogate
Name of chemical		
Amount added	$\mu\text{g/mL}$ (conc. in extract)	$\mu\text{g/mL}$ (conc. in sample)
Average recovery	(%)	(%)

## Method Blank (Reference Section 6, paragraph 1)

What was the average concentration in your method blanks during the determination of precision and accuracy (reference paragraphs 2 and 3).

$\text{CHCl}_3$ : \_\_\_\_\_ BDCM: \_\_\_\_\_ CP: \_\_\_\_\_ TCP: \_\_\_\_\_  
 TCAN: \_\_\_\_\_ CH: \_\_\_\_\_ DBCM: \_\_\_\_\_  $\text{CHBr}_3$ : \_\_\_\_\_  
 DCAN: \_\_\_\_\_ DCP: \_\_\_\_\_ BCAN: \_\_\_\_\_ DBAN: \_\_\_\_\_

**NOTE: Please attach an example chromatogram of your method blank. (Be sure to label the potential position of the method analytes and detector attenuation.)**

What is your lab's normal (non-ICR) reporting limit ( $\mu\text{g/L}$ )?

$\text{CHCl}_3$ : \_\_\_\_\_ BDCM: \_\_\_\_\_ CP: \_\_\_\_\_ TCP: \_\_\_\_\_  
 TCAN: \_\_\_\_\_ CH: \_\_\_\_\_ DBCM: \_\_\_\_\_  $\text{CHBr}_3$ : \_\_\_\_\_  
 DCAN: \_\_\_\_\_ DCP: \_\_\_\_\_ BCAN: \_\_\_\_\_ DBAN: \_\_\_\_\_

Briefly describe how these reporting limits are established.

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Laboratory Name:

ICR Lab No.:

**Primary Column MDL:** Using the minimum detection limit procedure described in the DBP/ICR Analytical Methods Manual, Section 6, paragraph 4., enter in the table below, the data and the MDLs ( $\mu\text{g/L}$ ) for this analysis.

	Spike Conc. ( $\mu\text{g/L}$ )	Concentration Determined in Replicate Samples ( $\mu\text{g/L}$ )							MDL ( $\mu\text{g/L}$ )
		1	2	3	4	5	6	7	
$\text{CHCl}_3$									
TCAN									
DCAN									
BDCM									
CH									
DCP									
CP									
DBCM									
BCAN									
TCP									
$\text{CHBr}_3$									
DBAN									
Date of Analysis of Replicate Sample									

Although not specifically required, have these MDLs been confirmed by analysis of a reagent water spiked near the MDL? ☐ Yes ☐ No

**NOTE:** Please attach an example chromatogram from one of the above determinations. Be sure to label each analyte, giving its retention time, concentration, and detector attenuation.

## CALIBRATION CURVE

List the approximate concentrations ( $\mu\text{g/L}$ ) of the calibration standards currently used to establish the standard curve. (Note: The concentrations used to establish the calibration curve may be revised for the ICR monitoring period.)

	Std #1	Std #2	Std #3	Std #4	Std #5
CHCl <sub>3</sub>					
TCAN					
DCAN					
BDCM					
CH					
DCP					
CP					
DBCM					
BCAN					
TCP					
CHBr <sub>3</sub>					
DBAN					

Does this calibration provide you with a linear curve? ☐ Yes ☐ No

Was this curve generated by a data system \_\_\_\_\_ or calibrated manually \_\_\_\_\_ ?

Laboratory Name:

ICR Lab No.:

## PERFORMANCE EVALUATION

Has your lab analyzed EPA WS PE samples using this method? ☐ Yes ☐ No. If yes, please list in both tables below, the results, in  $\mu\text{g/L}$ , from the three most recent studies in which you participated.

	Study#_____ Date:	Study#_____ Date:	Study#_____ Date:
CHCl <sub>4</sub>			
BDCM			
DBCM			
CHBr <sub>4</sub>			

	Study#_____ Date:	Study#_____ Date:	Study#_____ Date:
CH			

## ADDITIONAL INFORMATION

Using this Analytical Method, how many samples can your laboratory analyze per week? \_\_\_\_

List the personnel who will be performing these analyses for the ICR and give their duties (extraction, GC Analyst, etc.).

Name

Duties

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Laboratory Name:

ICR Lab No.:

## ICR Method Approval: Haloacetic Acids

**DESCRIPTION:** This analysis determines the concentration of 6 haloacetic acids (HAAs) in water, monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA), dibromoacetic acid (DBAA), and bromochloroacetic acid (BCAA).

Which HAA method is used in your laboratory? ☐ EPA 552.1 ☐ SM 6251 B  
☐ EPA 552.2 ☐ Other

If "Other", please give the name, number or description of the method used by your laboratory.

Does your lab have a written SOP for this analysis? ☐ Yes ☐ No

Is your lab certified for chlorinated acids (e.g. 2,4D) and/or other similar methods?  
☐ Yes ☐ No

### EQUIPMENT

Please list the equipment to be used in this analysis.

	Manufacturer	Model & Serial #
Gas Chromatograph		
Detector(s)		
Injector(s)		Type:
Analytical Column		Type:
Confirmation Column		Type:
Sample Storage Unit		
Extract Storage Unit		
Standard Storage Unit		
Diazomethane Generator		
Solid Phase Extraction Apparatus		
Temperature Bath		

## SAMPLE HANDLING INFORMATION

What is the sample container made from? \_\_\_\_\_ bottles \_\_\_\_\_ septa, liner, or cap  
(whichever contacts sample)

Sample bottle volume? \_\_\_\_\_

Storage Temp: \_\_\_\_ °C      Maximum Holding Time: \_\_\_\_ Days

Are samples dechlorinated? \_\_Yes \_\_No ; with \_\_\_\_\_ (\_\_\_\_ mg/mL concn in sample)

Are samples acidified? \_\_Yes \_\_No ; with \_\_\_\_\_ (\_\_\_\_ mg/mL concn in sample)

## EXTRACT HANDLING INFORMATION

Storage Temp: \_\_\_\_ °C      Maximum Holding Time: \_\_\_\_ Days

## QC INFORMATION

**Initial Demonstration of Capability:** Using the procedure outlined in the DBP/ICR Analytical Methods Manual, Section 6, paragraphs 2 and 3, enter in the table below, the data, and resultant calculated values, for your initial determination of precision and accuracy.

	Spike Conc. ( $\mu\text{g/L}$ )	Concentration Determined in Replicate Samples ( $\mu\text{g/L}$ )					Mean % Recovery (accuracy)	% RSD (precision)
		1	2	3	4	5		
MCAA								
MBAA								
DCAA								
TCAA								
BCAA								
DBAA								
Date of Analysis of Replicate Sample								

**NOTE:** Please attach an example chromatogram from one of these determinations. Be sure to label each analyte, giving its retention time, concentration, and detector attenuation. All peaks should be "on scale."

**Laboratory Name:**

**ICR Lab No.:**

**Internal Standard and Surrogate**

If you used an internal standard and/or surrogate in the determination of precision and accuracy (see preceding paragraph) please identify in the table below, the name of the chemical, the amount used, and average recovery.

	Internal Standard	Surrogate
Name of chemical		
Amount added	$\mu\text{g/mL}$ (conc. in extract)	$\mu\text{g/mL}$ (conc. in sample)
Average recovery	(%)	(%)

**Method Blank (Reference Section 6, paragraph 1)**

What was the average concentration in your method blanks during the determination of precision and accuracy (reference paragraphs 2 and 3).

MCAA: \_\_\_\_\_

DCAA: \_\_\_\_\_

BCAA: \_\_\_\_\_

MBAA: \_\_\_\_\_

TCAA: \_\_\_\_\_

DBAA: \_\_\_\_\_

**NOTE: Please attach an example chromatogram of your method blank. (Be sure to label the potential position of the method analytes and detector attenuation.)**

What is your lab's normal (non-ICR) reporting limit ( $\mu\text{g/L}$ )?

MCAA: \_\_\_\_\_

DCAA: \_\_\_\_\_

BCAA: \_\_\_\_\_

MBAA: \_\_\_\_\_

TCAA: \_\_\_\_\_

DBAA: \_\_\_\_\_

Briefly describe how these reporting limits are established.

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**Primary Column MDL:** Using the minimum detection limit procedure described in the DBP/ICR Analytical Methods Manual, Section 6, paragraph 4., enter in the table below, the data and the MDLs ( $\mu\text{g/L}$ ) for this analysis.

	Spike Conc. ( $\mu\text{g/L}$ )	Concentration Determined in Replicate Samples ( $\mu\text{g/L}$ )							MDL ( $\mu\text{g/L}$ )
		1	2	3	4	5	6	7	
MCAA									
MBAA									
DCAA									
TCAA									
BCAA									
DBAA									
Date of Analysis of Replicate Sample									

Although not specifically required, have these MDLs been confirmed by analysis of a reagent water spiked near the MDL? ☐ Yes ☐ No

**NOTE:** Please attach an example chromatogram from one of the above determinations. Be sure to label each analyte, giving its retention time, concentration, and detector attenuation.

### CALIBRATION CURVE

List the approximate concentrations ( $\mu\text{g/L}$ ) of the calibration standards currently used to establish the standard curve. (Note: The concentrations used to establish the calibration curve may be revised for the ICR monitoring period.)

	Std #1	Std #2	Std #3	Std #4	Std #5
MCAA					
MBAA					
DCAA					
TCAA					
BCAA					
DBAA					

Does this calibration provide you with a linear curve? ☐ Yes ☐ No  
 Was this curve generated by a data system ☐ or calibrated manually ☐ ?

**Laboratory Name:**

**ICR Lab No.:**

## PERFORMANCE EVALUATION

Has your lab analyzed EPA WS PE samples using this method? ☐ Yes ☐ No. If yes, please list in the table below, the concentrations reported to EPA, in  $\mu\text{g/L}$ , from the three most recent studies in which you participated.

	Study# _____ Date: _____	Study# _____ Date: _____	Study# _____ Date: _____
MCAA			
MBAA			
DCAA			
TCAA			
BCAA			
DBAA			

## ADDITIONAL INFORMATION

Using this Analytical Method, how many samples can your laboratory analyze per week? \_\_\_\_\_

List the personnel who will be performing these analyses for the ICR and give their duties (extraction, GC Analyst, etc.).

Name

Duties

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Laboratory Name:

ICR Lab No.:

## ICR Method Approval: Total Organic Carbon

**DESCRIPTION** This analysis determines the total organic carbon (TOC) concentration in water.

Which TOC method is used in your laboratory?

☐ SM 5310 B    ☐ SM 5310 C    ☐ SM 5310 D    ☐ Other

If "Other", please give the name, number or description of the method used by your laboratory.

Does your lab have a written SOP for this analysis? ☐ Yes ☐ No

### EQUIPMENT

Please list the equipment used in this analysis.

	Manufacturer	Model & Serial #
Total Carbon Analyzer		
Sample Storage Unit		

### SAMPLE HANDLING INFORMATION

What is the sample container made from? \_\_\_\_\_ bottles \_\_\_\_\_ septa, liner, or cap  
(whichever contacts sample)

Sample bottle volume? \_\_\_\_\_

Storage Temp: \_\_\_\_\_ °C    Maximum Holding Time: \_\_\_\_\_ Days

Are samples acidified? ☐ Yes ☐ No ; with \_\_\_\_\_

Preserved sample pH? \_\_\_\_\_

## QC INFORMATION

**Initial Demonstration of Capability:** Using the procedure outlined in the DBP/ICR Analytical Methods Manual, Section 6, paragraphs 2 and 3, enter in the table below, the data, and resultant calculated values, for your initial determination of precision and accuracy.

	Spike Conc. (mg/L)	Concentration Determined in Replicate Samples (mg/L)					Mean % Recovery (accuracy)	% RSD (precision)
		1	2	3	4	5		
TOC								
Date of Analysis of Replicate Sample								

### Method Blank

What was the average concentration of TOC in your method blank during the determination of precision and accuracy? (Reference above paragraph) \_\_\_\_\_mg/L

What is your normal (non-ICR) minimum reporting limit for TOC? \_\_\_\_\_mg/L

Briefly describe how the reporting limit was established.

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Laboratory Name:

ICR Lab No.:

**MDL:** Using the minimum detection limit procedure described in the DBP/ICR Analytical Methods Manual, Section 6, paragraph 4, enter in the table below, the data and the MDL (mg/L) for this analysis.

	Spike Conc. (mg/L)	Concentration Determined in Replicate Samples (mg/L)							MDL (mg/L)
		1	2	3	4	5	6	7	
TOC									
Date of Analysis of Replicate Sample									

Although not specifically required, has this MDL been confirmed by analysis of a reagent water spiked near the MDL?      ☐ Yes    ☐ No

### CALIBRATION CURVE

List the approximate concentrations (mg/L) of the calibration standards currently used to establish the standard curve. (Note: The concentrations used to establish the calibration curve may be revised for the ICR monitoring period.)

	Std #1	Std #2	Std #3	Std #4	Std #5
TOC					

Does this calibration provide you with a linear curve?    ☐ Yes    ☐ No

Was this curve generated by a data system \_\_\_\_\_ or calibrated manually \_\_\_\_\_ ?

What compound is used to prepare your TOC standards? \_\_\_\_\_

### PERFORMANCE EVALUATION

Has your lab analyzed EPA WP PE samples for TOC using this method?    ☐ Yes    ☐ No. If yes, please list in the table below, the concentrations reported to EPA, in mg/L, from the three most recent studies in which you participated.

	Study#      Date:	Study#      Date:	Study#      Date:
TOC (mg/L)			

## ADDITIONAL INFORMATION

What types of quality control checks are performed for this analysis?

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At what concentration is the quality control check analyzed? \_\_\_\_\_

Using this analytical method, how many TOC samples per week can your laboratory analyze?  
\_\_\_\_\_/wk

List the personnel who will be performing this analysis for the ICR and list their duties.

Name	Duties
_____	_____
_____	_____
_____	_____

Laboratory Name:

ICR Lab No.:

## ICR Method Approval: Total Organic Halide

**DESCRIPTION:** This analysis determines the total organic halide (TOX) concentration in water.

Which TOX method is used in your laboratory?

☐ SM 5320 B

☐ Other

If "Other", please give the name, number or description of the method used by your laboratory.

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Does your lab have a written SOP for this analysis? ☐ Yes ☐ No

### EQUIPMENT

Please list the equipment used in this analysis.

	Manufacturer	Model & Serial #
Instrument		
Adsorption Module		
Sample Storage		

### SAMPLE HANDLING INFORMATION

What is the sample container made from? \_\_\_\_\_ bottles \_\_\_\_\_ septa, liner, or cap  
(whichever contacts sample)

Sample bottle volume? \_\_\_\_\_

Storage Temp: \_\_\_\_\_ °C      Maximum Holding Time: \_\_\_\_\_ Days

Are samples dechlorinated? ☐ Yes ☐ No ; with \_\_\_\_\_ (\_\_\_\_\_ mg/mL concentration in sample)

Are samples acidified? ☐ Yes ☐ No ; with \_\_\_\_\_

Preserved sample pH: \_\_\_\_\_

## QC INFORMATION

**Initial Demonstration of Capability:** Using the procedure outlined in the DBP/ICR Analytical Methods Manual, Section 6, paragraphs 2 and 3, enter in the table below, the data, and resultant calculated values, for your initial determination of precision and accuracy

	Spike Conc. ( $\mu\text{gCl}^-/\text{L}$ )	Concentration Determined in Replicate Samples ( $\mu\text{gCl}^-/\text{L}$ )					Mean % Recovery (accuracy)	% RSD (precision)
		1	2	3	4	5		
TOX								
Date of Analysis of Replicate Sample								

### Method Blank

What was the average concentration of TOX in your method blank during the determination of precision and accuracy? (Reference the above paragraph.) \_\_\_\_\_  $\mu\text{gCl}^-/\text{L}$

What is your normal (non-ICR) minimum reporting limit for TOX? \_\_\_\_\_  $\mu\text{gCl}^-/\text{L}$

Briefly describe how the reporting limits were established.

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**MDL:** Using the minimum detection limit procedure described in the DBP/ICR Analytical Methods Manual, Section 6, paragraph 4, enter in the table below, the data and the MDL ( $\mu\text{gCl}^-/\text{L}$ ) for this analysis.

	Spike Conc. ( $\mu\text{gCl}^-/\text{L}$ )	Concentration Determined in Replicate Samples ( $\mu\text{gCl}^-/\text{L}$ )							MDL ( $\mu\text{gCl}^-/\text{L}$ )
		1	2	3	4	5	6	7	
TOX									
Date of Analysis of Replicate Sample									

Although not specifically required, has this MDL been confirmed by analysis of a reagent water spiked near the MDL?      ☐ Yes    ☐ No

Laboratory Name:

ICR Lab No.:

### CALIBRATION CURVE

List the approximate concentrations ( $\mu\text{gCl/L}$ ) of the calibration standards currently used to establish the standard curve. (Note: The concentrations used to establish the calibration curve may be revised for the ICR monitoring period.)

	Std #1	Std #2	Std #3	Std #4	Std #5
TOX					

Does this calibration provide you with a linear curve? ☐ Yes ☐ No

Was this curve generated by a data system \_\_\_\_\_ or calibrated manually \_\_\_\_\_ ?

What compound is used to prepare your TOX standards? \_\_\_\_\_

### ADDITIONAL INFORMATION

What types of quality control checks are performed for this analysis?

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At what concentration is the quality control check analyzed? \_\_\_\_\_

Using this analytical method, how many TOX samples per week can your laboratory analyze?  
\_\_\_\_\_/wk

List the personnel who will be performing this analysis for the ICR and list their duties.

Name	Duties
_____	_____
_____	_____
_____	_____



Laboratory Name:

ICR Lab No.:

## ICR Method Approval: UV Absorbing Organic Constituents

**DESCRIPTION:** This analysis determines the UV absorbing organic constituents in water.

Which UV method is used in your laboratory?    ☐ SM 5910    ☐ Other

If "Other", please give the name, number or description of the method used by your laboratory.

\_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

Does your lab have a written SOP for this analysis?    ☐ Yes    ☐ No

### EQUIPMENT

Please list any equipment used in this analysis.

Equipment	Manufacturer	Model & Serial #
Spectrophotometer		
Filtration apparatus		Type:
Filter		Type:

### SAMPLE HANDLING INFORMATION

What is the sample container made from? \_\_\_\_\_ bottles \_\_\_\_\_ septa, liner, or cap  
(whichever contacts sample)

Sample bottle volume? \_\_\_\_\_

Storage Temp: \_\_\_\_\_ °C    Maximum Holding Time: \_\_\_\_\_ Days

Are samples dechlorinated? ☐ Yes    ☐ No ; with \_\_\_\_\_ ( \_\_\_\_\_ mg/mL conc. in sample)

Are samples acidified? ☐ Yes    ☐ No ; with \_\_\_\_\_

## QC INFORMATION

**Initial Demonstration of Capability:** Using the procedure outlined in the DBP/ICR Analytical Methods Manual, Section 6, paragraphs 2 and 3, enter in the table below, the data, and resultant calculated values, for your initial determination of precision and accuracy

	Conc of KHP (mg/L as DOC)	Analyzed Absorbance of Replicate Samples (cm <sup>-1</sup> )					Mean Absorbance at 254nm (cm <sup>-1</sup> )	% RSD (precision)
		1	2	3	4	5		
UV								
Date of Analysis of Replicate Sample								

### Method Blank

What was the average measurement of UV absorbance in your method blank during the determination of precision and accuracy? (Reference the above paragraph) \_\_\_\_\_ cm<sup>-1</sup>

What is your normal (non-ICR) minimum reporting limit for UV absorbance? \_\_\_\_\_ cm<sup>-1</sup>

Briefly describe how the reporting limits were established?

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Laboratory Name:

ICR Lab No.:

**MDL:** Using the minimum detection limit procedure described in the DBP/ICR Analytical Methods Manual, Section 6, paragraph 4, enter in the table below, the data and the MDLs for this analysis.

	Conc. of KHP (mg/L as DOC)	Analyzed Absorbance of Replicate Samples (cm <sup>-1</sup> )							MDL (cm <sup>-1</sup> )
		1	2	3	4	5	6	7	
UV									
Date of Analysis of Replicate Sample									

Although not specifically required, has this MDL been confirmed by analysis of a reagent water spiked near the MDL?      — Yes    — No

### ADDITIONAL INFORMATION

What types of quality control checks are performed for this analysis?

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At what concentration is the quality control check analyzed? \_\_\_\_\_

Using this analytical method, how many samples per week can your laboratory analyze? \_\_\_\_/wk

List the personnel who will be performing this analysis for the ICR and list their duties.

Name	Duties
_____	_____
_____	_____
_____	_____



Laboratory Name:

ICR Lab No.:

### ICR Method Approval: Total Hardness

**DESCRIPTION:** This analysis determines the total hardness concentration in water.

Which Total Hardness method is used in your laboratory?

☐ SM 2340 B    ☐ SM 2340 C    ☐ Other

If "Other", please give the name, number or description of the method used by your laboratory.

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Does your lab have a written SOP for this analysis? ☐ Yes ☐ No

#### STATE APPROVALS

Is your laboratory certified or approved by a State to perform Total Hardness analyses on water samples using one of the methods specified in the ICR? ☐ Yes ☐ No

**NOTE:** In some circumstances a laboratory may be performing this analysis and reporting data to a State Primary Agency with only de facto, and not documented, State approval. For purposes of the ICR, check "yes" to the above if this is your circumstance.

If you responded "no" to the above question, is your laboratory approved by a State to perform Calcium Hardness analyses on water samples using one of the methods specified in the ICR?

☐ Yes ☐ No

If your laboratory is State approved for Calcium Hardness, identify the method(s) for which your laboratory is approved.

<input type="checkbox"/> EPA 215.1	<input type="checkbox"/> SM 3111 B	<input type="checkbox"/> ASTM D511-93 B
<input type="checkbox"/> EPA 200.7	<input type="checkbox"/> SM 3120 B	
<input type="checkbox"/> EPA 215.2	<input type="checkbox"/> SM 3500-Ca D	<input type="checkbox"/> ASTM D511-93 A

**NOTE:** You must submit the ICR "Verification of State Certification/Approval" form to EPA if you are State approved for either Total Hardness or Calcium Hardness.



**Laboratory Name:**

**ICR Lab No.:**

### ICR Method Approval: Ammonia

**DESCRIPTION:** This analysis determines the concentration of ammonia in water.

Which ammonia method is used in your laboratory?

☐ SM 4500-NH<sub>3</sub> D (19th edition)    ☐ SM 4500-NH<sub>3</sub> G (19th edition)    ☐ EPA 350.1    ☐ 379-75 WE    ☐ Other

If "Other", please give the name, number or description of the method used by your laboratory.

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Does your lab have a written SOP for this analysis? ☐ Yes ☐ No

#### STATE APPROVALS

Is your laboratory certified or approved by a State to perform this analysis on water samples using one of the methods specified in the ICR? ☐ Yes ☐ No

**NOTE:** In some circumstances a laboratory may be performing this analysis and reporting data to a State Primacy Agency with only de facto, and not documented, State approval. For the purposes of the ICR, check "yes" to the above question if this is your circumstance.

If you responded "yes" to the above question, you need only submit the "Verification of State Certification/Approval" form to EPA. You do not need to submit the rest of the information requested in this application. If you responded "no", you must complete the remainder of this application.

## EQUIPMENT

Please list the equipment used in this analysis.

	Manufacturer	Model & Serial #

## SAMPLE HANDLING INFORMATION

Storage Temp: \_\_\_\_ °C      Maximum Holding Time: \_\_\_\_ Days

Are samples acidified? \_\_ Yes \_\_ No ; with \_\_\_\_\_

## QC INFORMATION

What is your normal (non-ICR) minimum reporting limit for ammonia? \_\_\_\_ mg/L

## CALIBRATION CURVE

List the approximate concentrations (mg/L) of the calibration standards currently used to establish the standard curve.

	Std #1	Std #2	Std #3	Std #4	Std #5
Ammonia					

Does this calibration provide you with a linear curve? \_\_ Yes \_\_ No

Was this curve generated by a data system \_\_\_\_ or calibrated manually \_\_\_\_ ?

## PERFORMANCE EVALUATION

Has your lab analyzed EPA WP PE samples? \_\_ Yes \_\_ No. If yes, please list in the table below, the concentrations reported to EPA, in mg/L, from the three most recent studies in which you participated.

	Study# ____ Date: ____	Study# ____ Date: ____	Study# ____ Date: ____
Ammonia			

**Laboratory Name:**

**ICR Lab No.:**

**Initial Demonstration of Capability:** Using the procedure outlined in the DBP/ICR Analytical Methods Manual, Section 6, paragraphs 2 and 3, enter in the table below, the data, and resultant calculated values, for your initial determination of precision and accuracy

	Spike Conc. (mg/L)	Concentration Determined in Replicate Samples (mg/L)					Mean % Recovery (accuracy)	% RSD (precision)
		1	2	3	4	5		
Ammonia								
Date of Analysis of Replicate Sample								

### Method Blank

What was the average concentration in your method blanks during the determination of precision and accuracy? (Reference previous paragraph) \_\_\_\_\_ mg/L

### ADDITIONAL INFORMATION

What types of quality control checks are performed for this analysis?

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At what concentration is the quality control check analyzed? \_\_\_\_\_

List the personnel who will be performing your analyses for the ICR and list their duties.

Name	Duties
_____	_____
_____	_____
_____	_____



Laboratory Name:

ICR Lab No.:

## ICR Method Approval: Bromide

**DESCRIPTION:** This analysis determines the concentration of bromide ( $\text{Br}^-$ ).

Which method is used in your laboratory for the analysis of bromide?

☐ EPA 300.0    ☐ Other

If "Other", please give the name, number or description of the method used by your laboratory.

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Does your lab have a written SOP for this analysis? ☐ Yes ☐ No

### EQUIPMENT

Please list the equipment to be used in this analysis.

	Manufacturer	Model & Serial #
Ion Chromatograph		
Guard Column		Type:
Sample Storage Unit		
Analytical Column		Type:
Detector(s)		
Suppressor		

## ELUENT AND SUPPRESSOR REGENERANT INFORMATION

	Concentration (mM)	Flow rate (mL/min)	Frequency prepared
Eluent	:		
Suppressor Regenerant	(N)		

## SAMPLE HANDLING INFORMATION

What is the sample container made from? \_\_\_\_\_ bottles \_\_\_\_\_ septa, liner, or cap  
(whichever contacts sample)

Sample bottle volume? \_\_\_\_\_

Storage Temp: \_\_\_\_\_ °C      Maximum Holding Time: \_\_\_\_\_ Days

Are samples preserved? ☐ Yes ☐ No ; with \_\_\_\_\_ (\_\_\_\_\_ mg/mL conc.in sample)

Sample injection volume (loop size) \_\_\_\_\_  $\mu$ L

## QC INFORMATION

**Initial Demonstration of Capability:** Using the procedure outlined in the DBP/ICR Analytical Methods Manual, Section 6, paragraphs 2 and 3, enter in the table below, the data, and resultant calculated values, for your initial determination of precision and accuracy.

	Spike Conc. (mg/L)	Concentration Determined in Replicate Samples (mg/L)					Mean % Recovery (accuracy)	% RSD (precision)
		1	2	3	4	5		
Br <sup>-</sup>								
Date of Analysis of Replicate Sample								

**NOTE:** Please attach an example chromatogram from one of these determinations. Be sure to label each analyte, giving its retention time, concentration, and detector attenuation.

**Laboratory Name:**

**ICR Lab No.:**

**Internal Standard**

If an internal standard is used, please list the name of the chemical, the amount used, and the average recovery.

Name of chemical	
Amount added	
Average recovery	

**Method Blank**

What was the average concentration of bromide in your method blanks during the determination of precision and accuracy ? (Reference earlier paragraph.) \_\_\_\_\_ mg/L

**NOTE:** Please attach an example chromatogram of your method blank. (Be sure to label the potential position of the method analytes and detector attenuation.)

What is your normal (non-ICR) minimum bromide reporting limit? \_\_\_\_\_ mg/L

Briefly describe how the reporting limits were established.

**MDL:** Using the minimum detection limit procedure described in the DBP/ICR Analytical Methods Manual, Section 6, paragraph 4, enter below, the data and the MDL (mg/L) for this analysis.

	Spike Conc. (mg/L)	Concentration Determined in Replicate Samples (mg/L)							MDL (mg/L)
		1	2	3	4	5	6	7	
Br <sup>-</sup>									
Date of Analysis of Replicate Sample									

Although not specifically required, has this MDL been confirmed by analysis of a reagent water spiked near the MDL?      ☐ Yes    ☐ No

**NOTE:** Please attach an example chromatogram from one of the above determinations. Be sure to label each analyte, giving its retention time, concentration, and detector attenuation.

## CALIBRATION CURVE

List the approximate concentrations (mg/L) of the calibration standards currently used to establish the standard curve. (Note: The concentrations used to establish the calibration curve may be revised for the ICR monitoring period.)

	Std #1	Std #2	Std #3	Std #4	Std #5
Br <sup>-</sup>					

Does this calibration provide you with a linear curve? ☐ Yes ☐ No

Was this curve generated by a data system \_\_\_\_\_ or calibrated manually \_\_\_\_\_ ?

## ADDITIONAL INFORMATION

What types of quality control checks are performed for this analysis?

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Using this analytical method, how many samples per week can your laboratory analyze? \_\_\_\_/wk

List the personnel who will be performing your bromide analyses for the ICR and give their duties.

**Name**

**Duties**

_____	_____
_____	_____
_____	_____

Laboratory Name:

ICR Lab No.:

### ICR Method Approval: Oxyhalides

**DESCRIPTION:** This analysis determines the concentration of the three oxyhalides, bromate ( $\text{BrO}_3^-$ ), chlorate ( $\text{ClO}_3^-$ ), and chlorite ( $\text{ClO}_2^-$ ). If bromate is determined separately from chlorate and chlorite, please indicate the differences in analytical conditions between the two analyses.

Which method is used in your laboratory for the analysis of the oxyhalides?

☐ EPA 300.0      ☐ Other

If "Other", please give the name, number or description of the method used by your laboratory.

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Does your lab have a written SOP for this analysis? ☐ Yes ☐ No

#### EQUIPMENT

Please list the equipment to be used in this analysis.

	Manufacturer	Model & Serial #
Ion Chromatograph		
Guard Column(s)		Type:
Concentrator Column		Type:
Analytical Column		Type:
Detector(s)		
Suppressor		
Sample Storage Unit		

## ELUENT AND SUPPRESSOR REGENERANT INFORMATION

	Concentration (mM)	Flow rate (mL/min)	Frequency prepared
Eluent	:		
Suppressor Regenerant	(N)		

## SAMPLE HANDLING INFORMATION

What is the sample container made from? \_\_\_\_\_ bottles \_\_\_\_\_ septa, liner, or cap  
(whichever contacts sample)

Sample bottle volume? \_\_\_\_\_

Storage Temp: \_\_\_\_\_ °C      Maximum Holding Time: \_\_\_\_\_ Days

Are samples preserved? ☐ Yes ☐ No ; with \_\_\_\_\_ (\_\_\_\_\_ mg/mL concentration in sample)

Sample injection volume (loop size) \_\_\_\_\_  $\mu$ L

Describe any sample pretreatment steps used prior to injection into the IC.

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## QC INFORMATION

**Initial Demonstration of Capability:** Using the procedure outlined in the DBP/ICR Analytical Methods Manual, Section 6, paragraphs 2 and 3, enter in the table below, the data, and resultant calculated values, for your initial determination of precision and accuracy.

	Spike Conc. ( $\mu$ g/L)	Concentration Determined in Replicate Samples ( $\mu$ g/L)					Mean % Recovery (accuracy)	% RSD (precision)
		1	2	3	4	5		
ClO <sub>2</sub> <sup>-</sup>								
BrO <sub>2</sub> <sup>-</sup>								
ClO <sub>2</sub> <sup>-</sup>								
Date of Analysis								

**NOTE:** Please attach an example chromatogram from one of these determinations. Be sure to label each analyte, giving its retention time, concentration, and detector attenuation.

**Laboratory Name:**

**ICR Lab No.:**

**Internal Standard**

If an internal standard is used, please list the name of the chemical, the amount used, and the average recovery.

Name of chemical	
Amount added	
Average recovery	

**Method Blank**

What was the average concentration in your method blanks (in  $\mu\text{g/L}$ ) during the determination of precision and accuracy? (Reference earlier paragraph)

$\text{ClO}_2^-$ :\_\_\_\_\_  $\text{BrO}_3^-$ :\_\_\_\_\_  $\text{ClO}_3^-$ :\_\_\_\_\_

**NOTE: Please attach an example chromatogram of your method blank. (Be sure to label the potential position of the method analytes and detector attenuation.)**

What is your normal (non-ICR) minimum reporting limit? ( $\mu\text{g/L}$ )

$\text{ClO}_2^-$ :\_\_\_\_\_  $\text{BrO}_3^-$ :\_\_\_\_\_  $\text{ClO}_3^-$ :\_\_\_\_\_

Briefly describe how the reporting limits were established.

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**MDL:** Using the minimum detection limit procedure described in the DBP/ICR Analytical Methods Manual, Section 6, paragraph 4, enter in the table below, the data and the MDLs ( $\mu\text{g/L}$ ) for this analysis.

	Spike Conc. ( $\mu\text{g/L}$ )	Concentration Determined in Replicate Samples ( $\mu\text{g/L}$ )							MDL ( $\mu\text{g/L}$ )
		1	2	3	4	5	6	7	
$\text{ClO}_2^-$									
$\text{BrO}_3^-$									
$\text{ClO}_4^-$									
Date of Analysis of Replicate Sample									

Although not specifically required, have these MDLs been confirmed by analysis of a reagent water spiked near the MDL?      ☐ Yes    ☐ No

**NOTE:** Please attach an example chromatogram from one of the above determinations. Be sure to label each analyte, giving its retention time, concentration, and detector attenuation.

## CALIBRATION CURVE

List the approximate concentrations ( $\mu\text{g/L}$ ) of the calibration standards currently used to establish the standard curve. (Note: The concentrations used to establish the calibration curve may be revised for the ICR monitoring period.)

	Std #1	Std #2	Std #3	Std #4	Std #5
$\text{ClO}_2^-$					
$\text{BrO}_3^-$					
$\text{ClO}_4^-$					

Does this calibration provide you with a linear curve?    ☐ Yes    ☐ No

Was this curve generated by a data system \_\_\_\_\_ or calibrated manually \_\_\_\_\_ ?

**Laboratory Name:**

**ICR Lab No.:**

### PERFORMANCE EVALUATION

Has your lab analyzed EPA WS PE samples? ☐ Yes ☐ No. If yes, please list in the table below, the concentrations reported to EPA, in  $\mu\text{g/L}$ , from the three most recent studies in which you participated.

	Study#_____ Date:_____	Study#_____ Date: _____	Study#_____ Date: _____
$\text{ClO}_2^-$			
$\text{BrO}_3^-$			
$\text{ClO}_3^-$			

### ADDITIONAL INFORMATION

What types of quality control checks are performed for this analysis?

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Using this analytical method, how many samples per week can your laboratory analyze? \_\_\_\_/wk

List the personnel who will be performing your oxyhalide analyses for the ICR and give their duties.

**Name**

**Duties**

_____	_____
_____	_____
_____	_____



## Appendix D



APPENDIX B TO PART 136—DEFINITION  
AND PROCEDURE FOR THE DETER-  
MINATION OF THE METHOD DETEC-  
TION LIMIT—REVISION 1.11*Definition*

The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

*Scope and Application*

This procedure is designed for applicability to a wide variety of sample types ranging from reagent (blank) water containing analyte to wastewater containing analyte. The MDL for an analytical procedure may vary as a function of sample type. The procedure requires a complete, specific, and well defined analytical method. It is essential that all sample processing steps of the analytical method be included in the determination of the method detection limit.

The MDL obtained by this procedure is used to judge the significance of a single measurement of a future sample.

The MDL procedure was designed for applicability to a broad variety of physical and chemical methods. To accomplish this, the procedure was made device- or instrument-independent.

*Procedure*

1. Make an estimate of the detection limit using one of the following:

(a) The concentration value that corresponds to an instrument signal/noise in the range of 2.5 to 5.

(b) The concentration equivalent of three times the standard deviation of replicate instrumental measurements of the analyte in reagent water.

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

(d) Instrumental limitations.

It is recognized that the experience of the analyst is important to this process. However, the analyst must include the above considerations in the initial estimate of the detection limit.

2. Prepare reagent (blank) water that is as free of analyte as possible. Reagent or interference free water is defined as a water sample in which analyte and interferent concentrations are not detected at the method detection limit of each analyte of interest. Interferences are defined as systematic errors in the measured analytical signal of an established procedure caused by the presence of interfering species (interferent). The interferent concentration is presupposed to

be normally distributed in representative samples of a given matrix.

3. (a) If the MDL is to be determined in reagent (blank) water, prepare a laboratory standard (analyte in reagent water) at a concentration which is at least equal to or in the same concentration range as the estimated method detection limit. (Recommend between 1 and 5 times the estimated method detection limit.) Proceed to Step 4.

(b) If the MDL is to be determined in another sample matrix, analyze the sample. If the measured level of the analyte is in the recommended range of one to five times the estimated detection limit, proceed to Step 4.

If the measured level of analyte is less than the estimated detection limit, add a known amount of analyte to bring the level of analyte between one and five times the estimated detection limit.

If the measured level of analyte is greater than five times the estimated detection limit, there are two options.

(1) Obtain another sample with a lower level of analyte in the same matrix if possible.

(2) The sample may be used as is for determining the method detection limit if the analyte level does not exceed 10 times the MDL of the analyte in reagent water. The variance of the analytical method changes as the analyte concentration increases from the MDL, hence the MDL determined under these circumstances may not truly reflect method variance at lower analyte concentrations.

4. (a) Take a minimum of seven aliquots of the sample to be used to calculate the method detection limit and process each through the entire analytical method. Make all computations according to the defined method with final results in the method reporting units. If a blank measurement is required to calculate the measured level of analyte, obtain a separate blank measurement for each sample aliquot analyzed. The average blank measurement is subtracted from the respective sample measurements.

(b) It may be economically and technically desirable to evaluate the estimated method detection limit before proceeding with 4a. This will: (1) Prevent repeating this entire procedure when the costs of analyses are high and (2) insure that the procedure is being conducted at the correct concentration. It is quite possible that an inflated MDL will be calculated from data obtained at many times the real MDL even though the level of analyte is less than five times the calculated method detection limit. To insure that the estimate of the method detection limit is a good estimate, it is necessary to determine that a lower concentration of analyte will not result in a significantly lower method detection limit. Take two aliquots of the sample to be used to calculate the method detection limit and process each

through the entire method, including blank measurements as described above in 4a. Evaluate these data:

(1) If these measurements indicate the sample is in desirable range for determination of the MDL, take five additional aliquots and proceed. Use all seven measurements for calculation of the MDL.

(2) If these measurements indicate the sample is not in correct range, reestimate the MDL, obtain new sample as in 3 and repeat either 4a or 4b.

5. Calculate the variance ( $S^2$ ) and standard deviation ( $S$ ) of the replicate measurements, as follows:

$$S^2 = \frac{1}{n-1} \left[ \frac{\sum_{i=1}^n x_i^2 - \left( \sum_{i=1}^n x_i \right)^2}{n} \right] \quad S = (S^2)^{1/2}$$

where:

$X_i$ ;  $i=1$  to  $n$ , are the analytical results in the final method reporting units obtained from the  $n$  sample aliquots and  $\Sigma$  refers to the sum of the  $X$  values from  $i=1$  to  $n$ .

6. (a) Compute the MDL as follows:

$$MDL = t_{(n-1, 1-\alpha = 0.99)} (S)$$

where:

MDL = the method detection limit

$t_{(n-1, 1-\alpha = .99)}$  = the students'  $t$  value appropriate for a 99% confidence level and a standard deviation estimate with  $n-1$  degrees of freedom. See Table.

$S$  = standard deviation of the replicate analyses.

(b) The 95% confidence interval estimates for the MDL derived in 6a are computed according to the following equations derived from percentiles of the chi square over degrees of freedom distribution ( $\chi^2/df$ ).

$$LCL = 0.64 \text{ MDL}$$

$$UCL = 2.20 \text{ MDL}$$

where: LCL and UCL are the lower and upper 95% confidence limits respectively based on seven aliquots.

7. Optional iterative procedure to verify the reasonableness of the estimate of the MDL and subsequent MDL determinations.

(a) If this is the initial attempt to compute MDL based on the estimate of MDL formulated in Step 1, take the MDL as calculated in Step 6, spike the matrix at this calculated MDL and proceed through the procedure starting with Step 4.

(b) If this is the second or later iteration of the MDL calculation, use  $S^2$  from the current MDL calculation and  $S^2$  from the previous MDL calculation to compute the F-ratio. The F-ratio is calculated by substituting the larger  $S^2$  into the numerator  $S_A^2$  and the other into the denominator  $S_B^2$ . The com-

puted F-ratio is then compared with the F-ratio found in the table which is 3.05 as follows: if  $S_A^2/S_B^2 < 3.05$ , then compute the pooled standard deviation by the following equation:

$$S_{\text{pooled}} = \left[ \frac{6S_A^2 + 6S_B^2}{12} \right]^{1/2}$$

if  $S_A^2/S_B^2 > 3.05$ , respoke at the most recent calculated MDL and process the samples through the procedure starting with Step 4. If the most recent calculated MDL does not permit qualitative identification when samples are spiked at that level, report the MDL as a concentration between the current and previous MDL which permits qualitative identification.

(c) Use the  $S_{\text{pooled}}$  as calculated in 7b to compute the final MDL according to the following equation:

$$MDL = 2.681 (S_{\text{pooled}})$$

where 2.681 is equal to  $t_{(12, 1-\alpha = .99)}$ .

(d) The 95% confidence limits for MDL derived in 7c are computed according to the following equations derived from percentiles of the chi squared over degrees of freedom distribution.

$$LCL = 0.72 \text{ MDL}$$

$$UCL = 1.65 \text{ MDL}$$

where LCL and UCL are the lower and upper 95% confidence limits respectively based on 14 aliquots.

TABLES OF STUDENTS'  $t$  VALUES AT THE 99 PERCENT CONFIDENCE LEVEL

Number of replicates	Degrees of freedom (n-1)	$t_{(n-1, .99)}$
7	6	3.143
8	7	2.998
9	8	2.896
10	9	2.821
11	10	2.764
16	15	2.602
21	20	2.528
26	25	2.485
31	30	2.457
61	60	2.390
00	00	2.326

#### Reporting

The analytical method used must be specifically identified by number or title and the MDL for each analyte expressed in the appropriate method reporting units. If the analytical method permits options which affect the method detection limit, these conditions must be specified with the MDL value. The sample matrix used to determine the MDL must also be identified with MDL value. Report the mean analyte level with the MDL and indicate if the MDL procedure was iter-

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ated. If a laboratory standard or a sample that contained a known amount analyte was used for this determination, also report the mean recovery.

If the level of analyte in the sample was below the determined MDL or exceeds 10 times the MDL of the analyte in reagent water, do not report a value for the MDL.

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