

# Collaborative Study of EPA Method 317.0 for the Determination of Inorganic Oxyhalide Disinfection By-Products in Drinking Water Using Ion Chromatography with the Addition of a Postcolumn Reagent for Trace Bromate Analysis

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## Abstract

The development of the U.S. Environmental Protection Agency (EPA) Method 317.0 is initiated to provide a sufficiently sensitive and fundamental technique for the compliance monitoring of trace levels of bromate in drinking water. After a comparative evaluation of Method 317.0 and elimination of a chlorite interference, this method is tested by a collaborative study in order to determine the precision and bias of the method and evaluate its potential role as a future compliance-monitoring method for inorganic disinfection by-products (DBPs) and trace bromate. This technique provides a practical method for future compliance monitoring for all of the inorganic oxyhalide DBPs including trace concentrations of bromate.

## Introduction

In order to accumulate bromate occurrence data, the U.S. Environmental Protection Agency (EPA) initiated bromate sampling and analysis during the Information Collection Rule established in July 1997 (1,2). The samples were analyzed at EPA's Technical Support Center using a modified version of the selective-anion concentration (SAC) method (3) and by EPA-approved contract laboratories using a modified version of EPA Method 300.0 (4). In December 1998, EPA promulgated a maximum contaminant level (MCL) for bromate in drinking water under Stage I of the Disinfectants/Disinfection By-Products (D/DBP) Rule (5). The current bromate MCL is 10 µg/L (5). At the same time, the MCL goal for bromate was set at zero under Stage I of the D/DBP Rule (5). Limitations in acceptable compliance-monitoring

methods for bromate was one of the significant factors for establishing the Stage I bromate MCL at 10 µg/L.

In September 1997, EPA published Method 300.1 (6), and this method was promulgated as the Stage I compliance-monitoring method for bromate in December 1998 (5). The complexity of the SAC method and the limited sensitivity of Method 300.1 to detect bromate concentrations at or below 5 µg/L inspired EPA to develop a less complex, more sensitive method for the analysis of trace concentrations of bromate in drinking water. This work cumulated in publications involving the addition of a postcolumn reagent (PCR)—*o*-dianisidine dihydrochloride—to EPA Method 300.1 for trace bromate analysis (7), a comparative study of bromate methods (8,9), and the elimination of chlorite interference in the postcolumn method (10).

In order to assess the feasibility for using what has since been designated as EPA Method 317.0 (published in June 2000) (11) as a potential future compliance-monitoring method for all of the inorganic oxyhalide DBPs and trace bromate levels for Stage II of the D/DBP Rule, the method underwent collaborative testing in the fall of 1999 to determine the precision and bias of the method. This manuscript summarizes the statistical assessment of that data.

## Experimental

Because it involved the addition of a PCR to an existing EPA method (EPA Method 300.1), this collaborative study was specifically designed to evaluate the precision and accuracy of the method only and exclude potential errors associated with the

preparation of the test samples. In order to eliminate the potential for bias introduced as a result of analyst error or differences in analytical procedures or abilities in the various participating laboratories, all samples were prepared, packaged, and sent to the participants ready for direct analysis. The one exception was for those samples that required laboratory fortification as part of the chlorite-removal evaluation. The simulated chlorine dioxide treated samples (which contained chlorite and trace bromate as native samples) were sent to the participants along with a bromate spiking solution of uniform concentration. In addition to pretreating these samples to remove chlorite, the participants were asked to prepare laboratory-fortified matrices (LFMs) for those samples that required the addition of specified volumes of the bromate spiking solution prior to treatment with ferrous iron, or Fe (II).

The analysis array for this validation study was comprised

**Table I. Detection Limits for EPA Method 317.0 Analytes**

Lab	ClO <sub>2</sub> <sup>-</sup> (µg/L)	Br <sup>-</sup> (µg/L)	(µg/L) (cond*)	BrO <sub>3</sub> <sup>-</sup> (µg/L)	BrO <sub>3</sub> <sup>-</sup> (µg/L) (PCR)
1	1.1	1.5	1.5	1.0	0.16
2	2.5	2.9	1.2	4.0	0.19
3	1.3	2.2	1.9	2.1	0.41
4	1.2	1.5	4.1	3.1	0.18
5	2.1	5.8	2.2	4.9	0.98 <sup>†</sup>
<b>Average</b>	1.6	2.8	2.2	3.0	0.24

\* cond, conductivity detection.  
<sup>†</sup> Rejected using Dixon's outlier test.

**Table II. Precision and Bias for Chlorite by Conductivity Detection**

Matrix	Amount added (µg/L)	Amount found (µg/L)	Bias* (%)	S <sub>o</sub> <sup>†</sup> (%)	S <sub>t</sub> <sup>‡</sup> (%)
Reagent water (n = 5)	108	106	-1.7	1.9	2.8
	126	124	-1.9	-	3.2
	306	304	-0.7	1.2	4.3
	357	359	0.6	-	3.6
Bottled water (n = 5)	108	109	0.6	2.8	2.5
	126	122	-2.9	-	4.0
	306	303	-9.0	0.9	2.9
	357	354	-0.8	-	2.7
Tap water (n = 5)	108	111	2.6	4.1	7.8
	126	125	-0.6	-	6.7
	306	310	1.3	0.6	5.3
	357	359	0.7	-	4.6

\* The difference between the measured value and the known value expressed as a percentage equal to the measured concentration minus the known concentration and then divided by the known concentration.  
<sup>†</sup> The analyst relative standard deviation.  
<sup>‡</sup> The total relative standard deviation.

primarily of samples that were prepared as Youden pairs (12). The Youden "paired sample" approach to collaborative testing and data analysis (12) was incorporated into this study to evaluate the Method 317.0 analytes chlorite, bromide, chlorate, and bromate above 10 µg/L by conductivity detection as well as trace bromate levels by PCR UV-vis detection in three sample

**Table III. Precision and Bias for Bromate by Conductivity Detection**

Matrix	Amount added (µg/L)	Amount found (µg/L)	Bias* (%)	S <sub>o</sub> <sup>†</sup> (%)	S <sub>t</sub> <sup>‡</sup> (%)
Reagent water (n = 5)	11.3	10.8	-4.2	12.6	15.5
	13.2	13.8	4.8	-	5.0
	24.9	25.0	0.2	7.8	5.1
	29.0	29.3	1.0	-	9.4
Bottled water (n = 4)	13.1	13.1	0.0	16.9	24.7
	15.2	15.9	4.3	-	5.6
	23.4	28.1	5.1	3.7	6.8
	30.8	30.1	-2.2	-	4.6
Tap water (n = 4)	11.3	11.2	-0.7	14.3	15.3
	13.2	12.7	-0.4	-	16.0
	24.9	25.9	4.1	7.1	17.9
	29.0	26.7	-7.8	-	12.5

\* The difference between the measured value and the known value expressed as a percentage equal to the measured concentration minus the known concentration and then divided by the known concentration.  
<sup>†</sup> The analyst relative standard deviation.  
<sup>‡</sup> The total relative standard deviation.

**Table IV. Precision and Bias for Bromide by Conductivity Detection**

Matrix	Amount added (µg/L)	Amount found (µg/L)	Bias* (%)	S <sub>o</sub> <sup>†</sup> (%)	S <sub>t</sub> <sup>‡</sup> (%)
Reagent water (n = 5)	36.0	36.9	2.6	3.9	7.0
	42.0	41.3	-1.7	-	9.4
	144	143	-0.7	2.9	5.4
	168	165	-1.5	-	8.1
Bottled water (n = 5)	54.6	51.3	-6.0	9.6	14.1
	60.6	60.8	0.5	-	7.3
	163	169	3.7	6.9	5.3
	187	183	-1.8	-	6.3
Tap water (n = 5)	134	131	-2.2	1.3	4.8
	140	138	-1.0	-	5.2
	242	236	-1.2	0.6	5.6
	266	263	-1.1	-	4.7

\* The difference between the measured value and the known value expressed as a percentage equal to the measured concentration minus the known concentration and then divided by the known concentration.  
<sup>†</sup> The analyst relative standard deviation.  
<sup>‡</sup> The total relative standard deviation.

matrices—reagent water, bottled water, and chlorinated tap water. A simulated chlorine dioxide disinfected matrix was also included to evaluate the detection of trace bromate following the chlorite-removal process. The actual levels evaluated for each target analyte and matrix will be listed in a statistical summary.

Twelve laboratories were solicited to participate in the validation study. Seven labs responded favorably and data were provided by five of these laboratories. The data from the five laboratories were subjected to outlier testing using Dixon's test for outlying observations (13).

**Table V. Precision and Bias for Chloride by Conductivity Detection**

Matrix	Amount added ( $\mu\text{g/L}$ )	Amount found ( $\mu\text{g/L}$ )	Bias* (%)	S <sub>t</sub> † (%)	
				S <sub>o</sub> † (%)	S <sub>t</sub> † (%)
Reagent water (n = 5)	72.0	74.1	2.9	3.9	3.3
	84.0	84.6	0.7	–	2.8
	396	398	0.5	1.3	5.0
	462	469	1.5	–	3.5
Bottled water (n = 5)	72.0	74.9	4.0	6.1	6.0
	84.0	89.0	6.0	–	5.4
	396	397	0.3	0.7	4.0
	462	464	0.5	–	4.4
Tap water (n = 5)	160	161	0.7	1.6	5.2
	171	173	1.1	–	5.1
	483	486	0.8	0.7	4.6
	549	552	0.7	–	4.9

\* The difference between the measured value and the known value expressed as a percentage equal to the measured concentration minus the known concentration and then divided by the known concentration.

† The analyst relative standard deviation.

‡ The total relative standard deviation.

## Results and Discussion

### Detection limits

The detection limits were calculated using EPA protocols (14). The conductivity detection limits were determined using seven replicate analyses containing 5.0  $\mu\text{g/L}$  chlorite, bromate, bromide, and chlorate in reagent water, and the bromate PCR detection limit was determined by analyzing seven replicates of a 1.0- $\mu\text{g/L}$  bromate addition in reagent water. One PCR data set for bromate was higher than the other values, and consequently this data set was subjected to Dixon's test for outliers. This specific

**Table VI. Precision and Bias for Bromate by PCR and Absorbance Detection**

Matrix	Amount added ( $\mu\text{g/L}$ )	Amount found ( $\mu\text{g/L}$ )	Bias* (%)	S <sub>t</sub> † (%)	
				S <sub>o</sub> † (%)	S <sub>t</sub> † (%)
Reagent water (n = 5)	1.50	1.60	6.8	10.0	15.1
	2.20	2.14	-0.3	–	3.2
	4.20	4.36	3.9	3.8	8.8
	5.10	5.24	2.9	–	10.9
	6.89	7.27	5.5	–	5.3
Bottled water (n = 4)	3.29	3.26	-0.2	9.9	10.4
	3.99	3.96	-0.7	–	5.9
	5.99	6.25	4.3	1.2	6.5
	6.89	7.27	5.5	–	5.3
Tap water (n = 5)	1.50	1.74	15.9	10.1	15.2
	2.20	2.38	8.2	–	16.3
	4.20	4.63	10.3	8.7	5.0
	5.10	5.16	1.1	–	13.0

\* The difference between the measured value and the known value expressed as a percentage equal to the measured concentration minus the known concentration and then divided by the known concentration.

† The analyst relative standard deviation.

‡ The total relative standard deviation.

**Table VII. Precision and Accuracy for Chlorite Removal**

Lab	Sample #1		Sample #2		Sample #3		Sample #4		Sample #5	
	Spike (level)	%Recovery (2 $\mu\text{g/L}$ )	Spike (level)	%Recovery (2 $\mu\text{g/L}$ )	Spike (level)	%Recovery (4 $\mu\text{g/L}$ )	Spike (level)	%Recovery (6 $\mu\text{g/L}$ )	Spike (level)	%Recovery (8 $\mu\text{g/L}$ )
1	0.0	98.5	1.74	119	2.34	107	4.55	104	5.43	98.4
2	0.0	90.5	1.11	77.5	1.77	74.5	3.18	81.2	4.09	75.1
3	0.0	104	1.67	107	1.93	54.5*	4.05	19.7*	5.46	25.9*
4	0.0	98.0	1.63	83.5	2.83	59.5	4.41	94.8	4.86	88.0
5	0.0	95.0	2.20	110	87.0†	-115†	4.70	21.7†	7.10	7.5†
<b>Mean</b>										
%Recovery		97.1	111	99.0	101	36.2	103	54.3	94.8	49.1
%Relative standard deviation		4.9	23.2	17.9	21.4	30.2	16.1	12.3	23.8	13.4
Average native bromate recovery (sample #2, 3, 4, and 5) = 103%										
Average fortified bromate recovery (all five %recovery values) = 67%										

\* Laboratory 3 appeared to fortify the samples at a constant level of approximately 2  $\mu\text{g/L}$  instead of increasing the bromate fortification level.

† Laboratory 5 rejected as outlier after applying Dixon's test for outlying observations.

data point was classified as an outlier and thus the data set rejected. The results are presented in Table I.

#### Chlorite by conductivity detection

Two sample pairs for each matrix included chlorite and were subjected to ion chromatographic (IC) analysis using EPA Method 317.0 protocols (11). The chlorite results provided acceptable precision and accuracy and can be found in Table II.

#### Bromate by conductivity detection

Two sample pairs for each matrix included bromate and were subjected to IC analysis using EPA Method 317.0 protocols (11). One data set for bromate by conductivity detection in both the bottled water and tap water matrix was rejected after applying Dixon's test for outlying observations. One laboratory reported lower values for bromate by conductivity detection in these two matrices even though their reagent water results were acceptable. Consequently, the data were subjected to Dixon's testing and the values rejected as outliers. The results are located in Table III and indicate that acceptable precision and accuracy were obtained after the exclusion of these two data points.

#### Bromide by conductivity detection

Two sample pairs for each matrix included bromide and were subjected to IC analysis using EPA Method 317.0 protocols (11). The bromide conductivity results were acceptable in terms of precision and accuracy and are tabulated in Table IV.

#### Chlorate by conductivity detection

Two sample pairs for each matrix included chlorate and were subjected to IC analysis using EPA Method 317.0 (11). The results are listed in Table V and suggest that the method provided acceptable precision and accuracy for the analysis of chlorate using conductivity detection.

#### Bromate by PCR and absorbance detection

Two sample pairs for each matrix included bromate and were subjected to IC analysis using EPA Method 317.0 protocols (11). One laboratory submitted a bromate concentration that was higher in the native sample compared with the fortified sample. Consequently, this data set for bromate by PCR UV-vis detection in bottled water was subjected to Dixon's test for outlying observations and the data point rejected as an outlier. After rejection of

this data, acceptable results in terms of precision and accuracy were obtained for the analysis of bromate by PCR detection and are presented in Table VI.

#### Chlorite removal in simulated chlorine dioxide treated water

A series of simulated chlorine dioxide treated water samples were included to evaluate the precision and accuracy of the trace bromate measurement following the chlorite removal process in Method 317.0 (11). These samples all contained a background chlorite concentration of approximately 100 µg/L that had to be removed by treatment with Fe (II) prior to analysis. The samples (found in Table VII) were designed to contain increasing native levels of bromate (0.0, 1.5, 2.2, 4.2, and 5.1 µg/L). They were analyzed after treatment with Fe (II) in order to determine the native bromate level and again after fortification with 2.0, 4.0, 6.0, and 8.0 µg/L bromate, respectively, prior to the treatment with Fe (II) and IC analysis according to Method 317.0 quality assurance/quality control protocols. The results and fortification recoveries (expressed as a percentage) are presented in Table VII.

## Conclusion

This validation study of Method 317.0 provided an average single analyst precision of better than 10% relative standard deviation (RSD), an average interlaboratory precision of better than 12% RSD, and an average bias of better than 1.6% for chlorite, bromate, bromide, and chlorate by conductivity detection (Table VIII). Also, an average single analyst precision of better than 8.0% RSD, an average interlaboratory precision of better than 10% RSD, and an average bias of better than 5.0% were reported for the trace-level analysis of bromate by PCR (Table VIII).

The Fe (II) treatment protocols for the simulated chlorine dioxide treated water provided an average precision of better than 21% RSD and an accuracy of 103% average recovery of the native bromate for the five samples that were not fortified by the participants but were analyzed after treatment with Fe (II). However, the Fe (II) LFM recoveries were less than desirable and (as indicated by the poor fortification recoveries averaging 67% in Table VII) appeared to be technique related rather than method related. Because the samples that required only the Fe (II) treatment were satisfactory and those that required fortification by the participants prior to Fe (II) treatment were not, the difficulty can be attributed to the fortification process rather than the Fe (II) removal process.

The method provides excellent bromate sensitivity and offers a practicable method for future compliance monitoring for all of the inorganic oxyhalide DBPs and trace levels of bromate.

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**Table VIII. Average Precision and Bias for Method 317.0\***

Analyte	%Bias (and range)	%Single analyst precision and range (RSD)	%Interlaboratory precision and range (RSD)
Bromate (cond <sup>†</sup> )	0.35 (-7.8 to 5.1)	10 (3.7 to 17)	12 (4.6 to 25)
Chlorite	-0.98 (-9.0 to 2.6)	1.9 (0.6 to 4.1)	4.2 (2.5 to 7.8)
Bromide	-0.87 (-6.0 to 3.7)	4.2 (0.6 to 9.6)	6.9 (4.7 to 14)
Chlorate	1.6 (0.30 to 6.0)	2.4 (0.7 to 6.1)	4.5 (2.8 to 6.0)
Bromate (PCR)	4.8 (-0.20 to 16)	7.3 (1.2 to 10)	9.6 (3.2 to 16)

\* Ranges appear in parentheses.  
<sup>†</sup> cond, conductivity detection.

ucts does not constitute endorsement or recommendation for use.

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