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Suppressor current switching: a simple and effective means to reduce background noise in ion chromatography

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Abstract

Background noise in ion chromatography with suppressed conductivity detection was significantly reduced for the period of time when the electric current to an anion self regenerating suppressor (ASRS) running in the recycle mode was turned-off. With high capacity AS11-HC columns, it was possible to maintain current free conditions from the beginning of the run past the chloride peak, which enables routine high sensitivity analysis of early to mid eluting peaks. This suppressor current switching was utilized for the analysis of bromate in drinking water with large volume injection using on-line removal of chloride by an On-Guard Ag⁺-cartridge. The method detection limit (MDL) was 0.21 µg/l in fortified reagent water. Coelution of bromate with an unknown compound was observed, but it was solved by the optimization of gradient program.

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1. Introduction

The lowest achievable background noise in ion chromatography with suppressed conductivity detection is defined by electronic noise of the detector and pump pulsation. Electronic noise of the detector cannot be reduced by the chemist, but the contribution of pump pulsation to background noise is strongly dependent on the background conductivity and thus should be minimized. The aim of suppressor technology which has been in use since 1975 [1] is simultaneously to reduce background conductivity

and to increase the analyte signal. In anion analysis using aqueous eluents, hydroxide based mobile phases are preferred, since this eluent is converted to low conducting water after suppression. Other traditional eluents like solutions of tetraborate and carbonate–hydrogencarbonate still contain higher levels of conducting tetraboric and carbonic acid in the eluent stream after suppression. It must be noted that recent advances in suppressor technology have enabled both the conversion of eluents to carbonic acid and its subsequent removal from the eluent inside a single suppressor unit resulting in background conductivity similar to that achieved with hydroxide eluents [2]. For the first time this has made it possible to make effective use of carbonate–hydrogencarbonate gradients to solve complex separation problems [3].

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Despite these benefits, this technology is not yet in widespread use.

Most common suppressors for hydroxide eluents in use today are micromembrane based units. These have traditionally used 10–25 mM sulfuric acid regenerants at flow rates of 5–10 ml/min enabling gradient elution [4], but also requiring frequent preparation of regenerant solutions and thus interruptions in operation. Full automation of sulfuric acid regenerated micromembrane suppressor has been achieved recently in the displacement chemical regeneration (DCR) mode of operation where eluent from conductivity cell replaces sulfuric acid from the regenerant reservoir. Since the regenerant flowrate is dictated by the eluent flow rate, more concentrated sulfuric acid has to be used. This results in higher background conductivity because more unwanted sulfate ions penetrate through membranes to the eluent stream [5]. Micromembrane suppressors using electrolysis of water from the conductivity cell as a source of hydronium ions produce very low background conductivity since no chemical regenerant is needed and the electric field effectively pushes eluent counterions through ion-exchange membrane away from the eluent stream. In conjunction with the fact that this recycle mode of operation simplifies IC operation even more than that achieved with DCR mode of chemical regeneration, it is no wonder that these “self regenerating suppressors” (SRS) have gained great popularity in routine applications. The main drawback of the recycle mode is that there is more high frequency background noise generated because electrolysis products and eluent counter-ions are slowly swept out of the device only by the flow rate of the eluent [6]. Two techniques to achieve a faster sweep out have been presented. In the external water mode of operation, water from pressurized bottle is directed through regenerant chambers at 4–10 ml/min in exactly the same manner as in chemical regeneration. In this way a significant reduction in baseline noise can be achieved but regenerant consumption is high [6]. The gas assisted recycle mode of operation uses 100 ml/min flow of an inert gas to assist in sweeping out. Gas flow is connected with a T-piece to the eluent stream from the detector cell just before it enters the regenerant-in-port of the suppressor. This mode of operation has been shown to produce even lower noise than external water with less system complexity and thus can be used for unattended operation [5]. The

lowest noise of all forms of micromembrane suppressors should be achieved with chemical regeneration in the DCR mode [7,8], despite the slight increase in background conductivity [5]. From the above discussion it can be concluded that an ideal micromembrane suppressor would have background conductivity and ease of operation as with SRS in the recycle mode and background noise as low as that achievable with micromembrane suppressor in the DCR mode, i.e. without noise caused by electrolytic processes. Yet, due to the nature of suppression, the noise caused by the heat of the neutralization reaction is always present with every mode of suppression.

This paper demonstrates that by removing the contribution of electrolysis to the background noise by simply turning off the suppressor current, great reductions in baseline noise can be achieved when running SRS in the recycle mode. This method to reduce background noise has been studied under the title “Intermittent Electrolytic Membrane Suppressor Regeneration for Ion Chromatography”, but for some reason it has not found wider use [9]. The power of this method was applied for the determination of bromate, a disinfection by-product often present at sub $\mu\text{g/l}$ levels in drinking water. With a large loop injection and on-line removal of chloride, the method detection limit (MDL) in simulated drinking water was 0.21 $\mu\text{g/l}$, i.e. comparable to that which can be achieved with IC-post column reagent [10–13]. Spiked Finnish real water samples were also analyzed.

2. Experimental

2.1. Reagents and standard stock solutions

MQ-water of 18.2 M Ω and analytical grade reagents were used to make all eluents, standard stock solutions, and dilutions. The 1000 mg/l standard stock solutions were made from sodium bromate (Aldrich, Steinheim, Germany, Cat. No.: 22,487-1), sodium chloride (Riedel-de Haën, Seelze, Germany, Cat. No.: 31434), and sodium sulfate (Merck, Darmstadt, Germany, Cat. No.: 1.006649.5000) in water. All standard stock solutions were stored at 4 °C and were stable for 6 months after preparation. Ethylenediamine (EDA) (Fluka, Buchs, Switzerland, Cat. No.: 03550) sample preservation solution (5%; v/v) was prepared

by diluting 10 ml of EDA to 200 ml with MQ-water. A 1022 mg/l stock solution of trifluoroacetic acid (TFAA) (Aldrich, Steinheim, Germany, Cat. No.: 30,203-1) internal standard was made by weighing one drop and diluting with water to 50 ml.

2.2. Standard and sample preparation

Serial dilutions of 10 and 1 mg/l were made from 1000 mg/l bromate standard stock solution. Bromate working standards between 0.5 and 50 $\mu\text{g/l}$ were prepared by dilution of 1 mg/l solution. Chloride (10 mg/l) and sulfate (50 mg/l) were added as background ions to working standards by dilution of 1000 mg/l stock standards. Bromate was also spiked to tap water from Kuopio and Uusikaupunki. These cities use surface water as raw water and have chlorination in the water purification process. In the Finnish scale, Kuopio represents low and Uusikaupunki high ionic strength chlorinated drinking water. These spiked samples were made to test the method in real samples. A total of 100 μl of preservation solution/100 ml was added to all standards and samples. Preserved standards and samples were stable at 4 °C at least for a week. A 24 mg/l dilution of TFAA was made and 50 μl of this internal standard solution plus 6 ml of standard/sample were pipetted into autosampler vials. The filter caps of the vials were used to filter all standards and samples. Dionex OnGuard-Ag (P/N 39637) and OnGuard-H (P/N39596) cartridges were attached in series between

autosampler and injection valve to automatically remove interfering chloride ion and chelate leached silver ions. AS40 automated sampler was operated in the Concentrator mode to push 5 ml of water sample slowly (at 1 ml/min) to the sample loop to enhance the efficiency of the chloride removal.

2.3. Instrumentation

A Dionex DX 600 IC system (Dionex, Sunnyvale, CA, USA) consisting of a GP50-2 standard bore gradient pump, an EG40 eluent generator, a LC25 chromatography module, AS40 automated sampler, and an ED50A electrochemical detector in conductivity mode was used. The temperature of LC25 chromatography module containing columns and the conductivity cell was set to 30 °C. Chromeleon 6.4 chromatography software was used for instrument control, data acquisition, and processing. A combination of ED50A and Chromeleon 6.4 software enable suppressor current switching as timed events in 1 mA increments. Carbonate free KOH-eluent was prepared from EGC-KOH-cartridge installed in the EG40 eluent generator. To remove hydrogen gas formed in the electric eluent preparation process, nitrogen gas flow through the eluent degas unit of EG40 was used [14].

To reduce pump pulsation, a GM3-gradient mixer, and 4.8 m of 0.5 mm i.d., 1.59 mm o.d. Teflon tubing were attached in series to serve as a pulse dampener immediately after the pump. With the normal oper-

Table 1
IC system operating parameters

Run program						
Time (min)	Flow (ml/min)	A (%)	B (%)	Valve	EG40 concentration (mM)	Suppressor current (mA)
-6.1	1.5	50	50	Load	50	186
-3.0	1.5	50	50	Load	2	186
0.0	1.5	50	50	Inject	2	186
1.0	1.5	50	50	Inject	2	90
1.5	1.5	50	50	Load		90
2.5	1.5	50	50	Load		0
9.0	1.5	50	50	Load	11	0
9.5	1.5	50	50	Load		186
14.0	1.5	50	50	Load	50	186
20.0	1.5	50	50	Load	50	186

Columns: IonPac AS11-HC, 9.0 μm (250 mm \times 4 mm); IonPac AG11-HC, 13.0 μm (50 mm \times 4 mm). Trap columns: IonPac ATC-HC, 750 μm (75 mm \times 9 mm). Eluent: KOH (source EG40), deionised water from bottles A and B. Injection volume: 1000 μl . Detection: Suppressed conductivity. Suppressor: Anion Self Regenerating Suppressor, ASRS-ULTRA.

ation pressure of 2150 psi we have not encountered problems with the durability of the Teflon tubing. To remove dissolved carbon dioxide and other trace contaminants from the MQ-water, a Dionex ATC-HC anion trap column (75 mm × 9 mm; i.d.) packed with high capacity anion-exchange resin in the hydroxide form was installed between pulse the dampener and the EGC-KOH-cartridge. The sample loop (1000 μl) was prepared from a 226.3 cm length of 0.75 mm; i.d. PEEK-tubing. Hydroxide selective high capacity columns Dionex AG11-HC (90 mm × 4 mm; i.d.) and AS11-HC (250 mm × 4 mm i.d.) were used. The capacity of the AS11-HC column is 290 meq. per column enabling large injected sample volumes. The suppressor was Dionex anion self regenerating suppressor, ASRS-ULTRA (4 mm) operated in the recycle mode. Details of IC system and operation conditions are given in Table 1.

3. Results and discussion

3.1. Column selection and reduction of baseline pulsation

The initial aim of the study was to develop a gradient method that could analyze common inorganic anions,

organic acids, and bromate in a single run from drinking water. In these preliminary experiments it was realized that with the AS11-HC column we were using it was possible to run ASRS suppressor without current from the beginning of the run to well past the nitrite (and thus past the bromate) peak before the capacity of the suppressor was exhausted. Fig. 1 demonstrates the effect of different suppressor currents on the baseline noise with the KOH gradient. Noise was measured with Chromeleon software, which calculates a regression line using the method of least square, then determines the maximum distance of two datapoints above and below the line. No injection was made in the preparation of the chromatogram in Fig. 1.

In these initial experiments, 4 mm AS11-HC columns were selected instead of the 2 mm type, since separation of early eluting fluoride, lactate, and acetate was much better with 4 mm columns. Some peaks were also of better shape and higher with the 4 mm column. Unfortunately, it transpired that it was not possible to find a gradient program that could separate bromate from chloride with 4 mm AS11-HC columns when the concentration of chloride was higher than 30 mg/l (loop size 400 μl). For this reason, a separate method for simultaneous determination of common inorganic anions and organic acids was developed (P. Rantakokko et al., unpublished research) and method

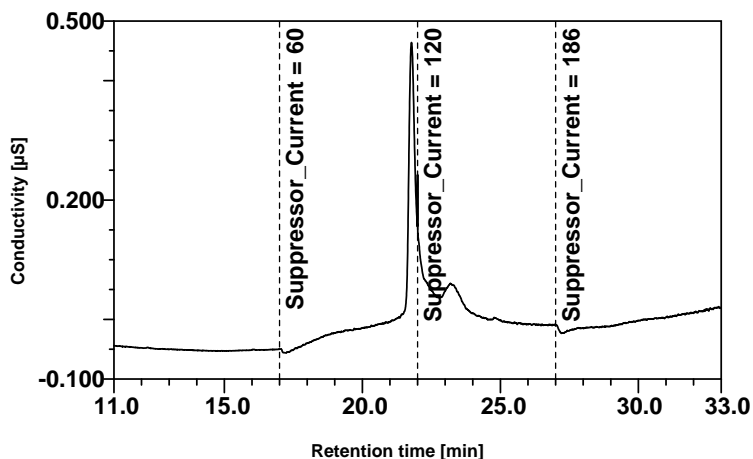


Fig. 1. A representative chromatogram showing the impact of suppressor current on baseline noise obtained for KOH-gradient without sample injection. Flow rate was 1.5 ml/min. Gradient program: 1 mM from 0 to 3 min, 3 mM at 8 min, 15 mM at 18 min, 30 mM at 27 min, 48 mM at 31 min, and 50 mM at 37 min. Suppressor was turned on at 17 min. Main peak around 22 min is trace carbonate from the system. The suppressor current on measured example noise sections were as follows: 0 mA 13.5–14.5 min: 0.56 nS/cm; 60 mA 19.5–20.5 min: 2.83 nS/cm; 120 mA 25.5–26.5 min: 3.53 nS/cm; 186 mA 30.5–31.5 min: 3.95 nS/cm.

development for bromate alone was continued. To avoid system downtime due to switching from 4 to 2 mm system, 4 mm columns were also selected for the analysis bromate. The size of the sample loop was increased to 1000 μl for bromate method, because this injection volume did not detectable broaden the bromate peak of spiked real water sample from the city of Uusikaupunki, tap water of which is one of the highest in salinity in Finland.

To minimize the contribution of pump pulsation to baseline noise, a pulse dampener consisting of two parts was constructed. First a GM3 gradient mixer was attached after the pump [15]. This was followed by 4.8 m of 0.5 mm i.d., 1.59 mm o.d. flexible walled Teflon tubing to provide further pulse dampening. Addition of this relatively large amount of dead volume after the pump does not cause any problem, since only deionized water flows through GM3 and Teflon tubing when EG40 is used to generate the eluent. It was also realized that the condition of the suppressor was crucial for low baseline pulse. An aging suppressor caused a clear baseline pulse of 2–3 nS/cm that followed pump cycle. The most likely reason for this pulse was that the aging suppressor “leaked” small electrolysis gas bubbles in to the eluent stream and these collected in the conductivity cell with a dynamic equilibrium determined by the backpressure after the cell. These bubbles amplified the pressure pulsation from the pump. When the amount of backpressure after the cell was increased from 27 to 40 psi, the pulse was reduced to 1–2 nS/cm with the old suppressor unit. When the aging suppressor was replaced, the noise was reduced to 0.3–0.5 nS/cm with 27 psi of backpressure after the cell. With a properly working suppressor, 0.5 $\mu\text{g/l}$ of bromate gave a clearly distinguishable peak from baseline noise as demonstrated in Fig. 2a. The same sample with the recommended current (186 mA) for the maximum eluent concentration (50 mM KOH) in the run program is shown for comparison in Fig. 2b.

The noise of a bromate run without sample injection was compared with the optimal case where only deionized water was pumped through backpressure tubing to the conductivity cell. Comparison of these two cases is shown in Table 2. It can be seen that the baseline noise achieved without suppressor current is close to that with deionized water. The noise values in Table 2 indicate, that further reductions in baseline noise will be difficult to achieve.

Table 2
Baseline noise in bromate runs without injection and with pure deionised water

Measured noise section	Baseline noise (nS/cm)	
	Bromate runs without injection ^a (1.0 min segment)	Pure deionised water ^b (1.0 min segments ^c)
1	0.41	0.24
2	0.44	0.28
3	0.44	0.32
4	0.80 ^d	0.33
5	0.55	0.29
6	0.39	0.33
Average	0.51	0.30

^a Baseline noise was measured from six consecutive runs, one measurement from each run, time segments cross the retention time of the bromate peak.

^b Only deionized water was pumped in one run through the cell at 1.5 ml/min for 20 min EG40, injection valve, columns, and suppressor were bypassed and replaced with enough PEEK-tubing to generate 2000 psi of backpressure.

^c Six 1.0 min segments with lowest noise were selected from 20 segments. Average of 20 segments was 0.37 nS/cm.

^d Sharp baseline disturbance doubled noise, with 0.9 min segment noise would have been 0.40 nS/cm.

3.2. Optimization of sample pretreatment and gradient program

Conductivity, post column reagent with spectrophotometric detection, and inductively coupled plasma mass spectrometry are the most commonly used methods of detection for bromate. In a study comparing these detection methods, it was found that under certain circumstances conductivity as a non-specific method gave higher results due to co-elution [16]. Especially when working with trace levels of analytes this places great demands on the chromatographic run program and requires experience on the part of laboratory personnel including knowledge of different sample matrices to be analyzed with their potential interferences. With this in mind, a gradient program and sample pretreatment were developed for optimal separation of interfering peaks.

It was realized that the use of on-line pretreatment for the removal of well-known chloride interference in contrast to conventional off-line removal would be a feasible solution. Ag^+ - and H^+ -cartridges attached in series between the autosampler and the injection loop effectively removed chloride and enabled fully

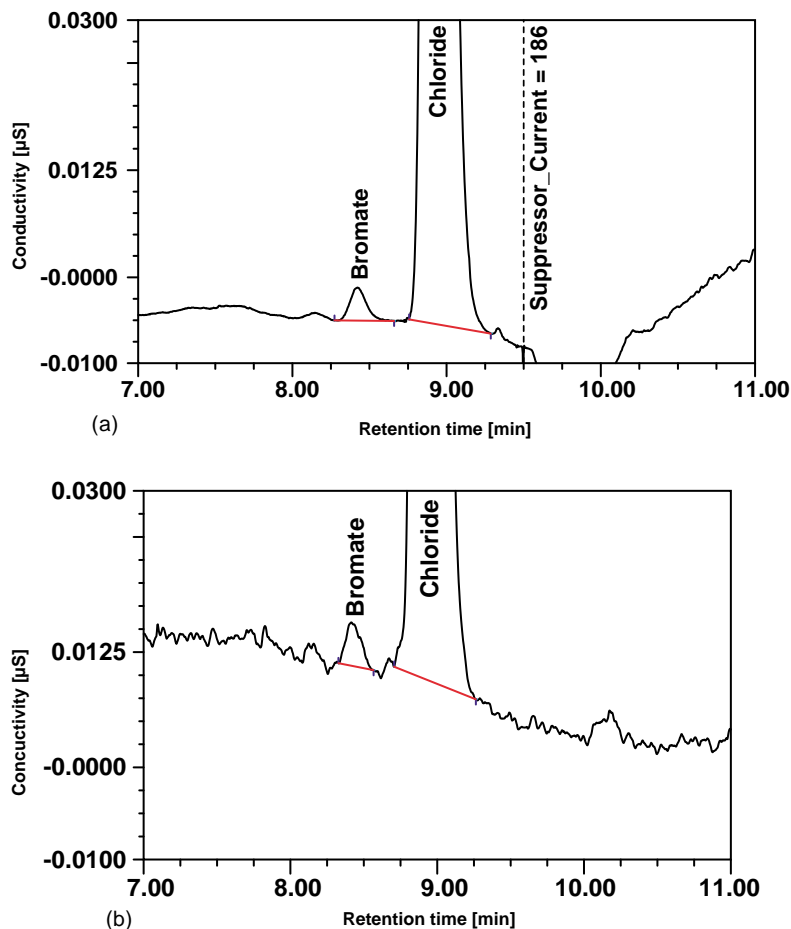


Fig. 2. A representative chromatogram showing injection of 0.5 µg/l of bromate in the presence 10 mg/l of chloride and 50 mg/l of sulfate, (a) conditions as in Table 1, (b) conditions as in Table 1, but the suppressor current was 186 mA during the whole run.

automatic operation. These cartridges have a capacity of 2 meq., which means that theoretically 1 l of water containing only 50 mg/l of chloride can be treated with one cartridge. In most cases this means that in practice these cartridges have to be replaced on a daily basis. Chloride removal was more complete when the autosampler was operated in the concentrator-mode pushing sample at 1 ml/min through the cartridges rather than at 4 ml/min in the loop-mode. Typical removal efficiency was between 99.5 and 99.9%. With on-line pretreatment it was not possible to remove carbonate by bubbling with helium, but this remaining carbonate had no impact on the results. Spike recoveries were acceptable for real samples using this method as demonstrated in Table 3.

Table 3
Spike recovery of bromate in different blank matrices^a

Spiked concentration (µg/l)	Average recovery (%) ± R.S.D. (%)	
	Kuopio tap water ^b : low ionic strength drinking water	Uusikaupunki tap water ^c : high ionic strength drinking water
1.0	107 ± 7.6	88 ± 2.3
2.5	105 ± 1.0	97 ± 6.8
10	103 ± 2.0	103 ± 3.7

^a Data were calculated from six replicate measurements ($n = 6$).

^b Kuopio tap water contained 0.1 mg/l F^- , 4.2 mg/l Cl^- , 0.6 mg/l NO_3^- , 28 mg/l SO_4^{2-} .

^c Uusikaupunki tap water contained 0.6 mg/l F^- , 39 mg/l Cl^- , 6.5 mg/l NO_3^- , 110 mg/l SO_4^{2-} .

The first attempts to find an optimal run program were made with isocratic elution using 8 mM KOH. In these experiments Kuopio tap water was spiked with 5 $\mu\text{g/l}$ of bromate, but close co-elution by an unknown compound was observed. Gradient program beginning with 2 mM KOH and increasing to 11 mM from 1 to 9 min gave the best results, but the differences in separation were not large when the elution time of bromate was kept to less than 10 min. After this KOH concentration was increased 50 mM to elute more strongly retained analytes. Instead of a one step gradient, it was necessary to employ a second gradient phase from 11 to 50 mM KOH from 9 to 14 min to separate the internal standard, TFAA, from bromide peak eluting after it. Fig. 3 shows an optimized separation of Kuopio tap water spiked with 1.0 $\mu\text{g/l}$ of bromate. The unknown peak eluting just before bromate did not prohibit quantification of this sample. In cases where the unknown peak would be larger and less bromate would be present, accurate quantification will be difficult or impossible. However, it is quite likely that many other conductivity based methods using columns with similar elution pattern as AS11-HC would encounter the same co-elution problem which is difficult to avoid if one wished to use suppressed conductivity detection. For example, we believe that EPA Method 300.1 using AS9-HC column and 9 mM carbonate eluent would not be able separate this co-elution any better [17]. Unfortunately AS9-HC column was not available to test this hypothesis.

3.3. Method performance

Linearity was tested from 1 to 50 $\mu\text{g/l}$ with bromate standards prepared in deionized water containing 10 mg/l of chloride and 50 mg/l of sulfate. The same concentration range was also spiked to Kuopio tap water. Correlation coefficients (r^2) were 0.9996 in deionized water and 0.9997 in Kuopio tap water, respectively.

Table 3 lists the spiking recoveries for Kuopio and Uusikaupunki chlorinated tap water between 1.0 and 10 $\mu\text{g/l}$. The recoveries are fully acceptable in terms of the trueness required by EU [18], even though there does seem to be some matrix dependent variation in recoveries especially at low concentrations. The high background ion concentration in water from Uusikaupunki caused slightly lower recoveries at low spiked concentrations. Co-elution in Kuopio tap water as demonstrated in Fig. 3, can lead to recoveries in excess of 100% at low concentrations.

Retention time reproducibilities were measured from 24 consecutive injections with bromate concentrations varying between 0.5 and 50 $\mu\text{g/l}$ in deionized ($n = 8$), Kuopio ($n = 7$), and Uusikaupunki ($n = 9$) waters. The retention times were between 8.41 and 8.47 min with a relative standard deviation of 0.21%.

The method detection limit (MDL) was determined from seven replicate injections of 0.5 $\mu\text{g/l}$ standard containing 10 mg/l of chloride and 50 mg/l of sulfate. When the standard deviation of these runs was multiplied with 3.143 (Student's t -value at 99% confi-

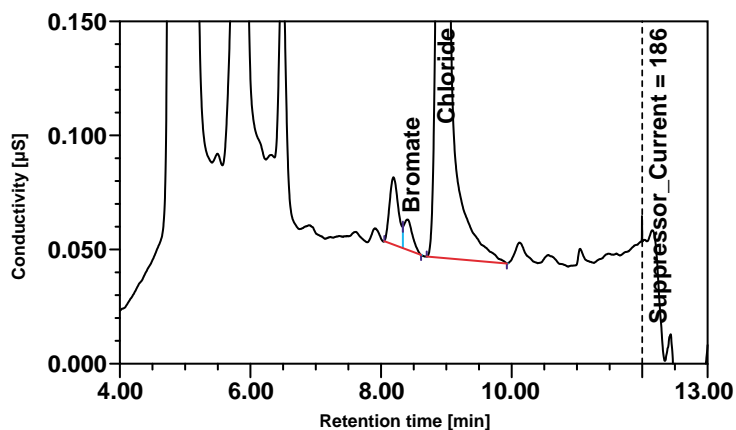


Fig. 3. A chromatogram obtained for Kuopio tap water spiked with 1.0 $\mu\text{g/l}$ of bromate. An unknown peak eluted just before bromate, the peak following bromate is chloride. Conditions as in Table 1, but the suppressor current was turned on at 12.0 min.

dence), MDL was found to be 0.21 $\mu\text{g/l}$. This value represents optimum conditions. As mentioned earlier, in the presence of co-eluting peaks, as in Fig. 3, MDL may be significantly increased. The low method detection limit will also be compromised if the capacity of the AS11-HC column is exceeded with a water sample of high salinity, requiring dilution of the sample or smaller injection loop.

4. Conclusions

The method detection limit achieved with the presented method is the lowest reported for bromate using suppressed conductivity detection with direct injection. This is in part due to the large injection volume, but is mainly attributable to the extremely low noise when running ASRS without current. The large injection volume caused no problems with a sample of relatively high ionic strength. The method can be fully automated with on-line removal of interfering chloride and uses the most simple recycle mode of the suppressor operation. It was also demonstrated that further reduction in baseline noise would be difficult to achieve. The main drawback of the method is the risk of interfering compounds, a problem common to most methods using conductivity detection at the trace level. Also, high salinity samples requiring a smaller injection loop will decrease the method detection limit.

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