METHOD 321.8

DETERMINATION OF BROMATE IN DRINKING WATERS BY ION CHROMATOGRAPHY INDUCTIVELY COUPLED PLASMA - MASS SPECTROMETRY

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John T. Creed, Carol A. Brockhoff and Theodore D. Martin
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NATIONAL EXPOSURE RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268
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1.0 SCOPE AND APPLICATION

1.1 This method provides a procedure for determination of bromate in drinking water.

Analyte	Chemical Abstract Services Registry Numbers (CASRN)
Bromate (BrO_3^-)	15541-45-4

1.2 For reference where this method is approved for use in compliance monitoring programs [e.g., Safe Drinking Water Act (SDWA)], consult both the appropriate sections of the Code of Federal Regulation (Part 141 § 141.23 for drinking water), and the latest Federal Register announcements.

1.3 This method should be used by analysts experienced in the use of inductively coupled plasma mass spectrometry (ICP-MS), and the interpretation of spectral and matrix interferences. A minimum of six months experience with commercial instrumentation is recommended. It is also recommended that the analyst have experience in liquid chromatography and the use of ICP-MS as a chromatographic detector.

1.4 Users of the method data should state the data-quality objectives prior to analysis. Users of the method must document and have on file the required Initial Demonstration of Performance data described in Section 9.2 prior to using the method for analysis.

2.0 SUMMARY OF METHOD

2.1 An aliquot of a finished drinking water is passed through a preparatory cartridge capable of removing the trisubstituted haloacetic acids which interfere with the analysis of bromate. The sample is then injected onto a column which separates the remaining brominated haloacetic acids and bromide from the bromate. The ICP-MS is interfaced to the ion chromatograph and both mass 79 and mass 81 are monitored in time as

bromate elutes from the column. The resulting signal is integrated and a concentration determined from a calibration curve. Mass 79 is used for quantitation while mass 81 provides isotope ratio information which can be used to screen for potential polyatomic interferences.

2.2 Chromatography: The chromatographic separation is based on an anion exchange resin. The sample is injected on the column and the matrix and analyte partition themselves between the mobile phase and the stationary phase as they move along the column. Early eluting analytes spend most of their time in the mobile phase while the late eluting compounds spend a larger percentage of their time interacting with the stationary phase. The matrix anions can influence retention times by blocking the interaction of the stationary phase with the analytes producing a shift in the retention time.

Inductively Coupled Plasma Mass Spectrometer: The detection technique is based on the use of an ICP-MS for the detection of trace elements[1-3]. The chromatographic eluent is introduced by pneumatic nebulization into a radio frequency plasma where energy transfer processes cause desolvation, atomization and ionization. The ions are extracted from the plasma through a differentially pumped vacuum interface and separated on the basis of their mass-to-charge ratio by the mass spectrometer having a minimum resolution capability of 1 amu peak width at 5% peak height. The ions transmitted through the mass spectrometer are detected by an electron multiplier or Faraday detector and the ion information is processed by the data system. Interferences relating to the technique (Sect. 4) must be recognized.

Although ICP-MS is typically used for multi-analyte determinations, it is used in 321.8 for species specific quantification. In this mode the signal response is recorded via chromatographic or time resolved software. The use of ion chromatography in combination with ICP-MS detection has been reported for the detection of bromate [4-7].

DEFINITIONS

3.1 **Calibration Blank** - A volume of reagent water pH adjusted (to 10) with the same base as in the calibration standards.

3.2 **Calibration Standard (CAL)** - A solution prepared from the dilution of stock standard solutions. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration. This solution is pH adjusted to 10.

3.3 **Instrument Performance Check (IPC) Solution** - A solution of method analytes, used to evaluate the performance of the instrumental system with respect to defined set of method criteria. Within this method, the IPC is identical to the laboratory fortified blank.

3.4 **Drift Standard**- A calibration standard added to a post column sample loop (via a second valve) which is transported into the plasma when the sample is injected. This analyte does not traverse the column and is used to compensate for instrumental (ICP-MS) drift during the analysis of a set of samples.

3.5 **Laboratory Duplicates (LD1 and LD2)** - Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analyses of a number of LD1 and LD2 indicates precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.6 **Laboratory Fortified Blank (LFB)** - An aliquot of LRB to which known quantities of the method analyte is added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements.

3.7 **Laboratory Fortified Sample Matrix (LFM)** - An aliquot of an environmental sample to which known quantities of the method analyte is added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

3.8 **Laboratory Reagent Blank (LRB)** - An aliquot of reagent water or other blank matrices that are treated exactly as a sample including exposure to all glassware, equipment, solvents, and reagents that are used with other samples. The LRB is used to determine if method analyte or other interferences are present in the laboratory environment, reagents, or apparatus.

3.9 **Linear Dynamic Range (LDR)** - The concentration range over which the instrument response to an analyte is linear.

3.10 **Method Detection Limit (MDL)** - The minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero.

3.11 **Quality Control Sample (QCS)** - A solution of the method analyte of known concentrations which is used to fortify an aliquot of LRB or sample matrix. The QCS is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check either laboratory or instrument performance.

3.12 **Stock Standard Solution** - A concentrated solution containing the method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

3.13 **Tuning Solution** - A solution which is used to determine acceptable instrument

performance prior to calibration and sample analyses.

3.14 **Water Sample** - For the purpose of this method, a sample taken from a finished drinking water supply.

4.0 INTERFERENCES

4.1 Several interference sources may cause inaccuracies or imprecisions in the determination of bromate by ICP-MS. These are:

4.1.2 Abundance sensitivity - This is a property defining the degree to which the ”wings” of a mass peak contribute to adjacent masses. The abundance sensitivity is affected by ion energy and operating pressure. “Wing” overlap interferences may result when a small ion peak is being measured adjacent to a large one. The potential for these interferences should be recognized and the mass spectrometer operating conditions adjusted to minimize the effect.

This interference is relevant in this method given the large $^{40}Ar^{40}Ar^{+}$ dimer adjacent to mass 79 which is present in conventional ICP-MS. The extent to which the dimer contributes to the signal on mass 79 can be determined by scanning over masses 76-83 using 20 points per amu (skipping mass 80) using a 5mM HNO_3 solution(See Figure 1). The interference signal from the argon dimer is apparent by examining the background signal at mass 79.4 relative to 76.4, 77.4 and 78.4. With proper mass calibration and adequate abundance sensitivity, the signal on masses 76.4, 77.4, and 78.4 should be close to normal photon background. The signal on 79.4 commonly is elevated relative to the above masses. This elevated signal is caused by the mass spectrometers insufficient abundance sensitivity.

The signal should decrease as the mass decreases from 79.5 to 79.3 etc. To determine if the instrument has adequate abundance sensitivity the decrease (79.5 to 79.3) in this signal should be extrapolated to mass 79.0 at which point it should be no higher than twice the normal photon background(See Figure 1). The signal may increase as mass 79.0 is approached depending on the bromide contamination in the 5mM $HNO_{3.}$ The resolution etc., should be adjusted to minimize the dimers contribution to mass 79.0.

> **Note:** If the decrease in the signal from 79.5 to 79.0 does not have an inflection point, this may indicate that the abundance sensitivity is insufficient to resolve $^{79}Br^{+}$ from $^{40}Ar^{40}Ar^{+}$

4.1.3 Isobaric polyatomic ion interferences are caused by ions consisting of more than one atom which have the same nominal mass-to-charge ratio as the isotope of interest, and which cannot be resolved by the mass spectrometer in use[8]. These ions are commonly formed in the plasma or interface system from

support gases or sample components. The two polyatomics which are inherent to conventional ICP-MS are the $^{40}Ar^{38}ArH$ and $^{40}Ar^{40}ArH$. $^{40}Ar^{40}ArH$ contributes to the background signal on mass 81. To minimize this, it is recommended that the sample flow rate remain on between injections. This will produce smoother baselines on mass 81 and thereby produce more reproducible integrations on mass 81 for the early eluting peaks.

The ICP-MS interferences which apply to the detection of bromate are listed in Table 1. These spectral interferences are common to the plasma or produced by matrix anions eluting from the column. These interferences are outside the retention window for bromate but may cause baseline shifts which will degrade integration precision.

4.1.4 Physical interferences are associated with the physical processes which govern the transport of sample into the plasma, sample conversion processes in the plasma, and the transmission of ions through the plasma-mass spectrometer interface. These interferences may result in differences between instrument responses for the sample and the calibration standards. Samples containing high concentration of chloride (which elutes immediately after bromate) may cause chromatographic baseline shift possibly from a small change in the $^{40}Ar^{40}ArH$ production during the chloride elution. In addition, the removal of high concentrations of sodium and potassium which may exist in the drinking water are removed by using an anion self regenerating suppressor. This minimizes their deposition on the sampling cone and thus improves long term stability.

> **Note**: The mobile phase in this method was chosen based on its ability to produce a stable baseline and sensitivity over a multiple week period. The long term stability of the instrument is monitored by injecting a post column drift standard with each chromatogram. The analyte concentration in a sample is corrected by using this drift standard in the same fashion that an internal standard is used in Method 200.8[9].

4.1.5 Baseline Drift - This results when a constituent from the sample matrix is not quantitatively removed from the column leading to a slow column bleed of the strongly retained species. If this is suspected, the column should be flushed according to the manufacturer's recommendations. A slowly rising baseline can be caused by trisubstituted brominated haloacetic acids.

4.1.6 Chromatographic Interferences - The known chromatographic interferences for the determination of bromate in drinking water via ICP-MS detection are listed in Table 1 and their approximate retention characteristics are reported in Figure 2. These known interferences have been chromatographically resolved using the procedure described in this method. Given the diversity of environmental samples, the possibility of unidentified interferences exist. The following

section is written to provide the analyst with some guidance if an interference is identified. The two possible interferences are chromatographic overlap with a bromine containing species or a co-eluting polyatomic. In the case of co-elution with a bromine containing anion it is recommended that the analyst try the following method modifications in the order presented in an attempt to resolve the co-elution.

1.) Use weaker mobile phases (i.e. lower NH_4NO_3 concentrations).
2.) Alternative columns.
3.) Pretreatment cartridge which selectively removes the interference.

This co-elution should be documented and the changes in the mobile and stationary phase should produce a method capable of meeting all requirements in Section 9.

In the case of a co-elution with a polyatomic interference (on mass 79), the recommendation to the analyst is to try the following method modifications in the order presented in an attempt to resolve the co-elution.

1.) Use mass 81 for quantitation.
2.) Use weaker mobile phases.
3.) Alternative columns
4.) Pretreatment cartridge to selectively remove the interference.

This co-elution should be documented and the changes in the mobile and stationary phase should produce a method capable of meeting all requirements in Section 9.

4.1.7 Samples that contain particles larger than 0.45 microns and reagent solutions that contain particles larger than 0.2 micron require filtration to prevent damage to instrument columns and HPLC pumping system.

4.1.8 The analyst should be aware of the potential for carryover peaks from one analysis which will effect the proper detection of bromate in the subsequent analysis. Carryover was not observed in the analysis listed in Table 3 using the column, mobile phase and flow rate reported in Table 2. However, the analyst should be aware of the potential for carryover peaks.

4.1.9 Retention time shifts in ion chromatography are possible do to weak eluent strengths and high ionic strength matrices. These shifts are minimized by the eluent system reported in table 2. However, the analyst should be aware of the potential for retention time shifts do to high ionic strength matrices. These effects can be minimized by dilution of the sample matrix.

5.0 SAFETY

5.1 The toxicity or carcinogenicity of bromate and reagents used in this method have not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable. Each laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method [10,11]. A reference file of material data handling sheets should also be available to all personnel involved in the chemical analysis. Specifically, concentrated nitric presents various hazards as it is moderately toxic and extremely irritating to skin and mucous membranes. Use these reagents in a fume hood whenever possible and if eye or skin contact occurs, flush with large volumes of water. Always wear safety glasses or a shield for eye protection, protective clothing, and observe proper mixing when working with these reagents.

5.2 Analytical plasma sources emit radio frequency radiation, in addition to intense UV radiation. Suitable precautions should be taken to protect personnel from such hazards. The inductively coupled plasma should only be viewed with proper eye protection from UV emissions.

5.3 It is the responsibility of the user of this method to comply with relevant disposal and waste regulations. For guidance see Sections 14.0 and 15.0.

6.0 EQUIPMENT AND SUPPLIES

6.1 Inductively coupled plasma mass spectrometer. This instrument must meet the following requirements:

6.1.1 An instrument capable of scanning the mass range 5-250 amu with a minimum resolution capability of 0.75 amu peak width at 5% peak height is required. This instrument may be fitted with a conventional or extended dynamic range detection system. The abundance sensitivity must be greater than 1.0×10^6 on the low side of mass 80 or such that the dimer's ($^{40}Ar^{40}Ar^+$)low mass shoulder does not influence mass 79.

6.1.2 Radio-frequency generator compliant with FCC regulations.

6.1.3 Argon gas supply - High purity grade (99.99%). When analyses are conducted frequently, liquid argon is more economical.

6.1.4 A variable-speed peristaltic pump may be used to pump the drain of the spray chamber to waste.

6.1.5 A mass-flow controller on the nebulizer gas supply is required. A water-cooled spray chamber may be of benefit in reducing the water vapor entering the

plasma and thereby minimizing the $^{40}Ar^{40}ArH^{+}$. A double-pass spray chamber is recommended to increase background stability on mass 81 if $^{40}Ar^{40}ArH^{+}$ is present in the spectrum generated while nebulizing the mobile phase.

6.1.6 If an electron multiplier detector is being used, precautions should be taken, where necessary, to prevent exposure to high ion flux. Otherwise, changes in instrument response or damage to the multiplier may result. This may be true for samples containing bromide in the parts per million range.

6.1.7 A nebulizer with a low dead volume is recommended.

6.2 Ion Chromatograph. This instrument must meet the following specifications:

6.2.1 Eluent Pump - Programmable flow high pressure pumping system capable of delivering pressures up to 3000 psi and flow rates up to 1.5 ml/min.

6.2.2 Control Valves - Inert double stacked pneumatic operated 4 way valves capable of withstanding 3000 psi.

6.2.3 Sample Loops- narrow bore, high pressure tefzel® tubing or equivalent.

6.2.4 Tubing- narrow bore high pressure tefzel® tubing or equivalent.

6.2.5 Guard and Analytical Column - Dionex PA-100 or equivalent.

6.2.6 Suppressor - Dionex (ASRS) anion self regenerating suppressor or equivalent.

6.2.7 Pretreatment Cartridges - Dionex On-Guard-RP or equivalent

6.3 Analytical balance, with capability to measure to 0.1 mg, for use in weighing samples and preparing standards.

6.4 An air displacement pipette capable of delivering volumes ranging from 50 to 2500 µL with an assortment of high quality disposable pipet tips. Calibration of the pipette should be verified frequently by weighing aliquots of distilled deionized water using the analytical balance to assure precision and accuracy of the pipette.

6.5 Labware - For determination of bromate, plastic labware has been used exclusively and measurable concentrations of bromate in the blank have not been observed.

6.5.1 Narrow-mouth storage bottles, FEP (fluorinated ethylene propylene) with ETFE (ethylene tetrafluorethylene) screw closure, 125-mL to 250-mL capacities.

6.5.2 One-piece stem FEP wash bottle with screw closure, 125-mL capacity.

6.5.3 Syringes- 10cc Becton-Dickinson plastic syringes or equivalent.

7.0 REAGENTS AND STANDARDS

7.1 Reagents may contain elemental impurities that might affect the integrity of analytical data. Due to the high sensitivity of ICP-MS, high-purity reagents should be used whenever possible. All acids used for this method must be of ultra high-purity grade. The acid used to prepare the 5mM HNO_3 in the mobile phase does contain some bromide background. Care should be taken to minimize this background intensity.

7.1.1 Nitric acid, concentrated (sp.gr. 1.41).

7.1.2 Nitric acid (1+1) - Add 500 mL conc. nitric acid to 400 mL of reagent grade water and dilute to 1L.

7.1.3 Ammonium Nitrate - Fisher ACS certified or equivalent.

7.1.4 Sodium Hydroxide - Fisher 50/50 liquid mixture or equivalent.

7.2 Reagent water - All references to reagent grade water in this method refer to ASTM type I water (ASTM D1193)[12]. Suitable water may be prepared by passing distilled water through a mixed bed of anion and cation exchange resins.

7.3 Standard Stock Solutions - Stock standards may be purchased from a reputable commercial source or prepared from ultra high-purity grade chemicals. These standards have extremely low ionic strengths and should be pH adjusted to 10 (with NaOH)in order to minimize bromate interaction with the plastic sample loop tubing[6]. Replace stock standards when they can not be verified with QC standards.

7.3.1 Preparation of calibration standards - a fresh bromate standard should be prepared once a month or as needed. Dilute the stock bromate standard solution to levels appropriate to the operating range of the instrument using reagent water and adjust the pH to 10 using NaOH. The bromate concentrations in the standards should be sufficiently high to produce good isotope ratio precision (<2%) and to accurately define the slope of the response curve. Depending on the sensitivity of the instrument, concentrations ranging from 10 µg/L to 50 µg/L are suggested.

> **Note:** A blank and one calibration standard or multi-point calibration can be utilized to calibrate the response of the instrument.

7.4 Drift standard - The drift standard should be made such that its concentration is approximately five times higher than the bromate calibration standard. (This will compensate for the sample loop volume difference between the sample and the drift standard.) The drift standard concentration should be chosen based on analytical

precision (< 5% rsd of replicate peak integration).

7.5 Blanks - The calibration blank is used to establish and verify the analytical calibration.

7.5.1 Calibration blank - Consists of reagent grade water which is pH adjusted to 10 with sodium hydroxide.

7.6 Tuning Solution - This solution is used for instrument tuning (lens, argon flows etc.), mass calibration and abundance sensitivity prior to analysis. The tuning solution should be approximately twice the bromate calibration standard concentration (producing greater than 30,000cps) and should be delivered to the plasma using a peristaltic pump at a flow rate of 1 mL/min. The instrument should be tuned for maximum signal-to-noise using mass 79. After tuning, the tuning solution should be analyzed by scanning over masses 76-84 using 20 points per amu (skipping mass 80). This data can be used to verify the mass calibration (mass shifts of greater than 0.1 amu should be corrected) and check the instrument sensitivity (approximately 35,000cps/100ppb bromate given the instrument conditions outlined in Table 2). The calibration blank or a 5mM HNO_3 solution should then be analyzed using the same scanning conditions to check the mass analyzer's abundance sensitivity. This preanalysis routine should be performed daily(see figure 1).

7.7 Quality Control Sample (QCS) - The QCS should be obtained from a source outside the laboratory. The concentration of the QCS solution analyzed will depend on the sensitivity of the instrument. To prepare the QCS dilute an appropriate aliquot bromate to a concentration which is approximately 75% of the concentration of the highest calibration standard. The QCS should be analyzed as needed to meet data-quality needs and a fresh solution should be prepared quarterly or more frequently as needed.

7.8 Laboratory Fortified Blank (LFB) - To an aliquot of Calibration Blank add an aliquot of the stock standard solution to prepare the LFB. The fortified concentration should produce percent relative standard deviations of 4-7% on replicate determinations. The LFB must be carried through the same entire preparation scheme as the samples. This solution should be pH adjusted to 10 with sodium hydroxide.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 The pH of all aqueous samples should be tested immediately prior to analysis to ensure the sample has been properly preserved. If the sample requires a pH adjustment throughly mix the sample after the sodium hydroxide has been added. The pH of the sample must be adjusted to 10. This pH adjustment should be performed just prior to analysis. This pH adjustment assures the solubility of bromate within the sample

loop[6].

8.2 If required by the data user, prepare a field blank using reagent water. Use the same sample containers (see section 6.5.1 for container recommendations)as used in sample collection.

9.0 QUALITY CONTROL

9.1 Each laboratory using this method is required to operate a formal quality control (QC) program. The minimum requirements of this program consist of an initial demonstration of laboratory capability, and the periodic analysis of laboratory calibration blanks, fortified blanks and calibration solutions as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of the data generated.

> **NOTE:** Because the sample preparation step of this method is limited to pH adjustment prior to analysis, the number of required solutions needed to verify data quality has been reduced. In this method the calibration blank (Section 7.5 and 9.3) is used to establish baseline calibration and is used to verify the absence of contamination. The laboratory fortified blank (Sections 7.8 and 9.3) is used to assess both method accuracy and instrument performance.

9.2 Initial Demonstration of Performance (mandatory)

9.2.1 The initial demonstration of performance is used to characterize instrument performance (determination of linear calibration range and analysis of quality control sample) and laboratory performance (determination of method detection limit) prior to analyses conducted by this method.

9.2.2 Linear dynamic range - Linear dynamic range is detector or chromatographic resolution limited.

The useable linear range must be determined for the instrument configuration to be used.

> **Note:** The linear dynamic range may be limited by the chromatographic resolution of bromate from bromoacetic acid or other interferences. In this situation, the linear calibration range is limited to a concentration of bromate which can be chromatographically resolved from bromoacetic acid. Given the experimental conditions in Table 2, the linear dynamic range was limited to 50µg/L based on chromatographic resolution.

9.2.3 Quality control sample (QCS) - When beginning the use of this method, on a quarterly basis or as required to meet data-quality needs, verify the calibration

standards and acceptable instrument performance with the preparation and analyses of a QCS. To verify the calibration standards, the determined mean concentration from three analyses of the QCS must be within ± 10% of the stated QCS value. If the calibration standards cannot be verified, the source of the problem must be identified and corrected before either proceeding on with the initial determination of method detection limits or continuing with on-going analyses.

9.2.4 Method detection limit (MDL)- This should be established using reagent water (blank) fortified at a concentration of two to five times the estimated detection limit[13]. To determine MDL values, take seven replicate aliquots of the fortified reagent water and process through the entire analytical method. Perform all calculations defined in the method and report the concentration values in the appropriate units. Calculate the MDL as follows:

$$MDL = (t)_{(n-1,1-alpha = 0.99)} \times (S)$$

where:

$(t)_{(n-1,1-alpha = 0.99)}$ = Student's t value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom (t=3.14 for seven replicates].

n = number of replicates

S = standard deviation of the replicate analyses.

The MDL should be determined annually, when a new operator begins work or whenever, in the judgement of the analyst, a change in analytical performance caused by either a change in instrument hardware or operating conditions would dictate they be redetermined.

The MDL for bromate using the conditions listed in Table 2 is 0.3 μg/L.

9.3 Assessing Laboratory Performance (mandatory)

9.3.1 Calibration blank - **Within this method a calibration blank and the laboratory reagent blank are operationally the same**. The calibration blank will be used as the LRB and a fresh calibration blank should be made daily to verify the lack of contamination.

Analysis of the calibration blank can be used to verify the calibration baseline and to assess chromatographic carryover interference or contamination. The calibration blank should be analyzed as a sample. If the calibration blank produces an integrable signal for bromate, the laboratory should find the source of this problem prior to analyzing samples. The laboratory must complete the analysis of one calibration blank with each batch of 20 samples.

9.3.2 Laboratory fortified blank (LFB) - **Within this method the LFB is used to assess both laboratory and instrument performance.** The laboratory must analyze at least one LFB (Sect. 7.8) immediately after calibration and after each 10 samples. Calculate accuracy as percent recovery using the following equation:

$$R = \frac{LFB - CB}{s} \times 100$$

where:

	R	=	percent recovery.
	LFB	=	laboratory fortified blank concentration.
	CB	=	calibration blank concentration.
	S	=	concentration equivalent of analyte added to fortify the CB solution.

If the recovery falls outside the required control limits of 85-115%, bromate is judged out of control, and the source of the problem should be identified and resolved before continuing analyses.

9.3.3 The laboratory must use LFB analyses data to assess laboratory performance against the required control limits of 85-115%. When sufficient internal performance data become available (usually a minimum of twenty to thirty analyses), optional control limits can be developed from the mean percent recovery (x) and the standard deviation (S) of the mean percent recovery. These data can be used to establish the upper and lower control limits as follows:

UPPER CONTROL LIMIT = x + 3S
LOWER CONTROL LIMIT = x - 3S

The optional control limits must be equal to or better than the required control limits of 85-115%. After each five to ten new recovery measurements, new control limits can be calculated using only the most recent twenty to thirty data points. Also, the standard deviation (S) data should be used to establish an on-going precision statement for the level of concentrations included in the LFB. These data must be kept on file and be available for review.

Note: Using the experimental conditions in Table 2, the average recovery of the LFB was 99.8% with a three sigma control limit of 10.2%

9.3.4 Instrument performance - For all determinations the laboratory must check instrument performance and verify that the instrument is properly calibrated on a continuing basis. This is accomplished via the recovery on the LFB (85-

115%,section 9.3.2) and monitoring the instrument drift standard injected with each sample.

9.3.5 Instrument Drift Standard - The analyst is expected to monitor the response from the instrument drift standard(in each sample) throughout the sample set being analyzed. The absolute response of any one drift standard must not deviate more than 70-130% of the original response associated with the calibration blank. If deviations greater than these are observed, the reason for the drift should be investigated. Possible causes of drift may be a partially blocked sampling cone or a change in the tuning condition of the instrument.

9.4 Assessing Analyte Recovery and Data Quality

9.4.1 The chemical nature of the sample matrix can affect analyte recovery and the quality of the data. Taking separate aliquots from the sample for replicate and fortified analyses can in some cases assess the effect. Unless otherwise specified by the data user, laboratory or program, the following laboratory fortified matrix (LFM) procedure is required.

9.4.2 The laboratory must add a known amount of analyte to a minimum of 10% of the routine samples. In each case the LFM aliquot must be a duplicate of the aliquot used for sample analysis. The added bromate concentration must be the same as that used in the laboratory fortified blank. Over time all routine sample sources should be fortified.

9.4.3 Calculate the percent recovery for bromate, corrected for background concentrations measured in the unfortified sample, and compare these values to the designated LFM recovery range of 70-130%. Percent recovery may be calculated using the following equation:

$$R = \frac{C_s - C}{s} \times 100$$

where: R = percent recovery.
C_s = fortified sample concentration.
C = sample background concentration.
s = concentration equivalent of bromate added to fortify the sample.

Note: The precision and recovery in six drinking water matrices are reported in Table 3.

9.4.4 If recovery falls outside the designated range and laboratory performance is

shown to be in control, the recovery problem encountered with the fortified sample is judged to be matrix related, not system related. The data user should be informed that the result for the unfortified sample is suspect due to an uncorrected matrix effect.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Operating conditions - Because of the diversity of instrument hardware, no detailed instrument operating conditions are provided. The analyst is advised to follow the recommended operating conditions provided by the manufacturer. It is the responsibility of the analyst to verify that the instrument configuration and operating conditions satisfy the analytical requirements of this method and to maintain quality control data verifying instrument performance and analytical results. Instrument operating conditions which were used to generate precision and recovery data for this method are included in Table 2.

10.2 Precalibration routine - The following precalibration routine must be completed prior to calibrating the instrument.

10.2.1 Initiate proper operating configuration of instrument and data system. Allow a period of not less than 30 min for the instrument to warm up. Conduct mass calibration and resolution checks using the tuning solution. The tuning solution should be analyzed by scanning over masses 76-83 using 20 points per amu (skipping mass 80). For good performance, adjust spectrometer resolution to produce a peak width of approximately 0.75 amu at 5% peak height. Adjust mass calibration if it has shifted by more than 0.1 amu from unit mass. The abundance sensitivity must be checked by analyzing the calibration blank(See Figure 1).

10.3 Instrument drift - An instrument drift solution must be injected into the column effluent at the same time a sample is injected onto the column to verify instrument drift throughout the analysis of a set of samples. This solution does not traverse the column. The correction factor is calculated by ratioing the drift standard response in the calibration solution to the drift standard response in the current sample. This correction factor is then multiplied by the sample concentration. This is similar to an internal standard correction used in EPA Method 200.8[9].

Note: The stability of the baseline on mass 81 is strongly influenced by the IC pump being turned on and off. Therefore it is recommended that this pump remain on throughout an analysis set.

10.4 Calibration - Prior to initial calibration, set up proper instrument software routines for the collection of time resolved data. (See Table 2 for the experimental parameters used to collect the data within the method.) The instrument must be calibrated using the

calibration blank and a calibration standard prepared at one or more concentration levels. If single point calibration is used, the standard concentration should be near the determined upper linear range.

10.5 The rinse blank should be used to flush the IC injection loop and by-pass loops. This procedure is recommended between injections.

11.0 PROCEDURE

11.1 Aqueous Sample Preparation - The sample must be adjusted to pH 10 prior to analysis. The sample must be room temperature and pretreated with an on-guard RP cartridge prior to analysis. The RP cartridges were used according to the manufacturer's recommendations. Trisubstituted haloacetic acids (removed by the RP cartridge) can cause a slowly rising baseline because these trisubstituted haloacetic acids are strongly retained on the column.

11.2 The sample is injected onto the column at the same time the instrument drift standard is injected into the post column mobile phase. For sample and drift standard sample loop volumes see table 2.

11.3 Samples having concentrations higher than the established linear dynamic range should be diluted into range and reanalyzed.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 Sample data should be reported in units of µg/L for aqueous samples. Do not report bromate concentrations below the determined MDL. Drift standard correction should be applied to all sample concentrations.

12.2 For data values less than ten, two significant figures should be used for reporting element concentrations. For data values greater than or equal to ten, three significant figures should be used.

12.3 If additional dilutions were made to any samples, the appropriate dilution factor should be applied.

12.4 The primary quantitative isotope should be 79 because it has the most stable background and is less prone to the known interferences. Mass 81 should be monitored to verify that the bromide isotope ratio within the retention window is near unity. A ratio of the two isotopes can provide useful information for the analyst in detecting a possible spectral interference.

12.5 The QC data obtained during the analyses provide an indication of the quality of the sample data and should be provided with the sample results.

13.0 METHOD PERFORMANCE

13.1 Instrument operating conditions used for single laboratory testing of the method are summarized in Table 2.

13.2 Data obtained from single laboratory testing of the method are summarized in Table 3 for six drinking water samples. The average concentrations reported in the second column are the native bromate concentrations. The percent relative standard deviations associated with the native concentrations are reported in the second column. The samples were then fortified with 25μg/L bromate. The average recovery and precision of this recovery is reported in the 4th and 5th columns respectively.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions, consult *"Less is Better: Laboratory Chemical Management for Waste Reduction"*, available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington D.C. 20036, (202)872-4477.

15.0 WASTE MANAGEMENT

15.1 The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management consult *"The Waste Management Manual for Laboratory Personnel"*, available from the American Chemical Society at the address listed in the Section 14.2.

16. References

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12. American Society for Testing and Materials. Standard Specification for Reagent Water,

D1193-77. Annual Book of ASTM Standards, Vol. 11.01. Philadelphia, PA, 1991.

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TABLE 1. SPECTRAL AND CHROMATOGRAPHIC INTERFERENCES

Spectral Interferences

Interferent Source	MASS 79	MASS 81
Plasma	$^{40}Ar^{38}ArH^+$	$^{40}Ar^{40}ArH^+$
Sulfate*		SO_3H^+
Phosphate**	PO_3^+	$PO_3H_2^+$
Potassium	$^{40}Ar^{39}K^+$	

* Determined in 300 μg/mL sulfate.
** Determined in 100 μg/mL phosphate.

Potential Chromatographic or Coelution Interferences

	Retention Time*
Bromate	230
Bromoacetic Acid	170
Dibromoacetic Acid	460
Bromochloroacetic Acid	400
Bromide	570
Phosphate Matrix (PO_3^+)	180
Sulfate Matrix (SO_3H^+)	400

*Based on experimental conditions listed in Table 2. Reported in seconds to the leading edge of the peak using the drift standard as t = 0.

TABLE 2. EXPERIMENTAL CONDITIONS FOR THE DETECTION OF BROMATE VIA ICP-MS

ICP-MS Experimental Condition and Detection Limit

Instrument	Upgraded VG Elemental PQ1
Power	1.4 KW
Cool Gas	12.0 L/min
Aux Gas	1.2 L/min
Nebulizer Gas	0.957 L/min (Concentric)
m/z Monitored	79 and 81
Analysis Mode	Time Resolved or Chromatographic
Time Slice	0.4 seconds
Spray Chamber	5°C
Sensitivity (100μg/L BrO_3^-)	35,000cps m/z 79
Background ($5mM\ HNO_3 + 25mM\ NH_4NO_3$)	100 cps m/z=79; 2500cps m/z=81
Detection Limit	0.3μg/L

Chromatographic Experimental Conditions

Chromatograph	Dionex Gradient GPM-2
Column	PA100 Guard and Analytical
Flowrate	1 mL/min.
Pretreatment Cartridge	On-Guard RP
Mobile Phase	$5mM\ HNO_3 + 25mM\ NH_4NO_3$ (Isocratic)
Sample Loop	580 μL (based on i.d. and length)
Drift Standard Loop	170 μL

TABLE 3. PRECISION AND RECOVERY DATA FOR BROMATE IN OZONATED DRINKING WATER*

WATER	AVERAGE CONCENTRATION ng/mL	%RSD Of AVG CONC.	AVG%** RECOVERY LFM	%RSD Of LFM RECOVERY
1	22.2	5.5	97	3.6
2	3.0	6.4	98	1.4
3	10.1	3.6	98	3.4
4	2.7	5.1	96	3.8
5	1.3	10.6	96	3.0
6	0.8	15.5	102	2.4

* n=5 for all analyses, determined using experimental conditions listed in Table 2.

** Fortified with 25μg/L Bromate

Figure 1: Abundance Sensitivity Considerations for Bromate Analysis

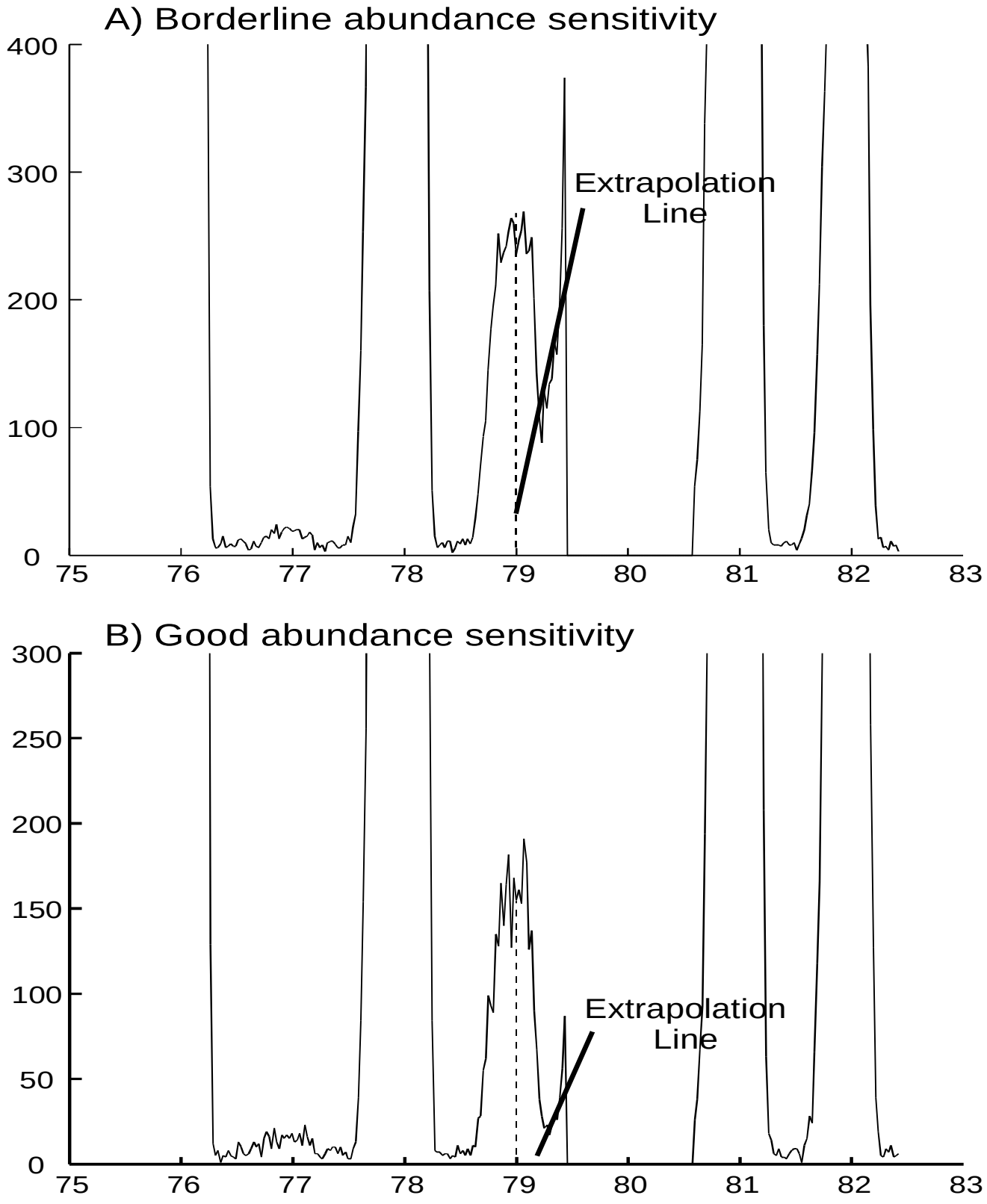

Figure 2: Sample Chromatogram Indicating Elution Order