Improving the performance of US Environmental Protection Agency Method 300.1 for monitoring drinking water compliance[☆]

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Abstract

In 1998, the United States Environmental Protection Agency (EPA) promulgated the maximum contaminant level (MCL) for bromate in drinking water at 10 μg/l, and the method for compliance monitoring of bromate in drinking water was established under Stage 1 of the Disinfectants/Disinfection By-Products Rule (D/DBP) as EPA Method 300.1. In January 2002, the United States Food and Drug Administration (FDA) regulated the bromate concentration in bottled waters at 10 μg/l. EPA anticipates proposing additional methods, which have improved performance for bromate monitoring, in addition to EPA Method 300.1, in the Stage 2 DBP Rule. Until the Stage 2 Rule is promulgated, EPA Method 300.1 will continue to be the only method approved for compliance monitoring of bromate. This manuscript describes the work completed at EPA's Technical Support Center (TSC) to assess the performance of recently developed suppressor technologies toward improving the trace level performance of EPA Method 300.1, specifically for the analysis of trace levels of bromate in high ionic matrices. Three different types of Dionex suppressors were evaluated. The baseline noise, return to baseline after the water dip, detection limits, precision and accuracy, and advantages/disadvantages of each suppressor are discussed. Performance data for the three different suppressors indicates that chemical suppression of the eluent, using the AMMS III suppressor, is the most effective means to reduce baseline noise, resulting in the best resolution and the lowest bromate detection limits, even when a high ionic matrix is analyzed. Incorporation of the AMMS III suppressor improves the performance of EPA Method 300.1 at and below 5.0 μg/l and is a quick way for laboratories to improve their bromate compliance monitoring.
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1. Introduction

In the USA and throughout the world, disinfection of municipal drinking water supplies is utilized to prevent human exposure to potentially hazardous microorganisms in drinking water. However, some disinfection processes have the potential to form inorganic oxyhalide disinfection by-products (DBPs); some of which also have potential health risks associated with them. When chlorine dioxide (ClO_2) is used to disinfect drinking water, chlorite (ClO_2^-)

and chlorate (ClO_3^-) are the DBPs potentially formed [1,2]. On the other hand, when drinking water is disinfected with hypochlorite (OCl^-), chlorate and bromate have been reported [3,4]. Also, when source waters containing bromide are ozonated (O_3), bromate (BrO_3^-) has the potential to be formed [5,6].

Bromate has been listed as an animal carcinogen by The National Cancer Institute [7] and has been classified as a group 2B, probable human carcinogen by the International Agency for Research on Cancer [8]. Health effects studies completed in 1995, established bromate as a suspected human carcinogen with a potential 10^{-4} risk of cancer after a lifetime exposure in drinking water at 5.0 µg/l [9]. Consequently, these findings prompted the US Environmental Protection Agency (EPA) to promulgate a maximum contaminant level (MCL) for bromate in drinking water of 10 µg/l in September 1998, under Stage 1 of the Disinfectants/Disinfection By-Products (D/DBP) Rule [10]. As well the maximum contaminant level goal (MCLG) was established at zero [10]. At the same time, EPA Method 300.1, which has a detection limit less than 2.0 µg/l [11], was designated as the Stage 1 compliance monitoring method for bromate [10].

In January 2002, the United States Food and Drug Administration (FDA) regulated the bromate concentration in commercially bottled waters at 10 µg/l and recommended EPA Method 300.1 as the compliance monitoring method for bottled waters [12].

Work completed at EPA's Technical Support Center (TSC) to improve sensitivity for the measurement of bromate at concentrations less than 5.0 µg/l, especially in high ionic matrices, resulted in publication of EPA Method 317.0 in January 2000 [13], and the development of EPA Method 326.0 [14]. Both of these methods coupled a postcolumn technique to Method 300.1 to reduce the bromate detection limit to approximately 0.12 µg/l [13,14]. EPA anticipates proposing Methods 317.0 and 326.0, as compliance monitoring methods in the Stage 2 DBP Rule. However, until approval of the Stage 2 DBP Rule, EPA Method 300.1 will remain the only acceptable compliance monitoring method for bromate.

High ionic matrices have, on occasion, been reported to have a negative impact on the detection of bromate concentrations at or below 5.0 µg/l when using EPA Method 300.1. This manuscript describes the work completed at EPA's TSC to evaluate recent developments in Dionex suppressor technology and summarizes how the individual suppressors affected the performance of EPA Method 300.1. The Ultra Anion Self Regenerating Suppressor (ASRS), which is the recommended suppressor for EPA Method 300.1, the Anion Micro Membrane Suppressor (AMMS III), which incorporates a new Displacement Chemical Regeneration (DCR) technique, and the Atlas Anion Electrolytic Suppressor (AES) were evaluated using EPA Method 300.1 protocols. The performance of the individual suppressors, in terms of baseline noise, return to baseline after the water dip, detection limits, precision and accuracy for chlorite, bromate, bromide and chlorate are discussed. The advantages/disadvantages of using each suppressor are also discussed.

2. Experimental

The Dionex (Sunnyvale, CA, USA) AMMS III suppressor incorporates a new, displacement chemical regeneration technique in which the suppressed eluent is used to displace the sulfuric acid regenerant from the reservoir and through the suppressor. Consequently, the regenerant flow-rate matches the eluent flow-rate. The recommended sulfuric acid concentration when using the new DCR technique with a 4-mm column and an eluent flow-rate of 1.5 ml/min is 37.5 mM. Since the eluent flow-rate used with EPA Method 300.1 is 1.3 ml/min with a 4-mm column, it was decided to evaluate a regenerant concentration at 75 mM. Acceptable baseline stability was obtained and this concentration was used throughout this study.

Sufficient quantities of all solutions were prepared to allow for comparison of the three suppressors with the same solutions using EPA Method 300.1 protocols. Prior to initiating the performance evaluation for the individual suppressors, normal EPA quality control (QC) protocols were used to validate instrument performance. The instrument was calibrated with each suppressor, using six calibration standards. The instrument calibration was validated by analysis of an external second source quality control sample. The low-, mid- and high-level calibration check standards to be used for QC in the various analysis batches were also validated prior to evaluating the

suppressor's performance. The suppressor perform-
ance was evaluated by determining the detection
limits using solutions containing 2.0 and 5.0 µg/l of
the four analytes in both reagent water (RW) and
simulated high ionic water (HIW). The suppressor
performance was further evaluated by assessing the
precision and accuracy, by analyzing solutions con-
taining 100 and 500 µg/l chlorite, bromide and
chlorate combined with 10 and 25 µg/l bromate,
respectively, in RW, HIW and simulated high organic
(HOW) water. The HIW and HOW matrices were
part of the development of EPA Method 300.1 to
evaluate the potential for matrix effects and conse-
quently, also evaluated in the suppressor comparison
work.

2.1. Reagents

The eluent, standards, stabilization solution, surro-
gate and all dilutions were prepared using 18 MΩ
water. American Chemical Society (ACS) reagent
grade Na_2CO_3 was used to prepare 9.0 mM carbon-
ate eluent (Aldrich, Catalog No. 22,348-4, Mil-
waukee, WI, USA), which was membrane filtered
(0.45 µm) and degassed with helium prior to use.
Ethylenediamine (EDA) preservation solution (100
mg/ml) was prepared from +99.5% EDA (Aldrich,
Catalog No. 39,108-5). Dichloroacetate (DCA) sur-
rogate solution was prepared from dichloroacetic
acid, potassium salt (Aldrich, Catalog No. 34,808-2;
0.065 g/100 ml reagent water). Sulfuric acid (Fisher
Scientific Certified ACS Plus, A 300-500, Fair Lawn,
NJ, USA) was used to prepare the 75 mM regenerant
solution. The HIW was prepared from reagent water,
which was fortified with the common anions of
chloride at 100 mg/l, carbonate at 100 mg/l, nitrate
at 10.0 mg/l as nitrogen, phosphate at 10.0 mg/l as
phosphorus, and sulfate at 100 mg/l [11]. The HOW
was prepared from reagent water fortified with 2.0
mg/l humic acid [11].

2.2. Standard and sample preparation

The calibration standards, continuing calibration
check standards and spiking solutions were prepared
using an EPA Information Collection Rule 1.0 mg/
ml National Exposure Research Laboratory stock
solutions. All calibration and continuing calibration
check standards were stabilized with the addition of

EDA stabilization solution (50 µl/100 ml of sam-
ple). Dichloroacetic acid (DCA) was used as the
surrogate and therefore was added to all standards
and samples just prior to analysis (10 µl/5.0 ml of
sample). Dionex autosampler vials were used to filter
all standards and samples prior to analysis.

2.3. Instrumentation

A Dionex autosampler and a rear-loading Rheo-
dyne Load/Inject valve with a 225-µl sample loop
were connected to the Dionex DX500 microbore
pump, which delivered the eluent (1.3 ml/min) to a
Dionex 4-mm IonPac AG9-HC guard and IonPac
AS9-HC analytical column for separation. Following
suppression, the suppressed eluent entered a Dionex
CD20 conductivity detector. The effluent from the
conductivity detector was directed to waste. A
personal computer (PC) with Peak Net software
(version 5.21) was utilized to control the instrument
and to process data.

3. Results and discussion

EPA Method 300.1 QC requirements, including
those defined above, were implemented and met for
successive analysis batches that were incorporated
for extended, 24-h overnight analyses.

During assessment of the suppressor performance
when using the AMMS III in the DCR mode,
baseline drift was observed when successive analysis
batches were analyzed during extended, overnight
24-h runs with both the 2- and 4-l reservoirs (see Fig.
1). The drift was both positive and negative and,
although it did not appear to affect the QC data
during the run, it was decided to evaluate the AMMS
III suppressor using normal chemical suppression
(CS) as well. Since in the DCR mode, the regenerant
flow-rate matched the eluent flow-rate (i.e. 1.3 ml/
min), it was decided to use a regenerant flow
delivered pneumatically at a rate of 1.3 ml/min. In
order to obtain a regenerant flow-rate of 1.3 ml/min
for evaluation of the AMMS III suppressor in the
normal chemical suppression mode, a 3-in. piece of
0.01 in. I.D. polyethylether ketone (PEEK) tubing
was connected to the suppressor waste line to
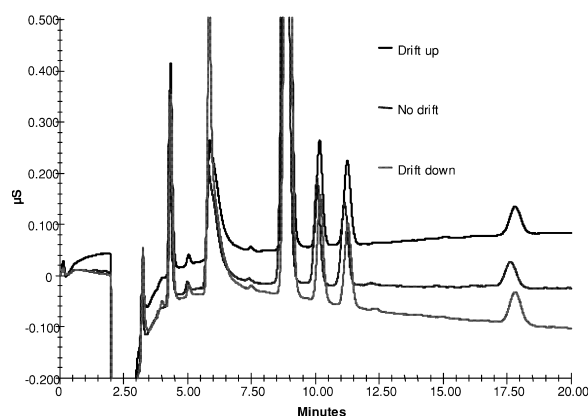provide the sufficient backpressure for constant flow

Fig. 1. Baseline drift observed during 24-h run using AMMS III suppressor in the DCR mode with a 2-l reservoir. No baseline drift was observed when the AMMS III suppressor was operated in the chemical suppression mode. Samples contained 100 µg/l chlorite, bromide and chlorate with 10.0 µg/l bromate.

(1 in.=2.54 cm). To avoid running out of regenerant solution in the CS mode, two, 2-l reservoirs were piggybacked in series. A single 4-l reservoir provided another alternative. Consequently, five comparative experiments were conducted and identified as: ASRS, AMMS III-DCR 2-l, AMMS III-DCR 4-l, AMMS III-CS and AES (see Tables 1–3).

The Ultra ASRS is an electrolytic suppressor and was configured using reverse osmosis water in the external water mode. The Atlas AES, which is also an electrolytic suppressor, was configured in the recycle mode. The AMMS III, when used in the DCR mode, was configured with the ''eluent out'' line connected to the regenerant reservoir and when used in the normal chemical suppression mode was configured with the ''eluent out'' line directed to waste. An overlay of the typical chromatograms obtained using a RW standard containing 5.0 µg/l of chlorite, bromate, bromide and chlorate with the three suppressors is shown in Fig. 2.

3.1. Comparison of suppressor return to baseline

When using suppressed conductivity detection, aqueous matrices produce a negative peak at the front of the chromatogram, commonly referred to as the ''water dip''. The size of the water dip, and consequently the time required to return to the starting baseline after the ''water dip'', is dependent upon several factors, including eluent strength, injection volume, sample matrix and suppressor void/ dead volume. As shown in Fig. 2, the baseline returns to its starting point faster with the Atlas

Table 1
Method detection limits in RW and a simulated HIW

Analyte and matrix (µg/l)[a]	Ultra ASRS (µg/l)	AMMS III DCR 2-l (µg/l)	AMMS III DCR 4-l (µg/l)	AMMS III CS (µg/l)	Atlas AES (µg/l)
Chlorite RW (2.0)	1.67	0.61	0.87	0.55	1.28
Chlorite HIW (2.0)	1.83	0.52	0.64	0.75	1.02
Chlorite RW (5.0)	1.28	0.78	0.93	0.72	0.94
Chlorite HIW (5.0)	2.41	0.98	1.24	0.51	1.14
Bromate RW (2.0)	1.62	0.75	1.02	0.61	1.74
Bromate HIW (2.0)	3.49	1.32	0.94	0.90	2.00
Bromate RW (5.0)	1.15	0.78	0.96	0.79	1.41
Bromate HIW (5.0)	3.36	1.07	1.34	0.92	1.68
Bromide RW (2.0)	3.77	0.60	1.90	0.83	1.19
Bromide HIW (2.0)	4.44	0.61	1.91	1.21	1.65
Bromide RW (5.0)	1.05	0.89	1.40	0.80	1.05
Bromide HIW (5.0)	4.00	1.51	1.66	1.25	1.36
Chlorate RW (2.0)	5.86	1.00	2.00	1.28	1.61
Chlorate HIW (2.0)	6.15	0.75	1.06	0.66	1.39
Chlorate RW (5.0)	2.03	0.67	1.33	0.78	1.98
Chlorate HIW (5.0)	4.11	0.66	2.08	1.81	1.36

[a] Number in parenthesis indicates the concentration fortified into each matrix.

Table 2
Method precision and accuracy (chlorite and bromate in RW, HIW and HOW)

Analyte and matrix (µg/l)	RSD, % (Recovery, %)				
	Ultra ASRS	AMMS III DCR 2-l	AMMS III DCR 4-l	AMMS III CS	Atlas AES
Chlorite RW	1.86	1.69	1.49	2.83	0.92
100+10[a]	(96.3)	(96.9)	(95.9)	(95.0)	(91.1)
Chlorite HIW	5.26	2.23	0.91	1.60	0.42
100+10	(96.8)	(95.3)	(94.7)	(95.0)	(91.4)
Chlorite HOW	1.09	0.28	0.79	1.06	1.80
100+10	(91.9)	(91.3)	(94.0)	(93.4)	(90.9)
Chlorite RW	0.89	1.31	0.66	0.80	0.20
500+25	(99.2)	(99.5)	(99.0)	(99.5)	(95.1)
Chlorite HIW	2.25	0.62	0.94	0.97	0.41
500+25	(98.2)	(98.0)	(99.5)	(98.5)	(95.8)
Chlorite HOW	0.64	0.56	0.67	0.71	0.74
500+25	(95.2)	(97.0)	(97.6)	(98.4)	(95.0)
Bromate RW	3.59	3.64	8.82	4.84	2.14
100+10	(99.7)	(97.9)	(99.6)	(97.4)	(99.6)
Bromate HIW	6.53	5.33	8.07	6.37	5.77
100+10	(98.9)	(99.0)	(97.5)	(95.9)	(101)
Bromate HOW	2.74	3.68	7.41	4.09	5.78
100+10	(99.0)	(102)	(97.9)	(96.1)	(102)
Bromate RW	2.22	2.89	2.05	3.12	3.62
500+25	(101)	(100)	(99.0)	(97.7)	(102)
Bromate HIW	5.04	2.08	3.51	3.11	1.93
500+25	(102)	(100)	(98.9)	(97.2)	(98.6)
Bromate HOW	3.63	2.67	2.72	1.50	1.85
500+25	(100)	(99.9)	(99.5)	(101)	(100)

[a] Fortification level in µg/l.

suppressor then with the other two suppressors. Consequently the chlorite and bromate peaks are not on the returning shoulder of the water dip. It is speculated that the faster return to baseline with the Atlas suppressor is attributable to the lower void/dead volume of this suppressor.

3.2. Comparison of suppressor baseline noise

Detection limits are dramatically affected by baseline noise and/or the signal-to-noise ratio. As shown in Fig. 2, the baseline noise (measured as peak-to-peak over a defined time) was determined to be 6.2 nS for the Ultra suppressor, 2.5 nS for the Atlas suppressor and 0.72 nS for the AMMS III suppressor. The lowest detection limits, as shown in Table 1, were obtained with the AMMS III suppressor. The AMMS III performance was essentially the same in either the DCR mode with 2- or 4-l

reservoirs or in the normal chemical suppression mode. However, baseline drift (see Fig. 1) was observed during extended, overnight runs in the DCR mode with both the 2- and 4-l reservoirs. The baseline drift was more noticeable with the 4-l reservoir. Due to volume limitations, when the DCR 2-l mode was used for extended, overnight operation, the run had to be paused after approximately 8–10 h. The regenerant and eluent reservoirs were re-filled and the system re-equilibrated before continuing with then next unattended 14–16 h of operation.

3.3. Determination of detection limits

The detection limits for each suppressor and combination were evaluated using EPA protocols according to Glaser et al. [15] and were determined by analyzing seven replicate solutions containing 2.0 and 5.0 µg/l of the four analytes in both RW and a

Table 3
Method precision and accuracy (bromide and chlorate in RW, HIW and HOW)

| Analyte and matrix (µg/l)	RSD, % (Recovery, %)				
	Ultra ASRS	AMMS III DCR 2-l	AMMS III DCR 4-l	AMMS III CS	Atlas AES
Bromide RW	1.84	1.75	1.18	1.58	1.02
100+10[a]	(100)	(101)	(99.2)	(99.5)	(96.4)
Bromide HIW	5.52	1.25	2.15	1.29	0.66
100+10	(105)	(103)	(104)	(104)	(103)
Bromide HOW	2.88	2.04	1.73	5.51	6.04
100+10	(104)	(104)	(97.7)	(102)	(104)
Bromide RW	1.03	1.76	0.61	0.84	0.26
500+25	(100)	(102)	(102)	(103)	(99.7)
Bromide HIW	2.05	0.85	0.74	0.76	0.25
500+25	(101)	(102)	(105)	(104)	(102)
Bromide HOW	0.57	1.10	1.43	0.65	0.80
500+25	(98.5)	(104)	(103)	(104)	(101)
Chlorate RW	2.24	2.12	2.41	1.66	0.80
100+10	(103)	(101)	(100)	(99.7)	(97.1)
Chlorate HIW	4.84	1.67	1.05	1.07	0.75
100+10	(100)	(93.6)	(94.3)	(94.4)	(93.4)
Chlorate HOW	1.67	1.96	4.02	1.95	2.10
100+10	(97.5)	(98.9)	(111)	(97.3)	(97.9)
Chlorate RW	1.13	1.49	0.49	1.17	0.15
500+25	(101)	(102)	(102)	(102)	(99.9)
Chlorate HIW	2.12	0.86	0.94	0.65	0.21
500+25	(97.9)	(96.9)	(98.3)	(99.1)	(97.2)
Chlorate HOW	1.08	0.66	1.76	1.17	0.86
500+25	(99.1)	(102)	(100)	(102)	(99.6)

[a] Fortification level in µg/l.
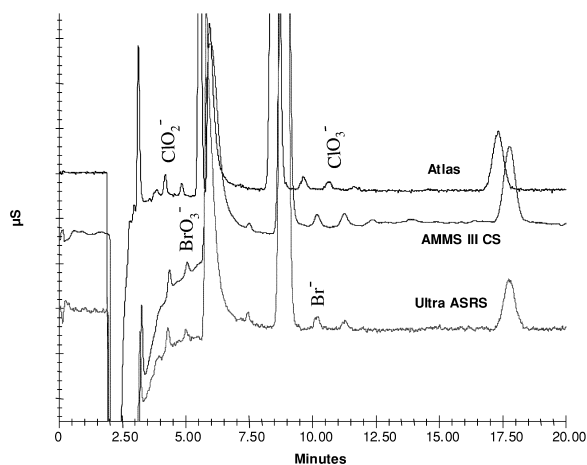
Fig. 2. Suppressor comparisons, Ultra ASRS, AMMS III in CS mode and Atlas AES using 5.0 µg/l of all four analytes. The baseline noise was determined to be 6.2 nS for the Ultra suppressor, 0.72 nS for the AMMS III suppressor and 2.5 nS for the Atlas suppressor. Chromatograms are offset 50% for clarity.

simulated HIW. The same day detection limits were calculated as 3.14 times the standard deviation (SD) of the seven replicates.

In general, as indicated in Table 1, the lowest detection limits were obtained with the AMMS III, followed by the Atlas AES and finally the Ultra ASRS. The bromate detection limits in Table 1 were the only data subjected to statistical evaluation since this work was initiated to determine if the different suppressors and/or combinations could improve the analysis of bromate, especially in high ionic matrices using EPA Method 300.1 protocols. Statistical analysis using Hartley's F-max test combined with pairwise F-tests confirmed that the AMMS III detection limits were statistically significantly lower, at the 95% confidence level, than the Ultra ASRS in three of the four matrices tested. The RW 5.0 µg/l comparison was not statistically significantly different.

No statistically significant differences were observed between the Ultra and the Atlas suppressors in the four matrices tested.

The AMMS III provided a statistically significant lower detection limit, at the 95% confidence level, in the RW 2.0 μg/l matrix compared to the Atlas suppressor. As well the AMMS III exhibited a 2.22 times lower detection limit in the HIW 2.0 μg/l matrix than the Atlas suppressor (0.90 vs. 2.00 μg/l). Albeit not statistically significantly different, this would be considered a significant difference by an experienced analyst. The other two matrices showed no significant differences between the AMMS III and Altas suppressors.

Although the AMMS III results were similar with all three combinations, DCR 2-l, DCR 4-l and with normal chemical suppression, the best results for baseline stability and bromate analyses, were obtained with the AMMS III suppressor in the CS mode. In fact, the simulated HIW matrix, at both the 2.0 and 5.0 μg/l concentrations had detection limits with no statistically significant differences compared to the RW detection limits with the AMMS III and Atlas suppressors. The 2.0 μg/l bromate peak in the HIW matrix was easily integrated using the AMMS III suppressor (see Fig. 3). Conversely, with the Ultra suppressor, the RW 5.0 μg/l detection limit was statistically significantly lower, at the 95% confidence level compared to the HIW matrix. The RW 2.0 μg/l matrix exhibited a 2.15 times lower

detection limit than the corresponding HIW matrix (1.62 vs. 3.49 μg/l). Again, although not statistically significant, this would be considered a significant difference by an experienced analyst. The elevated level of bromide (see Fig. 3) in the simulated HIW matrices is likely attributable to bromide impurities in the other salts used to prepare the HIW matrix.

3.4. Determination of suppressor performance (precision and accuracy)

The individual suppressor's performance in terms of precision (defined as percent relative standard deviation; RSD) and accuracy (defined as % recovery) was determined by analyzing seven replicates containing 100 μg/l chlorite, bromide and chlorate with 10.0 μg/l bromate, and 500 μg/l chlorite, bromide and chlorate with 25.0 μg/l bromate in RW, a simulated HIW and a simulated HOW using the five experimental combinations. The ranges chosen to evaluate the precision and accuracy were at the lower and mid levels of the calibration curve concentrations. As expected, the precision and accuracy, with the higher levels of analytes, was acceptable for all combinations and in all matrices. The chlorite precision ranged from 0.20 to 2.83% RSD and recovery ranged from 90.9 to 99.5%. The bromate precision ranged from 1.50 to 8.82% RSD and recovery ranged from 95.9 to 102%. The bromide precision ranged from 0.25 to 5.51% RSD and recovery ranged from 96.4 to 105%. The chlorate precision ranged from 0.15 to 4.84% RSD and recovery ranged from 93.4 to 111% (see Tables 2 and 3).

3.5. Comparisons of advantages and disadvantages of the three suppressors

The advantages and disadvantages observed with each suppressor and combination are listed in Table 4.

Fig. 3. AMMS III suppressor in chemical suppression mode with 2.0 μg/l of the four analytes in simulated HIW. The larger peak for bromide is likely attributable to bromide contamination in the salts used to prepare the HIW matrix.

4. Conclusions

The lowest baseline noise and detection limits were obtained with the AMMS III suppressor followed by the Atlas AES and finally the Ultra ASRS.
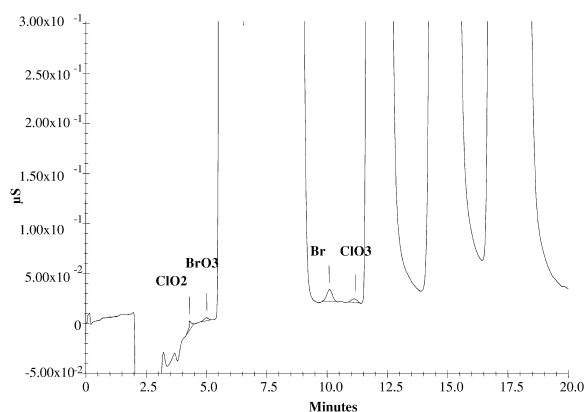
Table 4
Comparison of suppressor advantages and disadvantages

Suppressor	Advantage	Disadvantage
Ultra ASRS (external water mode)	RW as regenerant	Highest noise Highest detection limits In external water mode requires large reservoir More complex to use than the AMMS III
AMMS III DCR 2-l	Lowest noise Low detection limits Low regenerant flow 2-l regenerant reservoir	Sulfuric acid regenerant Baseline drift during extended runs Reservoirs need refilling and re-stabilization during extended runs Large void volume causes chlorite and bromate peaks to elute as the baseline is returning to starting point after the water dip
AMMS III DCR 4-l	Lowest noise Low detection limits Low regenerant flow 4-l regenerant reservoir	Sulfuric acid regenerant Baseline drift during extended runs Large void volume causes chlorite and bromate peaks to elute as the baseline is returning to starting point after the water dip
AMMS III CS	Lowest noise Low detection limits Low regenerant flow 4-l regenerant reservoir Easiest set-up and run for extended time	Sulfuric acid regenerant Large void volume causes chlorite and bromate peaks to elute as the baseline is returning to starting point after the water dip
Atlas AES (recycle mode)	Lowest void volume Baseline returns quickest Small void volume allows the baseline to return to starting point after the water dip and chlorite and bromate are essentially baseline resolved	Baseline noise higher than AMMS III detection limits higher than AMMS III Requires external controller for the suppressor More complex to use than the AMMS III and Ultra ASRS

The simulated HIW matrix had essentially no effect on the bromate detection limits using the AMMS III suppressor whereas the detection limits with the Atlas AES and Ultra ASRS were negatively impacted by the HIW matrix. The simulated HOW matrix had essentially no effect on the detection limits.

With the higher levels for the four analytes, acceptable precision and accuracy were obtained with all suppressors and combinations in all matrices.

The major difference among the three suppressors is their baseline noise and consequently, their ability to measure bromate accurately at concentrations at and below 5.0 µg/l. The AMMS III suppressor performed essentially the same in both the DCR and CS mode. However, in the DCR mode during extended overnight runs, both the 2- and 4-l reservoirs exhibited baseline drift. This baseline drift was eliminated when the AMMS III suppressor was used in the normal chemical suppression mode with the regenerant delivered pneumatically at a flow-rate of 1.3 ml/min.

Performance data for the three different suppressors indicate that chemical suppression of the eluent, using the AMMS III suppressor, is the most effective

means to reduce baseline noise, resulting in the best resolution and the lowest detection limits even when a high ionic matrix is analyzed. Incorporation of the AMMS III suppressor improves the performance of EPA Method 300.1 at and below 5.0 µg/l and is a quick way for laboratories to improve their bromate compliance monitoring.

Acknowledgements

References

[1] G. Gordon, R. Kieffer, D.H. Rosenblatt, The chemistry of chlorine dioxide, in: Progress in Inorganic Chemistry, Vol. 15, Wiley-Interscience, New York, 1972.

[2] E.M. Aieta, J.D. Berg, J. Am. Water Works Assoc. 78 (1986) 72.

[3] M. Bolyard, P.S. Fair, D.P. Hautman, Environ. Sci. Technol. 26 (1992) 1663.

[4] G. Gordon, L. Adam, B. Bubnis, Report on the American Water Works Association Research Foundation, AWWA, Denver, CO, 1995.

[5] E.A. Crecelius, Ozone News 5 (2) (1978) 1.

[6] W.R. Haag, J. Holgne, Environ. Sci. Technol. 17 (1983) 261.

[7] Y. Kurokawa, Y. Hayashi, A. Maekawa, M. Takahashi, T. Kokubo, S. Odashima, J. Natl. Cancer Inst. 71 (1983) 965.

[8] Y. Kurokawa, A. Maekawa, M. Takahashi, Y. Hayashi, Environ. Health Perspect. 87 (1990) 309.

[9] Fed. Reg. 59 (145) (1994) 38710.

[10] Fed. Reg 63 (241) (1998) 69390.

[11] D.P. Hautman, D. Munch, J.D. Pfaff, US EPA Method 300.1: Determination of Inorganic Anions in Drinking Water by Ion Chromatography, EPA/600/R-98/118, NTIS PB98-169196INZ, 1997.

[12] Fed. Reg 66 (60) (2001) 16858.

[13] H.P. Wagner, B.V. Pepich, D.P. Hautman, D.J. Munch, EPA Method 317.0: Determination of Inorganic Oxyhalide Disinfection By-Products in Drinking Water Using Ion Chromatography with the Addition of a Postcolumn Reagent for Trace Bromate Analysis, 2000.

[14] H.P. Wagner, B.V. Pepich, D.P. Hautman, D.J. Munch, U. von Gunten, EPA Method 326.0, Determination of Inorganic Oxyhalide Disinfection By-Products in Drinking Water Using Ion Chromatography Incorporating the Addition of a Suppressor Acidified Postcolumn Reagent for Trace Bromate Analysis, 2002.

[15] J.A. Glaser, D.L. Foerst, G.D. McKee, S.A. Quave, W.L. Budde, Environ. Sci. Technol. 15 (1981) 1426.