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Journal of Chromatography A, 847 (1999) 271–277

JOURNAL OF CHROMATOGRAPHY A

Ion chromatographic determination of bromate in drinking water by post-column reaction with fuchsin

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Abstract

Bromate deriving from ozonation treatment of bromide containing waters are analyzed by ion-exchange chromatography with spectrophotometric detection after post-column reaction with fuchsin in low pH medium. An anion-exchange column was used with 2.7 m*M* carbonate–0.3 m*M* hydrogencarbonate eluent. The eluent from the column was then allowed to react with a SO_2–reduced fuchsin solution and then with a diluted HCl solution at 65°C. The developed colour of the final product was measured spectrophotometrically at 530 nm. Linearity was checked up to 50 μg/l with a 200-μl injection loop (r^2=0.9997) and up to 100 μg/l of bromate with 100 μl loop (r^2=0.9939). Nitrate, sulfate, bromide, phosphate, fluoride did not interfere at 100 mg/l concentration level; only nitrite at concentration levels greater than 3 mg/l caused partial overlapping with bromate peak, but this value is not likely to occur in common drinking water. The detection limit (3σ) is 0.1 μg/l (1 μg/l propagation error approach).

Keywords: Derivatization, LC; Water analysis; Bromate; Fuchsin; Inorganic anions

1. Introduction

Bromate, a disinfection by-product of the ozonation of bromide containing waters [1], has been proved to be a carcenogenic substance with a concentration above 0.05 μg/l [2]. With respect to these toxic effects the World Health Organization (WHO) suggested (1993) 25 μg/l bromate as a limit value for bromate in drinking water [3]. The Drinking Water Commission of the European Union (EU) [4] proposed a parametric value of 10 μg/l, connected with a detection limit of 2.5 μg/l.

For these reasons trace analysis of bromate in water has received considerable attention in recent years.

Bromate determination is usually carried out by ion chromatography (IC) with conductivity detection, as also suggested by US Environmental Protection Agency (EPA) method 300.0. The detection limit is in the range 5–25 μg/l [1,5,6], depending on chloride concentration. With a preconcentration IC method a detection limit of 1 μg/l can be obtained [6–9]. This technique suffers from the existence of interferences which require time consuming step for elimination, clean-up and separation before the instrumental measurements. Very recently a new ion-exchange column has been developed [10] which seems to overcome interference problems without preconcentration.

Much lower detection limits are obtained using hyphenated techniques such as IC coupled with mass

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0021-9673/99/$ – see front matter
PII: S0021-9673(99)00190-9

spectrometry (MS) [11–13]. Diemer and Heumann [11] report a detection limit in the range 0.03–0.07 μg/l (using 50 ml sample) with anion-exchange chromatography coupled with negative thermal ionization isotope dilution mass spectrometry (NTI–IDMS) or inductively coupled (ICP) MS. The detection of bromate in ozonated drinking water by IC–ICP-MS does not suffer from chloride interferences associated with IC conductivity detection but tribromoacetic acid must be removed before analysis [12]. Detection limit as low as 0.8 μg/l can be achieved with direct injection of 170 μl sample volume.

These techniques are very sensitive but are highly sophisticated and the instrumentation is very expensive. Good sensitivity can also be reached following simple spectrophotometric methods. Bromate reacts with the SO_2–fuchsin adduct in acidic medium producing a red coloured product absorbing at 530 nm. The response is linear up to 20 μg/l and the detection limit is 1 μg/l. Cations interfere and have to be removed prior reagent addition [14]. Another colorimetric procedure is reported by Farrel et al. [15], including reduction of bromate with phenothiazine in acidic conditions to form a stable cation radical that strongly absorbs visible light at 504 nm in the range 1–700 μg/l with a detection limit of 0.67 μg/l. Nitrite and chlorite interfere. An automatic flow injection analysis (FIA) colorimetric procedure has been reported by Gordon et al. [16].

An alternative approach to avoid possible interferences in spectrophotometric methods is a preliminary separation by IC and post-column derivatization. Bromate can be converted to tribromide using hydrobromic acid and detected by UV absorption at 268 nm. With 0.1 ml sample volume a detection limit of 0.35 μg/l was obtained [17]. A similar detection limit (0.45 μg/l) was achieved by post-column reaction with chlorpromazine and absorption at 530 nm [18].

In this paper a very sensitive IC method with post-column derivatization, which overcomes the interferences commonly found in IC with conductimetric detection, is described. A very low detection limit is obtained without any preconcentration step or sample pretreatment.

2. Experimental

2.1. Reagents

All chemicals were analytical grade reagents.

Stock concentrated solution of fuchsin was prepared by dissolving 100 mg of basic fuchsin ($C_{19}H_{18}N_3Cl$, Carlo Erba RPE) in 100 ml of deionized water in a glass flask. This solution is stable for several months.

Fuchsin colour developing reagent was prepared by adding 0.5 ml of HCl (Carlo Erba RPE) solution (1:1, v/v) to 10 ml of stock fuchsin solution, followed by reduction with 400 mg of sodium metabisulfite (Carlo Erba RPE), in 100 ml final volume with water. This solution is stable for one month if stored in glass bottle, at room temperature and in the dark. It was further diluted 50 times with deionized water before use: the diluted solution must be prepared freshly every day.

Bromate standard solutions were obtained by dilution of a 1000 mg/l concentrated stock solution prepared by dissolving solid $KBrO_3$ (Carlo Erba RPE) in deionized water.

Anion stock standard solution for interferences studies were prepared from the corresponding salts (Fluka).

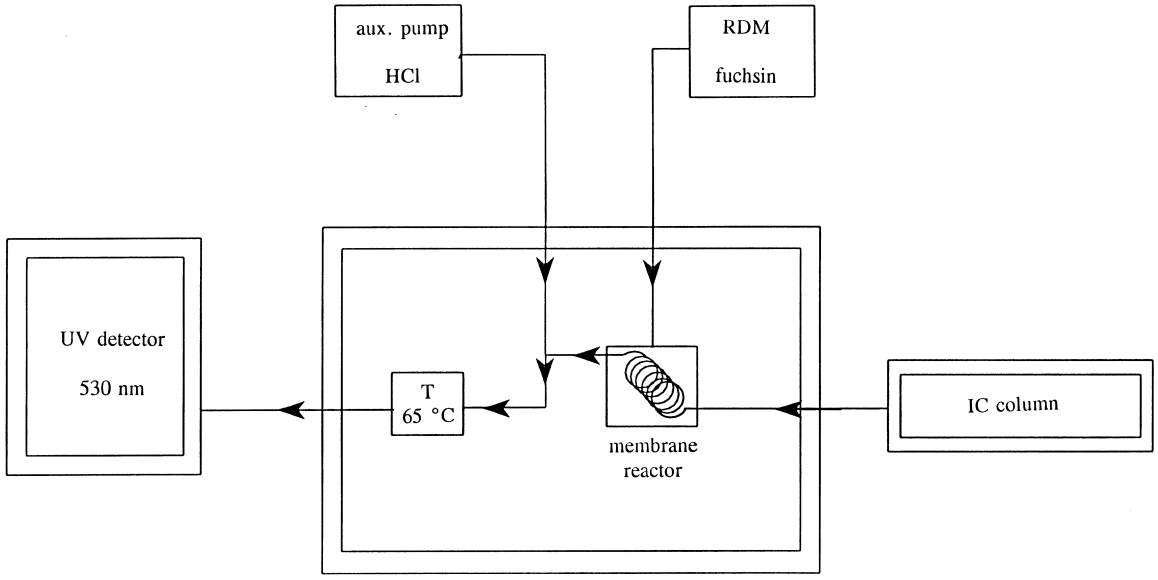
Anydrous sodium carbonate and sodium hydrogencarbonate (Merck) were used for eluent preparation (2.7 m*M* carbonate–0.3 m*M* hydrogencarbonate).

Twenty-five m*M* HCl was used for post-column derivatization.

2.2. Instrumentation

A Dionex system including APM isocratic pump, AG4A-SC (4 mm) guard column and AS4A-SC (4 mm) analytical column were used for IC measurements.

The post-column derivatization system is described in Fig. 1. A Dionex reagent delivery module with membrane reactor was used for fuchsin mixing along with an IC auxiliary pump (Dionex isocratic pump) for HCl addition. The effluent was heated with a thermostat (IDRONAUT, 650 cm coil length×0.8 mm I.D.).



RDM = Reagent Delivery Module

T = Thermostat

Fig. 1. Post-column detection system.

The spectrophotometric measurements were made using a Dionex VDM II variable-wavelength detector at 530 nm with a 6 mm optical path flow cell.

Acquisition of data and chromatogram and instrument remote control was performed with Dionex AI450 software on a personal computer station.

The experimental conditions are reported in Table 1.

3. Results and discussion

3.1. Post-column reaction

The reaction of bromate with fuchsin reagent is pH dependent [14], the optimum value being about 3. For this reason the reaction medium must be acidic and HCl must be added in the eluent flow after

Table 1
Experimental conditions

Column	AG4A-SC, AS4A-SC, 4 mm
Eluent	2.7 m*M* sodium carbonate
	0.3 m*M* sodium hydrogencarbonate
Flow-rate	1 ml/min
Injection volume	200 (100) μl
Derivatization reagent pressure	70 p.s.i. (1 p.s.i.=6894.76 Pa)
HCl flow	0.1 ml/min
Thermostat temperature	65°C
Detector	UV-VDM II
Wavelength	530 nm

fuchsin addition and before detection. From experimental tests it has been shown that optimum pH value is obtained with a 0.1 ml/min flow-rate of 25 m*M* HCl in the actual experimental conditions. The direct acidification of fuchsin reagent causes a decrease in absorbance signal for bromate, as shown in Fig. 2.

In a previous work [14] it was clearly demonstrated that the reaction of bromate with fuchsin is very slow at ambient temperature, with maximum colour development occurring at about 26 min. These conditions are not compatible with IC measurements. In this work it has been shown that an increase in temperature up to 65°C is effective in improving the spectrophotometric response, reducing the time needed for complete colour development. The best results were obtained at 65°C, as shown in Fig. 3: a further increase of temperature caused a reduction in absorbance signal.

3.2. Interferences

The interferences from common anions present in drinking water was checked. NO_3^-, Cl^-, SO_4^{2-} and PO_4^{3-} do not interfere at 100 mg/l concentration level. Br^-, F^- and ClO_3^- do not react with fuchsin under the experimental conditions. NO_2^- and ClO_2^- up to 3 and 5 ppm concentration levels, respectively do not interfere in the measurement because they are resolved from bromate (resolution factor higher than 1.3). Anyway, in ozonated drinking waters NO_2^- is not likely to be present.

3.3. Calibration and detection limit

Due to the absence of interferences the standard solutions for calibration were prepared in deionized water.

Absorbance signal for 100 μg/l bromate concentration was saturated using 200 μl sample injection loop. For this reason two calibration ranges were considered: (i) 2–50 μg/l bromate, using a 200-μl sample loop, (ii) 10–100 μg/l bromate, using a 100-μl sample loop. Good linearity was obtained in both cases. As reported in Tables 2 and 3

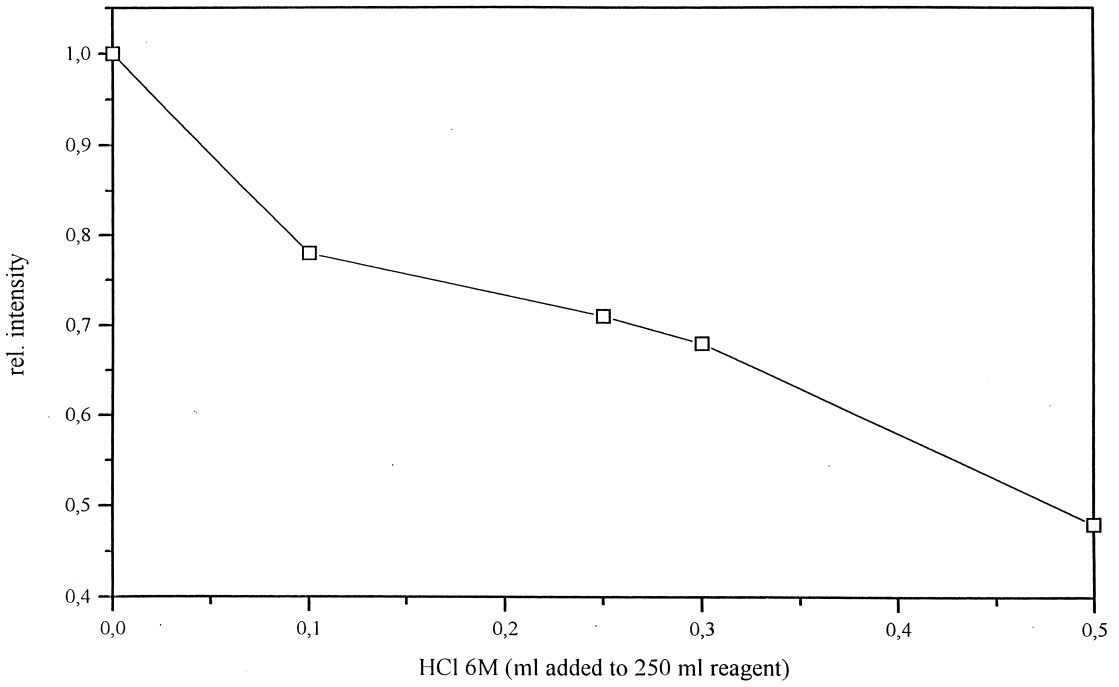


Fig. 2. Effect of direct addition of 6 *M* HCl to fuchsin reagent on relative signal intensity for a 100 μg/l bromate solution.

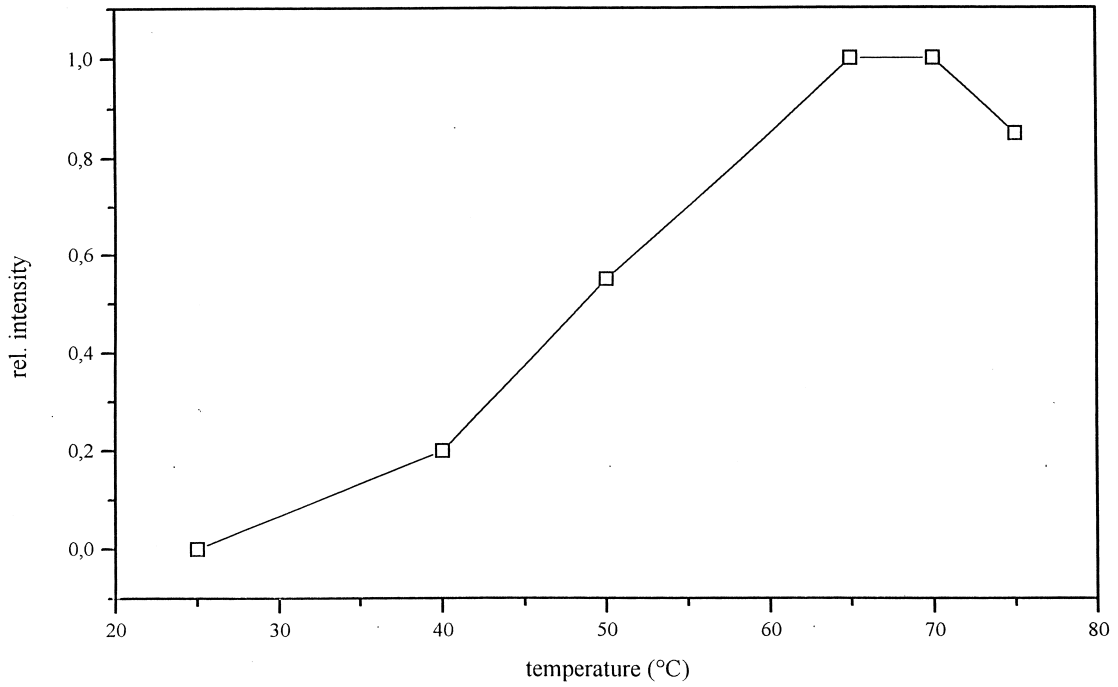


Fig. 3. Effect of temperature on relative signal intensity for a 100 μg/l bromate solution.

good correlation coefficients (r^2=0.9997 and 0.9939, respectively) and residual values were calculated.

A detection limit (3σ) of 0.1 μg/l was calculated. Following the propagation of errors approach and using the data reported in Table 2 for the calibration range 2–50 μg/l a detection limit of 1 μg/l was calculated. The relative standard deviations of five replicate measurements at 2 and 20 μg/l were 1.6 and 1.4%, respectively.

3.4. Application to real drinking water sample

The described method has been applied to the determination of bromate in drinking water. Chro-

Table 2
Regression data and statistical parameters for bromate calibration in the range 2–50 μg/l

	Expected value	Standard deviation
Slope	799.5	3.3
Intercept	−3.3	61.1

Number of points=18
Correlation coefficient (r^2)=0.9997

Residuals

x Value	Mean *y*	Predicted *y*	Residuals
2	1627	1596	31
5	3876	3994	−118
10	7968	7992	−24
20	16 189	15 987	202
50	39 914	39 972	−58

Table 3
Regression data and statistical parameters for bromate calibration in the range 10–100 μg/l

	Expected value	Standard deviation
Slope	402.9	8.7
Intercept	−1.4	445.2

Number of points=15
Correlation coefficient (r^2)=0.9939

Residuals

x Value	Mean *y*	Predicted *y*	Residuals
10	4451	4608	−157
20	9463	8637	826
50	22 479	20 726	1753
100	39 939	40 874	−935

matograms of drinking water sample, drinking water spiked with 50 μg/l of bromate and 50 μg/l standard solution in deionized water are reported in Fig. 4. Bromate is below the detection limit in real sample and no difference can be detected between spiked sample and standard solution. Table 4 shows replicate values for spiked real sample, showing good recovery and accuracy.

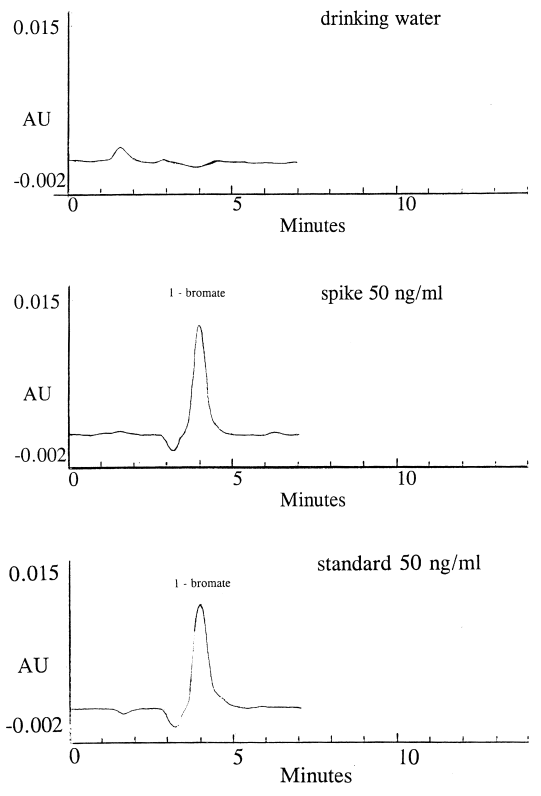


Fig. 4. Chromatograms of drinking water, spiked drinking water and bromate standard solution.

Table 4
Recoveries of bromate from spiked sample

Replicate No.	Spike (μg/l)	Found (μg/l)	Recovery (%)
1	50	47	94
2	50	49	98
3	50	48	96
4	50	50	100
5	50	47	94
Average	50	48.2	96.4

4. Conclusions

The method can be very easily applied to check for possible overcoming of EU limit values for bromate in drinking water (10 μg/l), without pre-concentration steps or clean-up to remove interferences. The analytical response is linear in the bromate concentration range 2–50 μg/l and the detection limit is 0.1 μg/l. Using a 100-μl sample injection loop the linearity is extended up to 100 μg/l bromate. This method is not influenced by interferences from common anions and gives better results than IC method with suppressed conductivity.

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