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Journal of Chromatography A, 890 (2000) 295–301

JOURNAL OF CHROMATOGRAPHY A

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Simultaneous determination of inorganic disinfection by-products and the seven standard anions by ion chromatography

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Received 17 January 2000; received in revised form 12 April 2000; accepted 22 May 2000

Abstract

For the first time, an ion chromatographic method for the simultaneous determination of the disinfection by-products bromate, chlorite, chlorate, and the so-called seven standard anions, fluoride, chloride, nitrite, sulfate, bromide, nitrate and orthophosphate is presented. The separation of the ten anions was carried out using a laboratory-made high-capacity anion-exchanger. The high capacity anion-exchanger allowed the direct injection of large sample volumes without any sample pretreatment, even in the case of hard water samples. For quantification of fluoride, chloride, nitrite, sulfate, bromide, nitrate, orthophosphate and chlorate, a conductivity detection method was applied after chemical suppression. The post-column reaction, based on chlorpromazine, was optimized for the determination of chlorite and bromate. The method detection limit for bromate measured in deionized water is 100 ng/l and for chlorite, it is 700 ng/l. In hard drinking water, the method's detection limits are 700 ng/l (bromate) and 3.5 μg/l (chlorite). The method's detection limits for the other eight anions, determined by conductivity detection, are between 100 μg/l (nitrite) and 1.6 mg/l (chlorate).

Keywords: Water analysis; Disinfection by-products; Bromate; Chlorite; Chlorate; Anions

1. Introduction

Disinfection of drinking, mineral and table water, as well as of pool water, is carried out to preserve public health. The chemically reactive disinfectants produce disinfection by-products (DBPs) by reacting with substances in the water. Many papers about the organic disinfection by-products, like the trihalomethanes (THMs), which are strong carcinogens, have been published. However, discussion about the inorganic DBPs, like bromate, chlorite and chlorate, is becoming more and more popular. The ozonation process partially oxidizes bromide to the potential carcinogen bromate [1]. Water treatment using chlorine dioxide leads to the inorganic DBPs chlorite and chlorate. Experiments with animals have proved that both show a toxicological effect and may lead to hemolytic anemia [2]. The concentration limit for bromate in drinking water according to the World Health Organization (WHO) is 25 μg/l [3] and the US EPA sets a concentration limit of 10 μg/l [4]. The European Commission suggests a concentration limit for bromate in drinking water of 10 μg/l and a method detection limit of less than 2.5 μg/l. An

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0021-9673/00/$ – see front matter
PII: S0021-9673(00)00606-3

interlaboratory trial for bromate was organized by the European Commission in 1999, to establish the ISO/DIS 15061 [5], which describes the ion chromatographic determination of bromate with conductivity detection. The German drinking water regulation sets no concentration limit for bromate, but includes a concentration limit of 200 μg/l for chlorite [6]. Control and monitoring of inorganic DBPs is mandatory and requires sensitive analytical methods at reasonable costs.

The majority of methods for the simultaneous determination of bromate, chlorite and chlorate utilize ion chromatography (IC) for the separation, combined with a variety of detection methods. Ion-chromatographic methods with direct injection and conductivity detection after chemical suppression have been published [7,8]. Under idealized conditions, the method detection limits (MDLs) for bromate, chlorite and chlorate are 1.73, 2.38 and 1.07 μg/l, respectively [7]. An ion-chromatographic method for the determination of bromate, chlorite, chlorate, nitrite, bromide and nitrate, by conductivity or UV detection, based on a $NaOH–H_3BO_3$ eluent, was developed by Hautman and Bolyard [9]. They achieved MDLs of 7.3 μg/l for bromate, 3.4 μg/l for chlorite, 9.4 μg/l for chlorate, 8.3 μg/l for bromide, and of 1.4 and 2.4 μg/l for nitrite and nitrate, respectively, using conductivity detection. Using UV detection at 195 nm, they achieved MDLs as follows: bromate, 10.3 μg/l; chlorite, 9.4 μg/l: bromide, 7.6 μg/l; nitrite and nitrate, 2.1 μg/l. On-line coupling of IC with inductively coupled plasma mass spectrometry (ICP–MS) was investigated by several authors [10–16]. The MDLs for bromate were at the low μg/l level, for example, 0.67 μg/l (50 μl sample loop) [15] or 60 ng/l (with an 885-μl sample volume and the use of a laboratory-made high-capacity anion-exchanger) [16]. The MDLs for chlorine species were between 47 μg/l [15] and 500 μg/l [10]. Lower MDLs have been attained by Charles and Pépin [17] using electrospray ion chromatography–tandem mass spectrometry (IC–MS/MS). They found MDLs of 0.05 μg/l for bromate and chlorate, 0.5 μg/l for iodate and 1.0 μg/l for chlorite. The application of atmospheric pressure ionization mass spectrometry (API–MS), coupled to IC, showed a performance comparable to that of IC–MS/MS and IC–ICP–MS [18].

Another technique for the simultaneous determination of inorganic disinfection by-products is a post-column reaction (PCR) followed by spectrophotometric detection. Weinberg et al. [19,20] developed a PCR system for the determination of bromate and other oxyhalides that was based on the conversion of the oxyhalides to the tribromide ion. A sample pretreatment step was not required. The MDL for bromate was 0.2 μg/l, for iodate, it was 0.1 μg/l and for chlorite, it was 0.4 μg/l. A PCR method based on *o*-dianisidine was developed by Wagner et al. [21]. The method, which was based on a single post-column reagent has been combined with the US EPA Method 300.1 [22], and a MDL of 0.1 μg/l for bromate was found. In addition, the method enables the analysis of bromide, chlorite and chlorate. A MDL for bromate of 0.5 μg/l was achieved by Walters et al. [23] using a PCR with chlorpromazine. Nowack and von Gunten [24] published information about a post-column reaction method using iodide for the determination of chlorate. Chlorate oxidizes the iodide into iodine, which reacts with excess iodide to give the triiodide, which is detectable at 288 nm. They achieved a MDL of 0.4 μg/l for chlorate. The method also allows the simultaneous determination of chlorite, bromate and nitrite at the low μg/l level [24]. Achilli and Romele [25] used Fuchsin as the post-column reagent for the determination for bromate and obtained a MDL of 0.1 μg/l.

Anion analysis of water samples should be performed using as few methods as possible, and they should be as inexpensive and simple as possible. None of the methods for bromate determination described previously are able to determine all other commonly analyzed anions in water, for two main reasons: sample pretreatment and column overloading in the case of real-world samples.

We tried to overcome this limitation using a laboratory-made high-capacity column with an elution system that could be applied to high-capacity columns, and conductivity detection together with a sensitive, post-column, detection method for the most critical analytes, bromate and chlorite. The first step is the separation of the ten anions using a laboratory-made high-capacity anion-exchanger, which allows the usage of large sample volumes (585 μl) without any sample pretreatment, besides

filtration. The seven standard anions, fluoride, chloride, nitrite, sulfate, bromide, nitrate and orthophosphate, as well as chlorate, were detected by conductivity detection after chemical suppression. The second step in the analysis is the PCR with chlorpromazine (CHP). CHP, a phenothiazine, is oxidized, in HCl-acidified medium, by chlorite, bromate and nitrite, into a radical cation [27] that exhibits an intense pink color, which allows for spectrophotometric detection at 530 nm.

2. Experimental

2.1. Conditions for IC and PCR

The chromatographic system consisted of a Separation Center 733, a conductivity detector 732 and an IC pump 709, with pulse dampener (Metrohm, Switzerland). The tubings and fittings were made of PEEK. The separation column was a laboratory-made PS/DVB anion-exchanger with 2-(dimethylamino)-ethanol as the functional group and a capacity of 715 μmol/column. The core of the anion-exchanger consisted of a highly pressure-stable PS/DVB polymer, with an average diameter of 5–6 μm. First, the material was functionalized by chloromethylation using dimethoxymethane, sulfuryl chloride and chlorosulfonic acid. Afterwards, the chlorine was replaced by a tertiary amine by an S_N reaction.

For chemical suppression of the eluent, an Anion Micro Membrane Suppressor AMMS-1 (Dionex, Germany) was applied in the external mode with 0.025 mol/l H_2SO_4. The pump system for delivering the post-column reagents consisted of a control unit (Liquino 711 with a Dosino 700) equipped with a 5-ml dispensing unit for each reagent (all from Metrohm, Switzerland). At a flow-rate of 0.2 ml/min, as used throughout the experiments (Table 1), the time window for PCR analysis with a single burette volume was slightly below 25 min.

Brown storage bottles were used as light-protecting devices for the CHP solution. The laboratory-developed post-column reactor consisted of two mixing coils filled with micro-glass pearls of 420–560 μm size (Worf, Germany). The mixing coils and all tubings used for the post-column reaction were made of poly-tetrafluoroethylene (PTFE), whereas T-connectors and fittings were made of PEEK. The first mixing coil (0.3 m×0.7 mm I.D.) was used for mixing the eluent with reagent I (CHP) and reagent II (hydrochloric acid) was added with the second coil (1.0 m×0.7 mm I.D.). The separate addition of hydrochloric acid as the second reagent enhances the sensitivity of the spectrophotometric detection [28]. Reaction temperatures did not have an influence on the sensitivity of the spectrophotometric detection

Table 1
Conditions for ion chromatography and post-column reaction

Parameter	Setting/Value
Column; dimensions	P 160497 I DMEA, 120×4 mm I.D. PEEK,
Particle size	5–6 μm
Eluent composition	70 mmol/l NaOH+0.5 mmol/l $HClO_4$
Flow-rate of eluent	1.0 ml/min
Injection volume	585 μl
Detection mode for standard anions and chlorate	Conductivity
Suppressor regenerant	0.025 mol/l H_2SO_4
Range	1000 μS/cm
Full Scale	500 μS/cm
Reagent I	15 mmol/l Chlorpromazine
Flow-rate, reagent I	0.2 ml/min
Reagent II	8 mol/l HCl
Flow-rate, reagent II	0.2 ml/min
Detection mode for chlorite and bromate	Spectrophotometry
Wavelength	λ=530 nm
Cell	Flow through cell (pathlength, 8 mm)

method, therefore, the PCR took place at ambient temperature. For the detection of chlorite and bromate, a VDM II UV–Vis detector (Dionex, Germany) was used. All further details of the chromatographic and PCR conditions are given in Table 1. Fig. 1 shows the equipment set-up.

2.2. Reagents

An eluent based on 70 mmol/l NaOH and 0.5 mmol/l $HClO_4$, made from sodium hydroxide pro analysi grade and suprapure perchloric acid (both from Merck, Germany), was used. PCR reagent I (15 mmol/l chlorpromazine) was prepared daily by dissolving 532 mg of chlorpromazine hydrochloride (Fluka, Switzerland) in 100 ml of deionized water (SG Reinstwassersystem, Germany). reagent II comprised 8 mol/l hydrochloric acid diluted from subboiled hydrochloric acid, 37% (Riedel de Haën, Germany). For the regenerant 0.025 mol/l H_2SO_4, a ULSI puranal sulfuric acid 95–97% (Riedel de Haën, Germany) was used. For the preparation of stock anion solutions (1000 mg/l), the different sodium salts of pro analysis grade chemicals (Merck, Darmstadt) were used. Only the chlorite stock solution was prepared from 80% technical-grade sodium salt (Aldrich, Germany). Calibration standards were prepared by diluting the stock solution with deionized water (SG Reinstwassersysteme, Germany). In addition, the spectrophotometric analysis was performed by a matrix-matched calibration method using drinking water (Hannover, Germany).

3. Results and discussion

3.1. Separation and conductivity detection

The application of the laboratory-made high-capacity anion-exchanger allowed the separation of the seven standard anions and of the three DBPs without any sample pretreatment, except for a 0.45-μm filtration step. Applied conductivity detection after chemical suppression did not show any interference. It was used for the quantification of fluoride, chloride, nitrite, sulfate, bromide, nitrate, orthophosphate and chlorate. The MDLs were calculated according to DIN 32645 (3σ-criterion: threefold standard deviation of background noise at the anion retention time) [29] and the results are shown in Table 2, together with the relative standard deviations (RSD) of *n* replicates for the eight anions. A chromatogram of a standard solution including all ten anions is shown in Fig. 2.

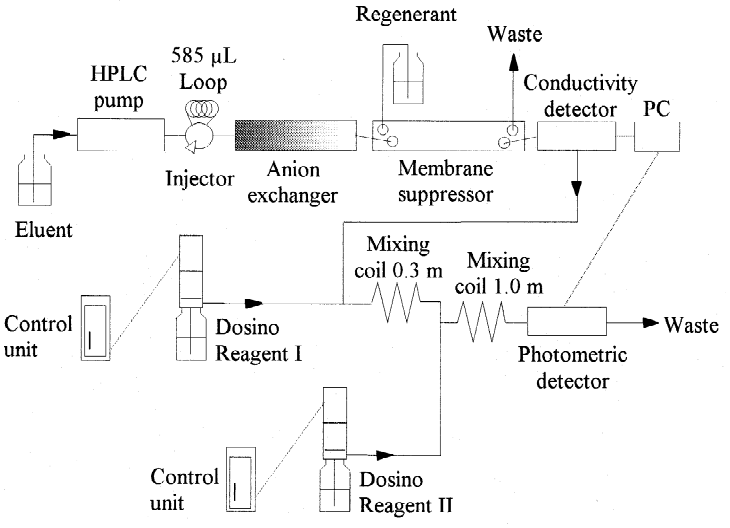

Fig. 1. Sketch of the combined conductivity and PCR detection system used for the simultaneous analysis of all common drinking water anions in disinfected water samples.

Table 2
Method detection limits and relative standard deviations for the anions determined with conductivity detection after chemical suppression[a]

Anion	MDL (mg/l)	RSD (n=5)	
		c (mg/l)	RSD%
Fluoride	0.2	5	0.6
Chloride	0.3	7.5	1.6
Nitrite	0.1	10	0.7
Sulfate	0.9	10	0.7
Bromide	0.2	20	0.4
Nitrate	0.9	20	0.5
Orthophosphate	0.8	30	1.7
Chlorate	1.6	20	1.0

[a] n=Number of replicate measurements.

3.2. Post-column reaction and spectrophotometric detection

Spectrophotometric detection after the PCR with chlorpromazine enables the sensitive determination of chlorite and bromate. CHP was selected due to the stability of its oxidation product, its water solubility and high molar absorption coefficient (1.5×10^4 l/mol/cm at 530 nm) [27]. The on-line coupling of IC with PCR, and a two-step detection method, represents a selective technique for the determination of the DBPs. This is an important advantage compared to the non-selective conductivity detection of DBPs. In addition, conductivity detection is less sensitive than spectrophotometric detection.

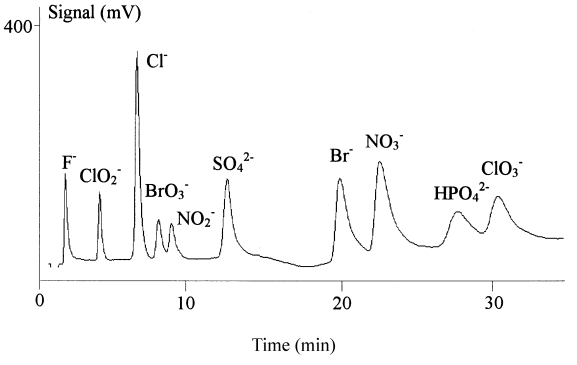

Fig. 2. Chromatogram of a standard solution containing 5 mg/l F^-, 10 mg/l ClO_2^-, 7.5 mg/l Cl^-, 10 mg/l BrO_3^-, 15 mg/l NO_2^-, 10 mg/l SO_4^{2-}, 20 mg/l Br^-, 20 mg/l NO_3^-, 30 mg/l HPO_4^{2-} and 20 mg/l ClO_3^-, obtained using conductivity detection. Chromatographic conditions were as listed in Table 1.

The instrumental parameters ‘concentration’ and ‘flow-rate’ of the two reagents (CHP, HCl) were optimized by a ‘Box-Behnken’ experimental design with 15 experiments using the signal-to-noise ratio (S/N). In this work, ‘Dosino’ motor burettes equipped with 5 ml dispensing units and control units were used as the a PCR system for the first time. In comparison to peristaltic pumps, the motor burettes improved the sensitivity of the spectrophotometric detection by reducing pump pulsation noise. Further advantages are the more precise setting of the flow-rate and the chemical robustness of the dispensing unit and tubings.

The flow-rates of the Dosino motor burettes were optimized at between 0.1 and 0.3 ml/min. Due to the back pressure of the ion chromatograph, higher flow-rates are unacceptable. Taking the results for the PCR from previously published work [23,26] into account, the concentration of CHP was optimized at between 10 and 30 mmol/l, and that for HCl was optimized at between 4 and 8 mol/l. Both parameters (concentrations of reagents) had only a minor influence on the sensitivity of the spectrophotometric detection.

The MDLs measured in deionized water were 100 ng/l for bromate and 700 ng/l for chlorite. The MDLs were also evaluated for chlorite and bromate in drinking water (Table 3).

Fig. 3 shows chromatograms of standard solutions containing chlorite and bromate. The rising baseline in the early part of the chromatogram is caused by the injection peak. The reproducibility of the spectrophotometric detection was determined in deionized water and drinking water. The results are also shown in Table 3.

3.3. Water samples

Several water samples, such as drinking water, mineral and table water, as well as swimming pool water, were analyzed using the method described. Fig. 4 shows chromatograms of the drinking-water sample ‘Hannover, Germany’, both unspiked, and spiked with chlorite and bromate. Drinking water usually contains high concentrations of chloride, sulfate and carbonate. A strong carbonate signal (7–8 min) appeared in front of the bromate peak, but integration was still possible. Therefore, removal of

Table 3
Method detection limits and relative standard deviation for the anions determined with spectrophotometric detection after PCR with chlorpromazine[a]

Anion	MDL[b] (μg/l)	MDL[c] (μg/l)	RSD[b] (n=8)		RSD[c] (n=8)	
			c (μg/l)	RSD%	c (μg/l)	RSD%
Chlorite	0.7	3.5	5.0	1.7	20	0.7
Bromate	0.1	0.7	1.0	2.6	5.0	3.2
Nitrite	0.2	–	1.0	2.5	–	–

[a] n=Number of replicate measurements.
[b] Measured in deionized water.
[c] Measured in drinking water.

carbonate is not necessary. Sulfate caused a negative absorption (13 min) without any interference on the observed anions. In the case of high concentrations of chloride, a negative absorption (7–8 min) appeared in front of the bromate peak, which had no effect on the analysis of chlorite, bromate and nitrite. In addition, all standard anions injected in higher concentrations appeared to cause a positive system-peak that interfered with the nitrite signal (retention time NO_2^-, t_R=10.10 min). Due to this interference, nitrite was determined by conductivity detection, but method detection limits for spectrophotometric detection using deionized water as the matrix are also given in Table 3.

4. Conclusion

The developed method is a sensitive tool for the analysis of the inorganic disinfection by-products bromate, chlorite and chlorate. The method enables the simultaneous determination of the disinfection by-products and seven standard anions by a single injection without any sample pretreatment step. Low method detection limits and a time of analysis below 40 min are advantages of the method compared to conventional, single analyte, methods. The use of motor burettes as the reagent-delivering system simplified the handling of the post-column reaction and improved the sensitivity of the spectrophotometric detection.

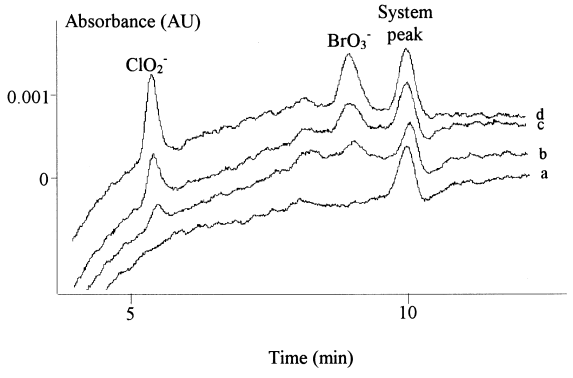

Fig. 3. Chromatograms of standard solutions containing chlorate, bromate and nitrite, determined by spectrophotometric detection after PCR with chlorpromazine. Chromatographic conditions were as listed in Table 1. (a) Deionized water; (b) 1 μg/l chlorite, 0.25 μg/l bromate; (c) 2 μg/l chlorite, 0.5 μg/l bromate; (d) 4 μg/l chlorite, 1 μg/l bromate.

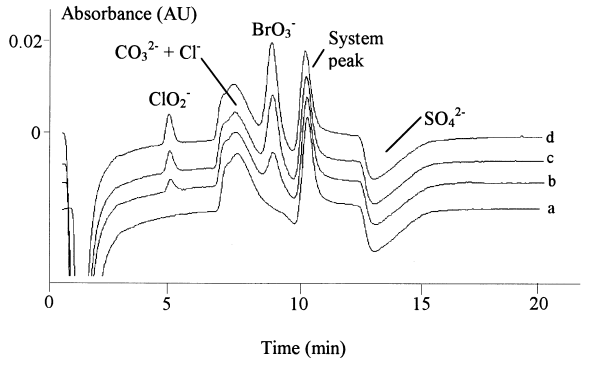

Fig. 4. Chromatograms of a drinking-water sample 'Hannover, Germany' determined by spectrophotometric detection after PCR with chlorpromazine. Samples: unspiked and spiked with ClO_2^- and BrO_3^- at between 5 and 15 μg/l in each case. Chromatographic conditions were as listed in Table 1. (a) Unspiked sample, (b) 5 μg/l each, (c) 10 μg/l each and (d) 15 μg/l each.

Acknowledgements

The authors are grateful for financial support from the Fonds der Chemischen Industrie (FCI) and for financial and material support from Metrohm AG., Dr. H. Schäfer, Herisau, Switzerland.

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