Determination of Bromate and Chloride and Bromide In Scrubber Water By Ion Chromatography With Suppressed Conductivity Detection

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Objectives

The objective of this application is to analyse bromate in scrubber solution by ion chromatography with suppressed conductivity detection on Integrion HPIC system. The sample matrix contains 0.64% NaCl, 0.16%NaBr, 0.35% Na_2CO_3, and 0.35% $SnO_2.2H_2O$, pH 10.5. This report shows that the bromate in this scrubber solution is very well analysed on IonPac AS19-4um, 2x250mm column using a KOH gradient as eluent. The chloride and bromide can be analysed under the same analytical condition with different sample prepare.
This report is considered proof of concept for purchasing IC system from Thermo Fisher Scientific.

Refer to: Thermo fisher scientific Application note 167 "Determination of Trace Concentrations of Oxyhalides and Bromide in Municipal and Bottled Water Using a Hydroxide-Selective Column with Reagent-Free Ion Chromatography System"

Instrumentation

Instrument:	Integrion with EG
Autosampler:	AS-AP
Data Management System:	Chromeleon 7.2.9

Analytical Condition

Column:	IonPac AS19-4um, 2x250mm (P/N: 083223) plus IonPac AG19-4um Guard, 2x50mm (P/N:083225)
Eluent:	KOH gradient by EG 10mM KOH, 0 to 10min; 10-45mM KOH, 10 to 25 min; 45mM KOH, 25-35min; Recondition column at 10mM KOH for 7min prior to injection
Flow rate:	0.25ml/min
Back Pressure:	~2800psi at 10mM KOH
Column Temperature:	30°C
Detection:	Suppressed Conductivity
Suppressor:	ADRS 600 2mm, recycle mode, constant current 28mA
Background:	<0.60 us
Injection:	100.0 µl
Standard:	1000 ppm bromate stock solution: 35.4mg $NaBrO_3$ dissolved in 30ml of DI water. 1000 ppm chloride stock solution: (P/N 037159) 1000 ppm bromide stock solution: 38.6mg NaBr dissolved in 30ml of DI water. 1000 ppm bicarbonate stock solution: 0.138g NaHCO3.anhydrous dissolved in 100ml DI water Simulated matrix: 40 ppm chloride, 15 ppm bromide

and 20 ppm bicarbonate (based on the sample concentration information that customer provided after 1:100 diluted)
Calibration working solutions are appropriately prepared for calibration solutions (see table1&2)

Sample: Scrubber water solution (lot VWRMJM-20, customer provided)

Sample prep: The sample was diluted 1:100 v/v in DI water prior to injection for bromate analysis (Density=1.011g/ml). The sample was diluted 1:1000 v/v in DI water prior to injection for chloride and bromide analysis.

DI water at 18.2MΩ-cm resistivity was used in standard preparation.

Table1. Concentration of bromate in simulated matrix for bromate calibration standards

Anions		level 1	level 2	level 3	level 4	level 5
Bromate	ppb	1.0	2.0	5	10	20
Chloride	ppm	40	40	40	40	40
Bromide	ppm	15	15	15	15	15
Bicarbonate	ppm	20	20	20	20	20

Table2. Concentration of chloride and bromide in DI water for chloride and bromide calibration standards

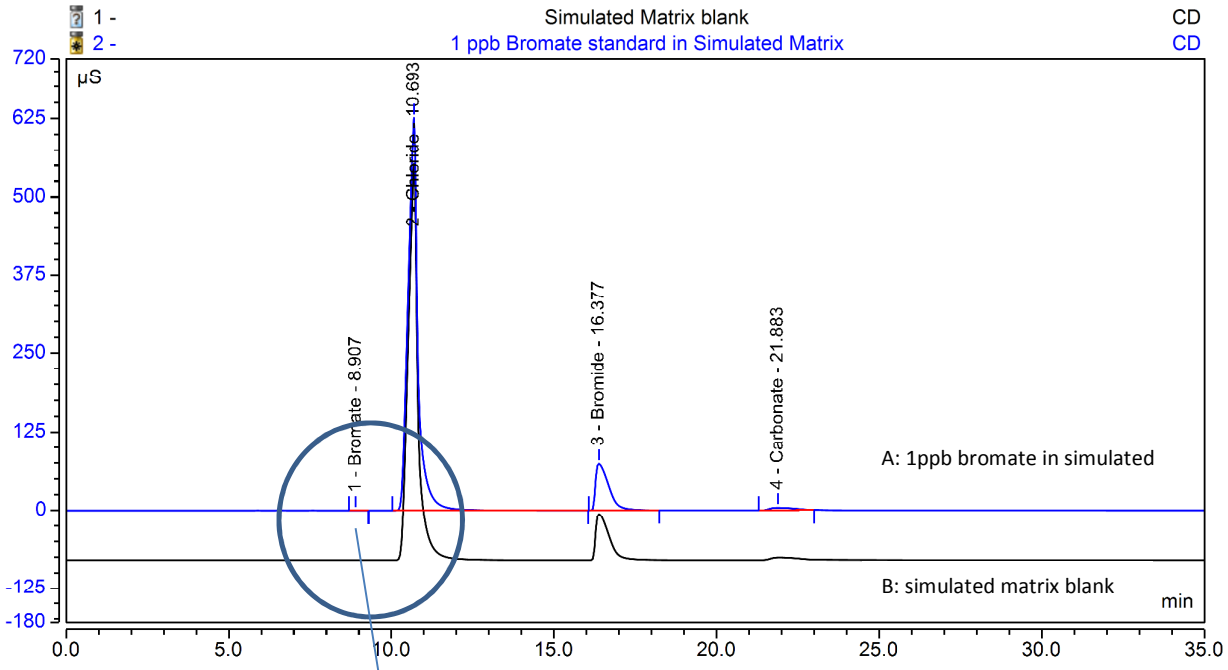
Anions		level 1	level 2	level 3	level 4
Chloride	ppm	0.4	2.0	4.0	8.0
Bromide	ppm	0.15	0.75	1.5	3.0

Results and Chromatograms

Table3. Quantification data (n=6, six replicates injection)

	Bromate-BrO3	Chloride-Cl	Bromide-Br
	ppm	ppm	ppm
Average (n=6)	0.400	3483.37	1166.52
RSD	1.44%	0.07%	0.11%

Figure1. Chromatograms of 1ppb bromate in simulated matrix (A) and simulated matrix (B)



1) Bromate-1.0ppb 2) Chloride-40ppm 3) Bromide-15ppm 4) Carbonate-20ppm

Zoom-In

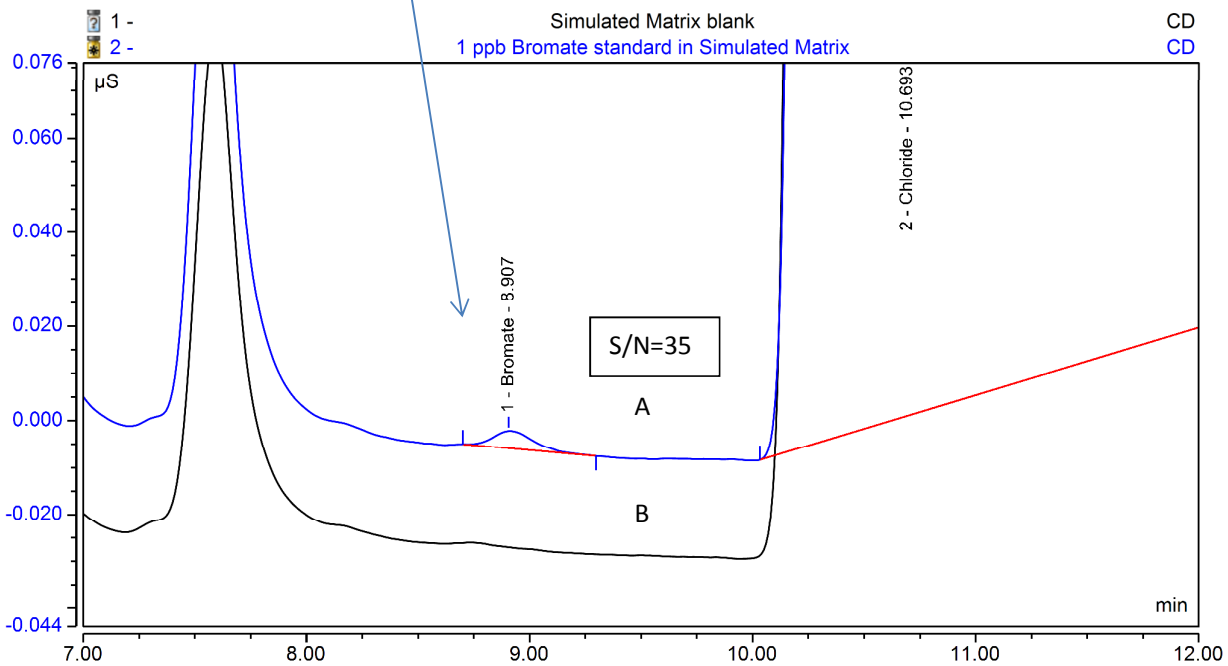


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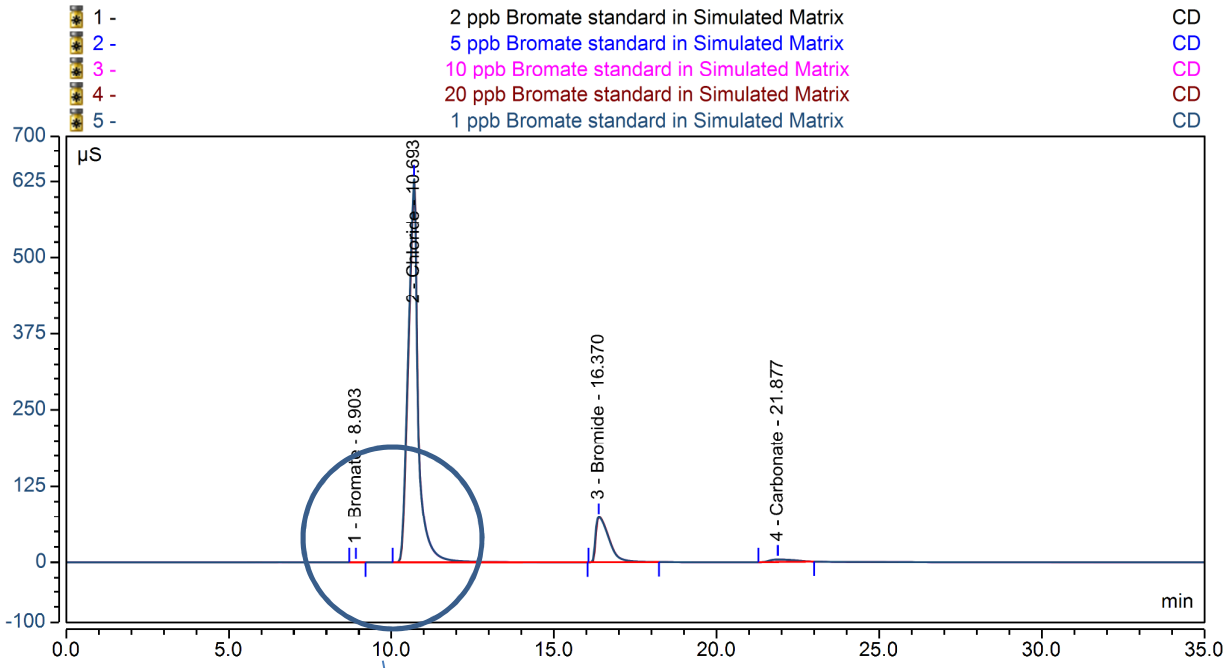
Figure2. Overlaid chromatograms of five levels of bromate in simulated matrix



Zoom-In

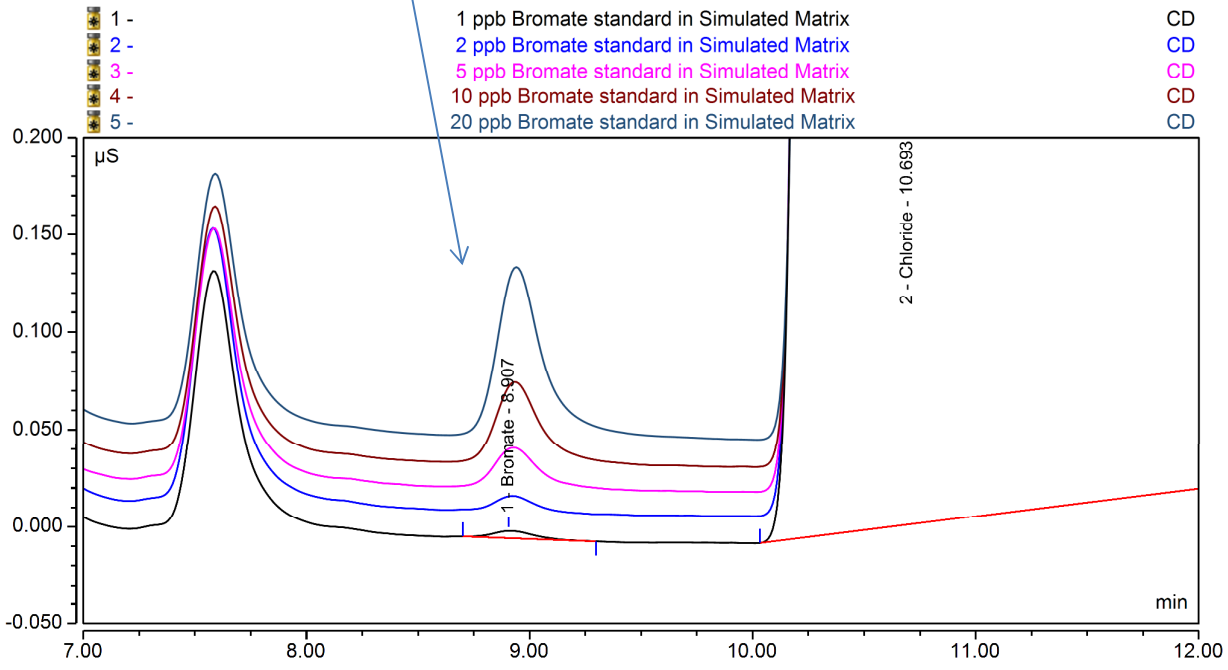


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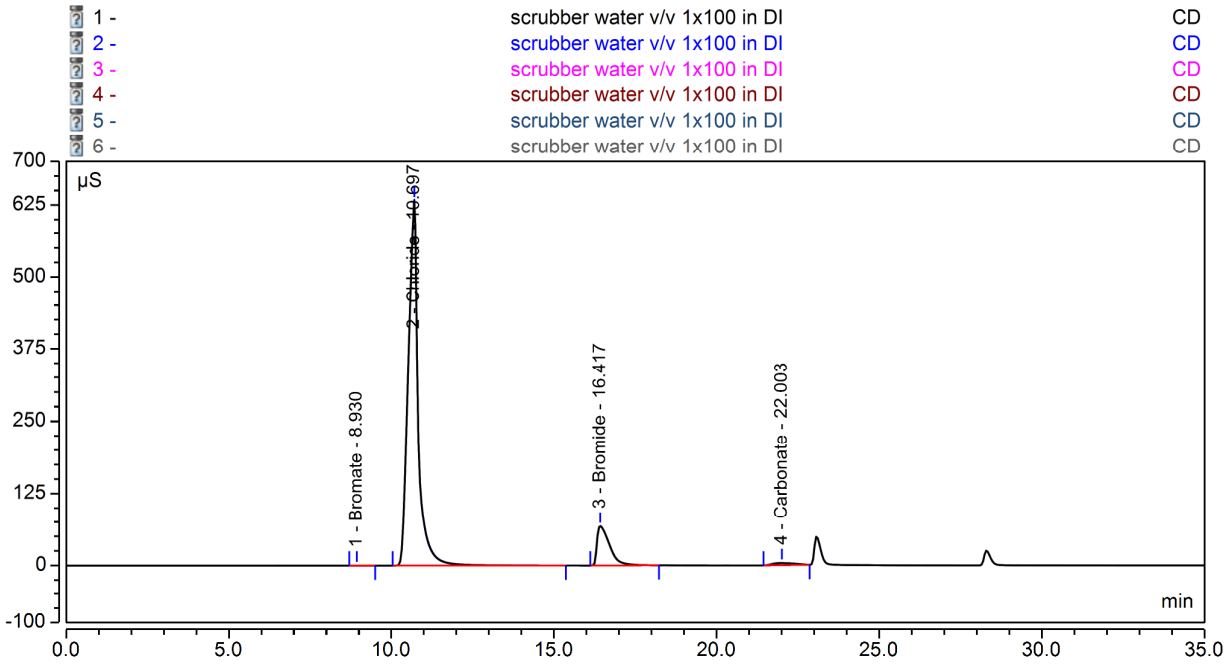
Figure3. Chromatogram of scrubber water solution 1:100 v/v diluted in DI water



Zoom-In

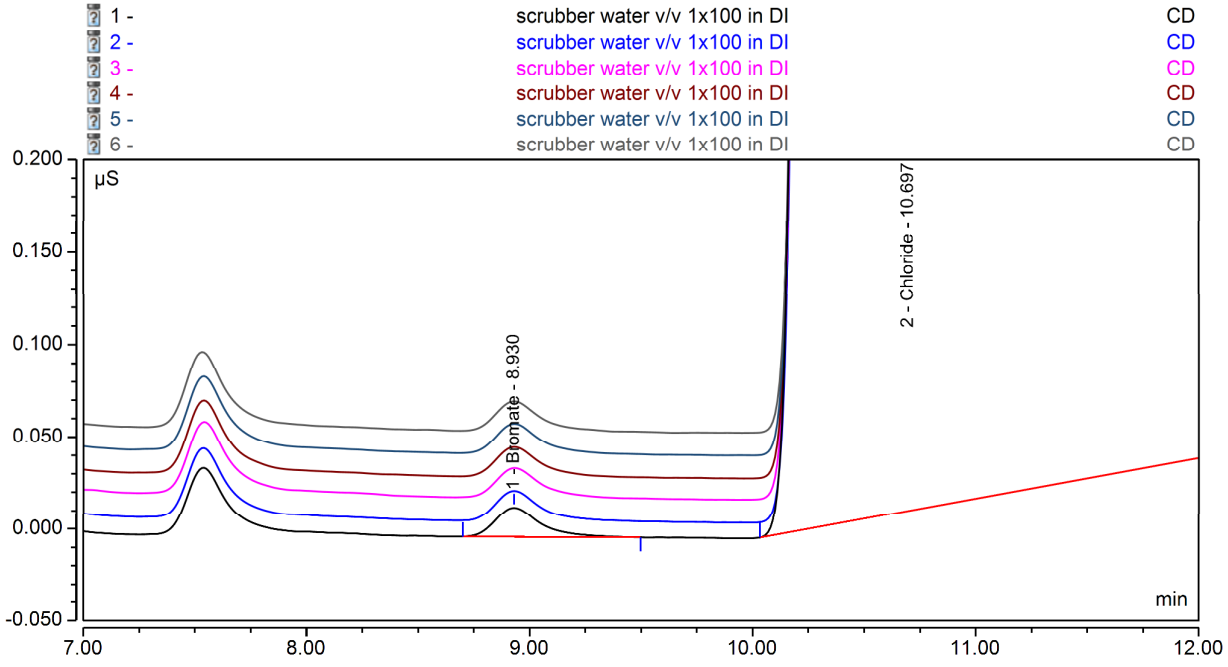


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Figure4. Recovery of bromate: 91.9% by spiked 5ppb bromate in scrubber water (sample 1:100 diluted in DI water)

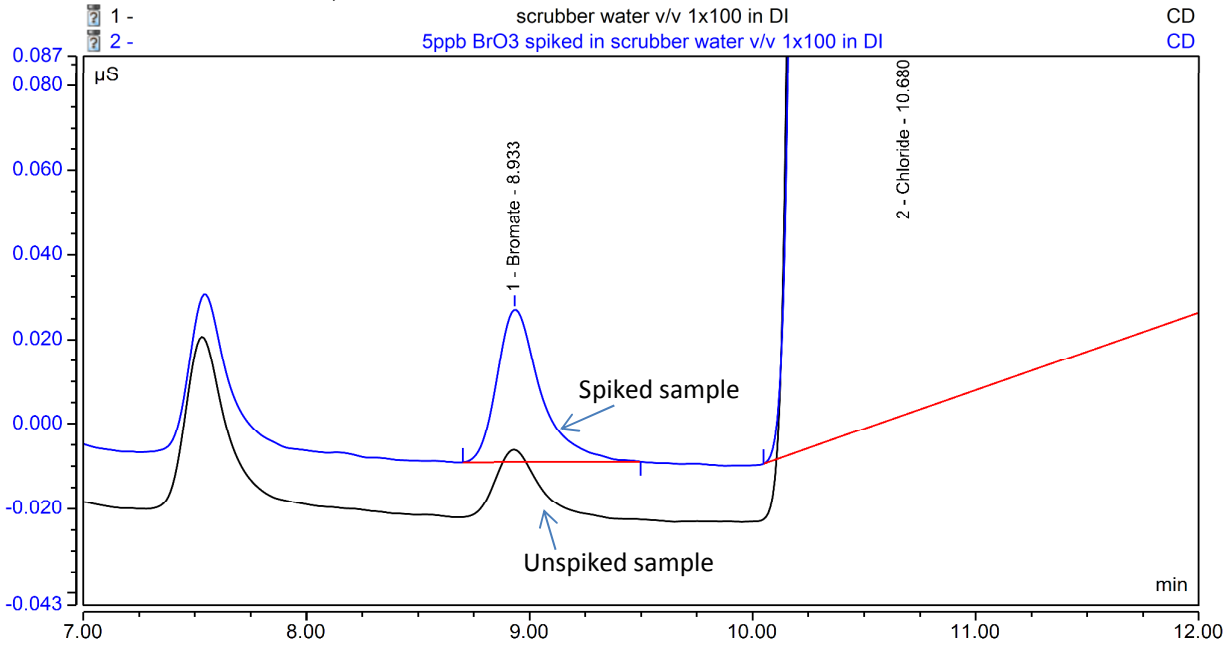

Figure5. Chromatogram of scrubber water solution 1:1,000 v/v diluted in DI water for chloride and bromide analysis

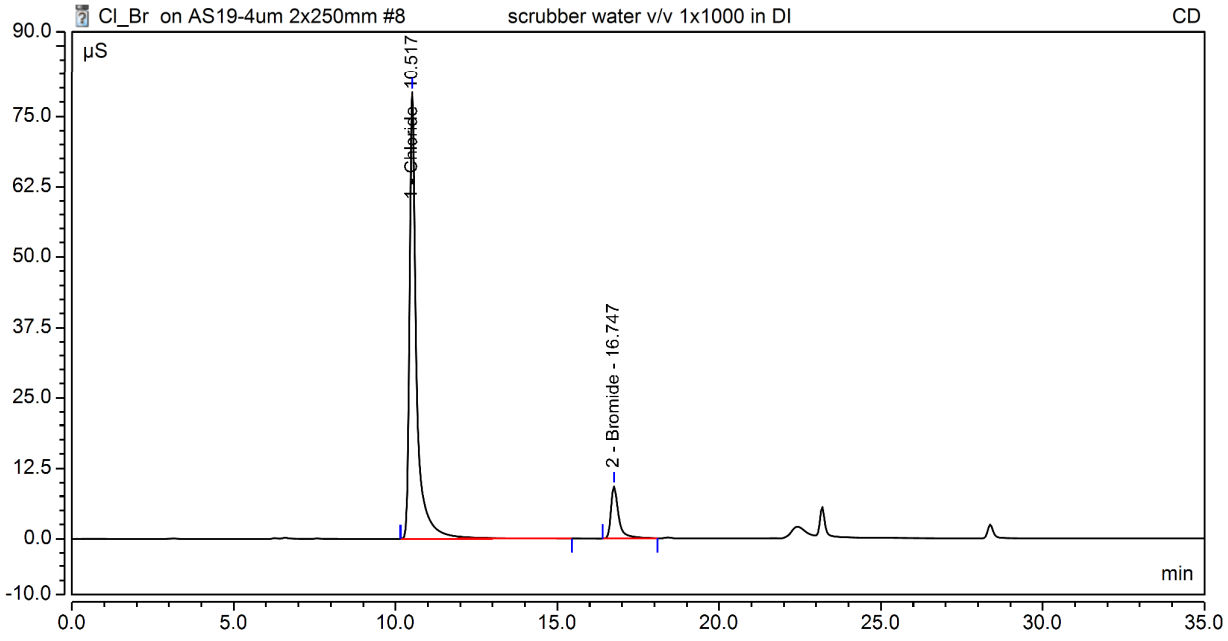

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Table4. Reproducibility of retention and peak area and MDL for bromate in simulated matrix (n=7, seven replicate injections)

Injection#	Peak Retention	Peak Area	Peak Amount
Bromate-1ppb	min	µs*min	ppb
1	8.91	0.0008	1.059
2	8.91	0.00082	1.074
3	8.91	0.00077	1.026
4	8.917	0.00082	1.080
5	8.913	0.00081	1.064
6	8.917	0.00083	1.086
7	8.92	0.00081	1.063
Average	8.914	0.0008	1.065
SD (Standard Deviation)	0.004	0	0.0199
RSD	0.05%	2.42%	1.87%
Calculated MDL in simulated matrix (ppb)			**0.062**
MDL=(t)x(SD), t=3.14 for seven replicates (n=7)			

Figure6. Calibration curves for bromate, chloride and bromide

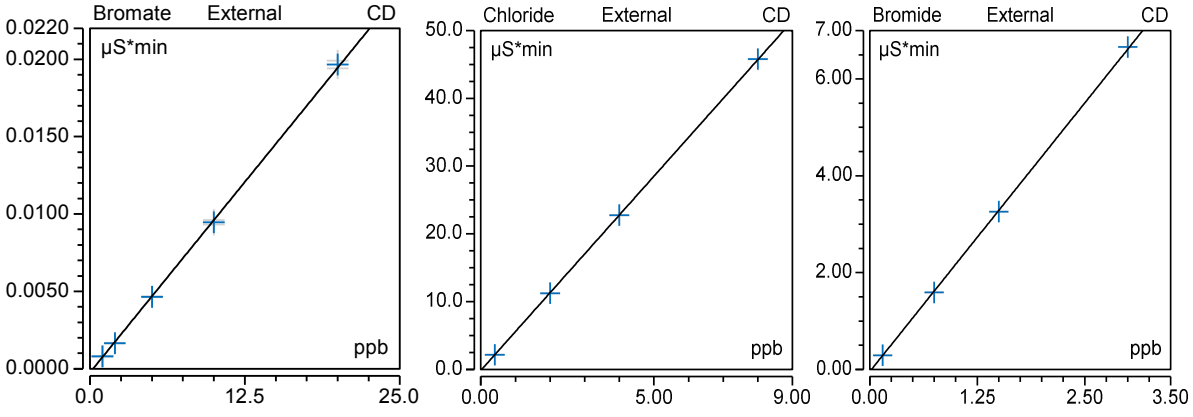

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Table5. Calibration summary

Bromate prepared in simulated matrix: 40ppm Chloride, 15ppm Bromide, 20ppm Bicarbonate

Peak Name	Ret.Time	Conc. Range	Cal.Type	Eval.Type	Number of Points	Coeff.of Determination	C0	C1
	min	ppb					(Offset)	(Slope)
Bromate	8.94	1.0-20.0	Lin, WithOffset, 1/A, Avg	Area	5	0.99958	-0.0002	0.001

Chloride and bromide prepared in DI water

Peak Name	Ret.Time	Conc. Range	Cal.Type	Eval.Type	Number of Points	Coeff.of Determination	C0	C1
	min	ppm					(Offset)	(Slope)
Chloride	10.513	0.4-8.0	Lin, WithOffset, 1/A, Avg	Area	4	0.99999	-0.1498	5.7331
Bromide	16.8	0.15-3.0	Lin, WithOffset, 1/A, Avg	Area	4	0.99987	-0.046	2.2198

Conclusions

1. Sub-ppm level of bromate in scrubber water can be very well analysed on IonPac AS19-4um, 2x250mm column using a KOH gradient by EG on Integrion HPIC system within 35 minutes (figure 1-3). High concentration of chloride and bromide in the sample with different dilution (1:1000 diluted in DI water) can be analysed under the same analytical condition (figure5). Table3 shows the quantification results.
2. Table4 shows the MDL result and reproducibility result of retention and peak area for seven replicate injections (1ppb bromate in simulated matrix). The RSD% of retention time is 0.05 and the RSD% of peak area is 2.42. The calculated MDL of bromate in simulated matrix (40ppm chloride, 15ppm bromide and 20ppm bicarbonate) is 0.062ppb. The MDL is estimated by injecting seven replicates of 1ppb bromate in simulated matrix. MDL is calculated as (t) X (SD), t=3.14 for seven replicates injection, SD is standard deviation of the replicate analysis. LOD is

0.10ppb (S/N=3) and LQD is 0.33ppb (S/N=10) which are determined by the S/N of 1ppb bromate in simulated matrix (figure1).

3. Calibration curve of bromate with concentration range 1.0ppb to 20 ppb in simulated matrix is excellent with coefficient determinations better than 99.9%. Calibration curve of chloride with concentration range 0.4 ppm to 8 ppm in DI water has 99.99% coefficient determination. Calibration curve of bromide with concentration range 0.15 ppm to 3.0 ppm in DI water has 99.98% coefficient determination. (seeTable6).
4. Recovery of bromate in scrubber water is 91.9% (figure 4). The result is obtained by spiking 5 ppb of bromate standard in the 1:100 diluted scrubber sample.