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A sensitive flow-based procedure for spectrophotometric speciation analysis of inorganic bromine in waters

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ABSTRACT

A flow-based system with solenoid micro-pumps and long path-length spectrophotometry for bromate and bromide determination in drinking water is proposed. The method is based on the formation of an unstable dye from the reaction between bromate, 2-(5-dibromo-2-pyridylazo)-5-(diethylamino)phenol (5-Br-PADAP) and thiocyanate ions. A multivariate optimization was carried out. A linear response was observed between 5.0 and 100 μg L^{-1} BrO_3^- and the detection limit was estimated as 2.0 μg L^{-1} (99.7% confidence level). The coefficient of variation ($n=20$) and sampling rate were estimated as 1.0% and 40 determinations per hour, respectively. Reagent consumption was estimated as 0.17 μg of 5-Br-PADAP and 230 μg of NaSCN per measurement, generating 6.0 mL of waste. Bromide determination was carried out after UV-assisted conversion with $K_2S_2O_8$ using 300 μL of sample within the range 20–400 μg L^{-1} Br^-. The generated bromate was then determined by the proposed flow system. The results for tap and commercial mineral water samples agreed with those obtained with the reference procedure at the 95% confidence level. The proposed procedure is therefore a sensitive, environmentally friendly and reliable alternative for inorganic bromine speciation.

1. Introduction

Ozonation is an efficient process for water disinfection and organic matter elimination. It is based on photochemical reactions due to UV irradiation of ozone [1]. Parallel reactions of common concomitants in water generates harmful species [2]. The oxidizing radicals yield bromide oxidation into bromate ions [3], which shows Class 3 carcinogenic potential according to the International Agency of Research on Cancer (IARC) [4].

The World Health Organization (WHO) [5] established the threshold limit for bromate in drinking waters as 10 μg L^{-1} which was followed by most national regulation agencies. Bromide limit in water has not been established but it generally varies from 0.01 up to 3.0 mg L^{-1} in natural waters. Bromide determination is important because it brings information about the potential bromate yield after disinfection.

Bromate determination has usually been based on ion-chromatographic [6–8] and spectrophotometric procedures [9–11]. Aiming at inorganic bromine speciation, selective and sensitive procedures are required. The analytical procedures based on ion-chromatography have commonly been proposed for this end [6,7]. The time per determination can reach up to 30 min and the acquisition and maintenance of the equipment have high costs. Additionally, with conductivity detection, strong chloride interference was observed due to band overlapping [3], requiring separations with ion-exchange resins or precipitation as AgCl. Post-column derivatization with fluorimetric detection has been exploited to increase selectivity [8], but sampling rate was not significantly improved.

Most non chromatographic procedures have not exploited bromine speciation analysis. A procedure based on X-ray fluorescence was proposed for bromate determination in drinking waters [12]. A polymeric membrane with immobilized *o*-dianisidine was immersed in the sample to retain the analyte prior to X-ray fluorescence determination. In spite of low detection limit, the retention process required 10 h to adsorb significant quantities of the analyte.

Lower-cost and faster chemiluminometric [13] and spectrophotometric [9–11] procedures have been proposed for bromate determination. In the chemiluminometric procedure, the resulting energy from sulphite oxidation by bromate ions was transferred to a sensitizer (hydrocortisone), which luminescence increased with bromate concentration. In spite of the simple instrumentation and fast determinations (*ca.* 120 h^{-1}), the detection limit (10 μg L^{-1}) was not suitable for water analysis, taking into account the threshold limits [5].

Spectrophotometric procedures have been based on discoloration of dyes due to reaction with bromate in acidic medium, such as methylene blue [9] and 2-(5-dibromo-2-pyridylazo)-5-(diethylamino)

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phenol (5-Br-PADAP) [10,11]. In order to achieve suitable sensitivity, the spectrophotometric methylene blue method required a 5.0 cm optical path [9]. The sample throughput was compromised by 10 min reaction time and the readings had to be performed up to 20 min after reagent addition due to the instability of the brominated product.

In view of the lack of stability of the brominated 5-Br-PADAP species, mechanized procedures have been proposed using flow [10] or sequential injection analysis (SIA) [11]. Flow-based procedures are characterized by high precision in view of controlled sample dispersion and residence time, high sampling rate, low reagent consumption and waste generation [14]. Sample contamination is also minimized because the process occurs in closed vessels. By using the FIA system [10], the sample was injected into a water carrier stream and mixed with acidic 5-Br-PADAP and afterwards with NaSCN solutions. The formed product showed maximum absorption at 560 nm. The low product stability did not hinder the detection due to precise timing of the flow system. The SIA procedure [11] was developed by mixing sample, 5-Br-PADAP and SCN^- in the retention coil and carrying the sample zone towards detection. In both procedures, the detection limits were unsuitable for bromate determination in water, applied to food extracts [10] and wastewaters [11].

The use of computer-controlled solenoid micro-pumps in flow-based systems promotes better analytical performance due to the independent solution handling. These devices actuate as both fluid propellers and injectors [15] by reproductively dispensing micro-amounts of solutions. Additionally, the inherent pulsed flow improves sample to reagent mixing [16]. In spite of the advantages, flow systems with solenoid micro-pumps have not been exploited yet for bromate determination.

Bromine speciation analysis requires separate approaches. Quantitative bromide conversion into bromate using UV irradiation in the presence of persulfate ions was previously demonstrated [17]. In spite of the potential, this strategy has not been exploited for bromine speciation analysis. The Standard Methods for Examination of Water and Wastewaters recommends the method based on the reaction between bromide ions and chloramine-T [18]. The generated Br_2 brominates phenol red to yield bromophenol blue, which is monitored by spectrophotometry at 590 nm. The measurements are taken after 20 min and the addition of $Na_2S_2O_3$ is necessary to decompose chlorinated species.

In this work, a multi-pumping flow system was developed for inorganic bromine speciation analysis. Bromate determination was based on the reaction between the analyte, 5-Br-PADAP and thiocyanate ions, which was monitored by spectrophotometry at 560 nm. A flow cell based on a liquid-core waveguide was used to increase the optical path and provide the required sensitivity for bromate determination. Bromide was quantified after sample photo-oxidation with persulfate prior to determination as bromate.

2. Experimental

2.1. Apparatus

The flow system was constructed with five solenoid micro-pumps (Biochem Valve Inc., Boonton, NJ, USA; model 090SP), dispensing volumes of 24 μL (P_1), 16 μL (P_2 and P_4), 17 μL (P_3) and 18 μL (P_5) with coefficients of variation $< 0.36\%$, two three-way solenoid valves (NResearch, West Caldwell, NJ, USA), 0.8 mm i.d. Teflon™ tubes and a Perspex™ joint point. A Pentium I microcomputer was used for system control and data acquisition. The active devices were computer-controlled through a parallel port of the microcomputer by using a power drive based on a ULN2803 integrated circuit. Spectrophotometric measurements were carried out with a multi-channel CCD spectrophotometer (Ocean Optics, Dunedin, FL, USA; model USB4000) coupled to a tungsten-halogen light source (Ocean Optics, Dunedin, FL, USA; model LS-1). Optical fibers (400 μm) were used to transmit the radiation from the light source to a 100 cm optical path (250 μL internal volume) liquid-core waveguide flow cell (Ocean Optics) and from the cell to the detection system. The control software was developed in Visual Basic 6.0 (Microsoft, Redmond, WA, USA), and the data acquisition was carried out with the software supplied by the manufacturer of the spectrophotometer. The software Statistica 10.0 (StatSoft, Tulsa, OK, USA, 2011) was employed for data analysis in the multivariate optimization of bromate determination.

The lab-made photo-reactor (Fig. 1) was constructed with a (a) 13-W low-pressure mercury vapor lamp (Philips, TUV PL-S), which shows high emission at 254 nm. The lamp was connected through (b) metallic contacts to a (c) 13 W reactor (Begli). A pair of watch glasses containing 300 μL sample aliquots (d and e) was positioned on a (f) metallic surface *ca.* 1.0 cm under the lamp bulb. The devices were inserted into a (g) dark box to avoid radiation loss.

2.2. Reagents and solutions

All solutions were prepared with analytical grade chemicals and distilled-deionized water. The reference solutions were prepared with sodium bromate and sodium bromide salts (both Sigma-Aldrich, St. Louis, MO, USA) by dilution of 6.60 mmol L^{-1} BrO_3^- and 9.70 mmol L^{-1} Br^- stock solutions in water.

A 10 mmol L^{-1} 2-(5-dibromo-2-pyridylazo)-5-(diethylamino) phenol solution was prepared in anhydrous ethanol and kept under 4 °C. R_1 reagent was prepared with 6.0 μmol L^{-1} 5-Br-PADAP by dilution of the stock solution in 1.0 mol L^{-1} H_2SO_4. A 50 mmol L^{-1} NaSCN solution was prepared by dissolution of the salt in water. All solutions were stable for at least three months. Stock solutions containing 5.7 or 860 mmol L^{-1} $NH_2OH \cdot HCl$ and 4.4 mmol L^{-1} $K_2S_2O_8$ were prepared daily. The effect of ClO^-, Fe^{3+} and Cl^- on the determinations was evaluated in concentrations up to, respectively, 20, 200 and 5000-fold higher than bromate, which was maintained at 50 μg L^{-1}.

2.3. Flow diagram and procedure

The flow manifold shown in Fig. 2 was operated according to the switching course described in Table 1. The binary sampling approach [19] was adopted for solutions handling. The volume of each solution was defined by the stroke volume and the number of pulses of the corresponding micro-pump.

The analytical cycle was started by inserting sample and reagents through two strokes of each P_4, P_3 and P_2 pumps (steps 1–3). These aliquots underwent fast mixing by dispersion at the interfaces, establishing the first sampling cycle. The sample zone was formed by two sampling cycles and then the flow was stopped

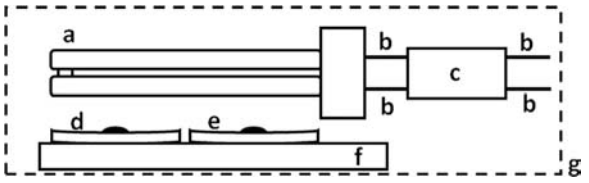

Fig. 1. Photo-reactor scheme for bromide conversion, constructed with a 13-W low-pressure mercury vapor lamp (a), powered through electrical contacts (b) by a lamp reactor (c). Sample aliquots (300 μL) were added onto glass watches at different distances (d and e) from the lamp filament. A metallic support (f) was employed to position the sample vessels. A dark box (g) was used to avoid radiation loss.

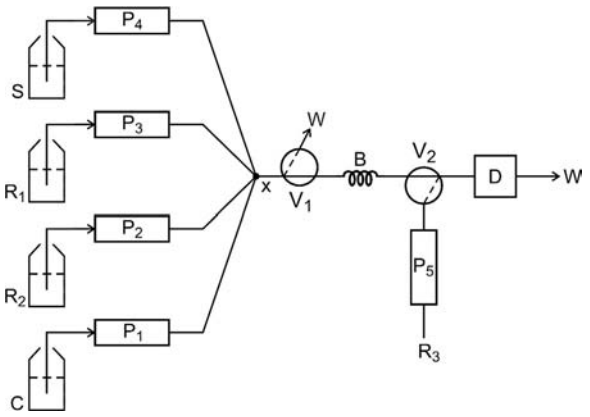

Fig. 2. Multi-pumping flow manifold for bromate determination. S: Sample; R_1: 6.0 μg L^{-1} 5-Br-PADAP in 1.0 mol L^{-1} H_2SO_4; R_2: 50 mmol L^{-1} NaSCN; C: Water; W: Waste vessels; P_1–P_5: Solenoid micro-pumps; V_1 and V_2: Three-way solenoid valves; x: Confluence point; B: 50 cm long reaction coil; D: 100 cm optical path cell coupled to spectrophotometric detection.

Table 1
Switching course of the active devices for bromate determination in waters.

Step	Description	Pump [a]	Pulses
1[b]	Sample insertion	P_4	2
2[b]	5-Br-PADAP insertion	P_3	2
3[b]	NaSCN insertion	P_2	2
4	Stopped-flow (45 s)	–	–
5	Sample zone transportation and detection	P_1	170
6[c,d]	Cleaning	P_5	2
		P_1	200
7[e]	Sample replacement	P_4	40
		P_1	40

[a] The stroke volumes of the micro-pumps were 24 μL (P_1), 16 μL (P_2 and P_4), 17 μL (P_3) and 18 μL (P_5) with coefficients of variation $<0.36\%$.
[b] Two sampling cycles.
[c] Solenoid valve V_2 switched on.
[d] After triplicates.
[e] Solenoid valve V_1 switched on.

for 45 s (step 4). Afterwards, the sample zone was carried out towards detection by actuation of P_1 (step 5). The analytical signal was based on peak height. After triplicates, an additional cleaning step was performed by switching valve V_2 on during KOH insertion by actuation of micro-pump P_5 (step 6). The flow cell was cleaned by switching V_2 off and applying 200 pulses to P_1.

Valve V_1 was used to replace solutions, avoiding the passage through the analytical path and minimizing the risks of contamination. Before analyzing another sample, valve V_1 was switched on while pump P_4 was actuated (40 pulses) to fill the connection tube with the new sample. Pump P_1 was then actuated (40 pulses) and the carrier removed the sample aliquot through valve V_1 (step 7).

2.4. Sample preparation

Four tap and three commercial mineral water samples were stored in 50-mL flasks previously decontaminated with a 10% HNO_3 bath for 24 h followed by washing with deionized water. For bromate determination, a 10 mL aliquot was collected and 100 μL of 5.7 mmol L^{-1} $NH_2OH \cdot HCl$ (400 mg L^{-1}) was added for elimination of ClO^- and Fe^{3+} ions. The sample was analyzed 10 min after hydroxylamine addition. For bromide determination, 300 μL of sample and 10 μL of 4.4 mmol L^{-1} $K_2S_2O_8$ (1.2 g L^{-1}) were added onto the center of a watch glass and submitted to UV irradiation for 15 min. Afterwards, the digest was quantitatively transferred to a 2.0 mL vial, in which 10 μL of 860 mmol L^{-1} $NH_2OH \cdot HCl$ (60 g L^{-1}) was added. The volume was made up to 1.5 mL followed by bromate determination.

2.5. Reference procedures

Accuracy assessment was carried out by spectrophotometric determinations of bromate [9] and bromide [18] separately because of the lack of spectrophotometric procedures for speciation analysis. For bromate determination, a 2.85 mmol L^{-1} $NH_2OH \cdot HCl$ (200 mg L^{-1}) was added to the samples to decompose hypochlorite. After 1 h, samples were analyzed by adding 2.0 mol L^{-1} HCl and 1.5 nmol L^{-1} methylene blue (50 μg L^{-1}), the discoloration of which was monitored by spectrophotometry. The measurements were carried out after 10 min. Additionally, a 100 cm flow cell was employed for sensitivity enhancement, reaching linear response between 10 and 30 μg L^{-1} bromate.

Bromide determination was carried out as recommended by the Standard Methods of Analysis of Waters and Wastewaters [18], based on the addition of 50 mL of sample, 2.0 mL of acetate buffer (pH=4.7), 2.0 mL of 590 μmol L^{-1} phenol red (210 mg L^{-1}) and 0.5 mL of 18 mmol L^{-1} chloramine T (5.0 g L^{-1}). After 20 min, 0.5 mL of 2.0 mol L^{-1} $Na_2S_2O_3$ (315 g L^{-1}) was added to eliminate possible chlorinated compounds, followed by spectrophotometric determination at 590 nm.

3. Results and discussion

A reliable alternative was developed based on the reaction between bromate, 5-Br-PADAP and thiocyanate ions to yield a brominated azo-dye with maximum absorption at 560 nm. Sample processing in a flow system with solenoid micro-pumps [15] was employed to improve mixing, minimize reagent consumption and circumvent the drawbacks due to the instability of the compound formed, which decomposes within minutes. The reaction was previously exploited for bromate determination in food extracts [10] and wastewaters [11]. Due to the small amounts of bromate usually found in drinking water and to the established limits of regulation agencies, sensitivity was improved with a liquid-core waveguide flow cell [20] with an optical path of 100 cm.

The speciation analysis of inorganic bromine was applied after bromide conversion into bromate ions and subsequent determination by the proposed flow-based procedure. The photo-oxidation of bromide ions was exploited in the presence of $K_2S_2O_8$, the efficiency of which was previously demonstrated [17]. The disadvantage of this sample preparation is the time required for quantitative conversion of bromide that can take several hours depending on persulfate concentration and irradiation efficiency. Therefore, a micro-digestion strategy [21] was adopted to accelerate the process, by employing micro amounts of solution and improving sample irradiation, resulting in faster sample treatment. Additionally, a low volume of waste was generated.

3.1. System optimization for bromate determination

System optimization was carried out with the flow system showed in Fig. 2, aiming at the best sensitivity and the highest sampling rate as well as minimization of reagent consumption and blank signals. The chromogenic reagent 5-Br-PADAP shows maximum absorption at 480 nm, and it easily impregnates onto the flow cell tubing, which caused baseline drift after a few determinations. Therefore, cleaning solutions were evaluated to circumvent this drawback. Ethanol (50% v/v) and KOH (5% m/v) were inserted by micro-pump P_5 (Fig. 2) while valve V_2 was switched on to redirect the flow stream into the cell. The insertion of 40 μL of

the alkali solution efficiently removed the impregnated reagent after triplicates, thus avoiding baseline drift.

After preliminary tests, a 2^5 factorial design was employed considering 5-Br-PADAD (0.5–2.0 μmol L^{-1}), H_2SO_4 (0.5–1.0 mol L^1), thiocyanate (5.0–20 mmol L^{-1}), reaction coil length (50–150 cm) and stopped flow interval (15–45 s). Both sample and blank signals were taken into account. The binary sampling approach [19] was exploited to improve sample and reagent mixing, and the aliquots (80 μL of each sample and chromogenic reagents) were distributed in two sampling cycles.

According to the Pareto charts presented in Fig. 3a, the analytical signal was mainly dependent on reagent concentrations and stopped flow interval. On the other hand, the blank increased with 5-Br-PADAP concentration due to the absorption of the remaining reagent that showed maximum absorption at 480 nm (Fig. 3b).

Aiming at higher sensitivity, a 3^3 factorial design was applied taking into account reagent concentrations (adopting 45-s stopped flow interval and 50 cm reaction coil length). Experimental results were fitted to statistical models for analytical (r^2=0.9984) and blank signals (r^2=0.9917) presented on the surface charts in Fig. 3c and d, respectively. Based on the models, the blank signals remained <0.3 and the analytical signal was improved by using 6.0 μmol L^{-1} 5-Br-PADAP, 1.0 mol L^{-1} H_2SO_4 and 50 mmol L^{-1} NaSCN. After the optimization, the analytical features were evaluated.

3.2. UV-assisted micro-digestion for bromide determination

Photo-oxidative processes are generally environmentally friendly due to the mild conditions of the process and generally yield compatible solutions with most techniques [21]. Bromide photo-oxidation in the presence of persulfate ions has shown quantitative bromate yields depending on the oxidant concentration and irradiation time [17].

The effects of sample volume, irradiation time and persulfate concentration on the analyte conversion and sample throughput were evaluated. A 5.0 mL sample aliquot containing 30 μg L^{-1} Br^-, 25 mg L^{-1} $S_2O_8^{2-}$ was submitted to 30 min UV-irradiation. Under these conditions, *ca.* 70% conversion efficiency to bromate was observed. Blank signal increased *ca.* 25% due to 5-Br-PADAP oxidation by persulfate. In order to increase conversion, persulfate concentration was increased to 40 mg L^{-1}. In this condition, blank signals increased *ca.* 230%, hindering bromate quantification. Therefore, a 5-fold dilution of the digest was exploited, yielding an increase of blank signals of *ca.* 0.9%. The need for dilution prior

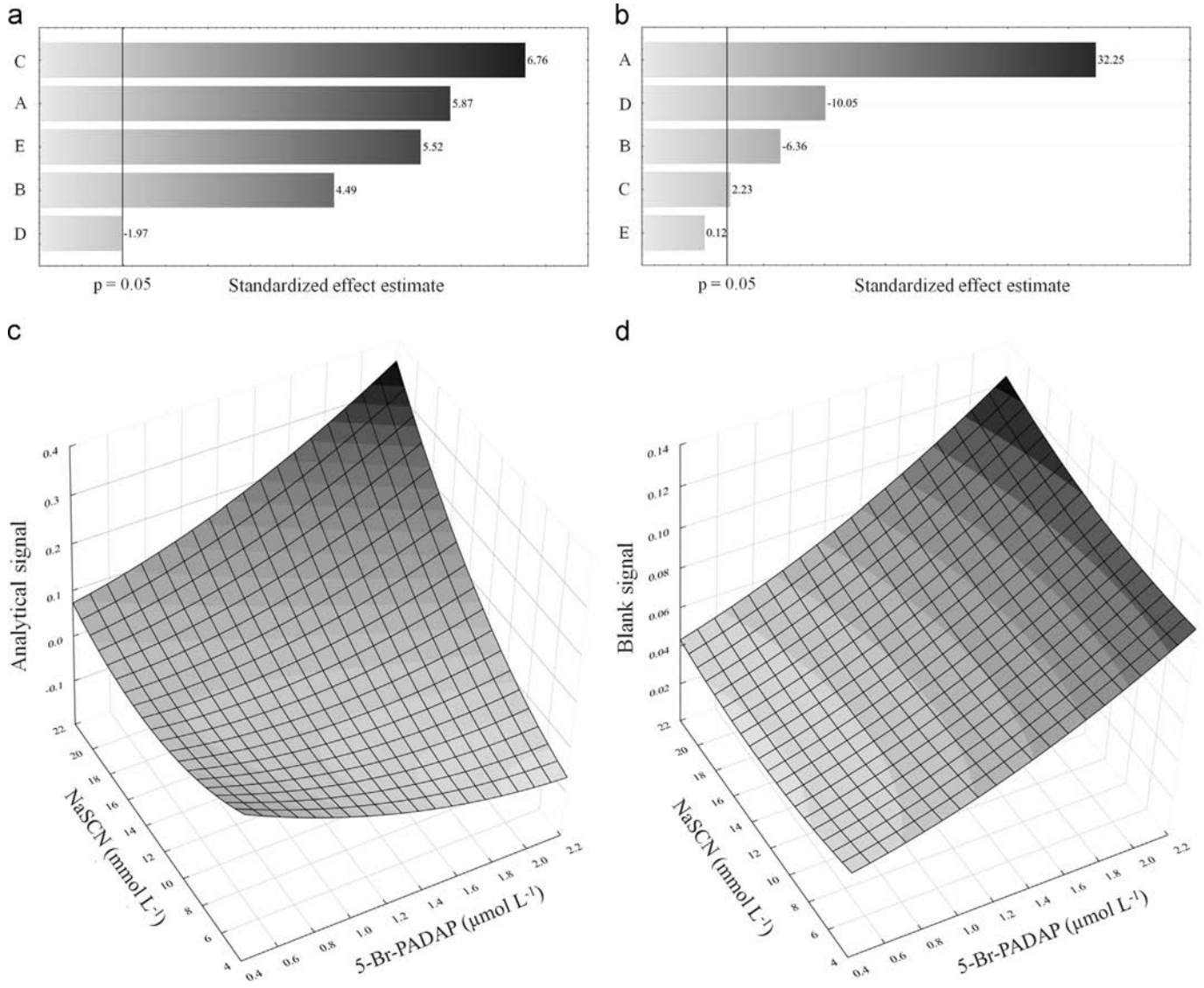

Fig. 3. Pareto charts and response surface for the analytical (a and c) and blank signals (b and d) obtained in the optimization of bromate determination. The pareto charts show the influence of 5-Br-PADAP (A), H_2SO_4 (B) and NaSCN (C) concentrations, reaction coil length (D) and stopping period (E).

to bromide determination is not a drawback because its concentration is generally higher than bromate in water. As a dilution was required, sample volume was reduced to 300 μL. This strategy enhanced the process efficiency due to lower light absorption by concomitants. Additionally, due to the light bulb length, it was possible to submit duplicates to the process simultaneously, increasing sample throughput (Fig. 1).

As previously reported [17], after 20 min UV-irradiation of bromide solutions, the conversion efficiency varied from 6 to 100% within 20–300 μmol L^{-1} (4.0–60 mg L^{-1}) persulfate concentration range. In this work, the use of 40 mg L^{-1} persulfate, 92% conversion was achieved. In this way, the time for photoconversion was evaluated (Fig. 4a) in order to increase sample throughput. The experiments were carried out in duplicate by submitting pairs of solutions to the treatment. Quantitative conversion was achieved in 15 min, remaining constant until 30 min irradiation time. Thus, a 15 min photoconversion time was chosen for further experiments.

The positioning of both sample aliquots in the photo-reactor could affect the conversion efficiency because light irradiation and temperature showed slight variation across the light bulb. In order to evaluate this effect, five duplicates of bromide determination were carried out. The signal variations for 30 μg L^{-1} Br^- were estimated at 3.2 and 2.0% between samples positioned away from (Fig. 1d) and close to (Fig. 1e) the filament, respectively. The coefficient of variation between both positions was estimated at 3.8% ($n=5$), indicating similar conversion efficiency and allowing the process to be carried out in duplicate simultaneously. An additional study was carried out with a 2.0 mL sample volume and an estimated coefficient of variation of *ca.* 20% between positions was observed. This drawback was not observed with micro amounts of sample because the variations on irradiation intensity and temperature were not significant.

The effect of persulfate concentration was also evaluated (Fig. 4b). Quantitative conversion was achieved with 40 mg L^{-1} persulfate, as previously described in the literature [17]. Smaller quantities of the oxidant did not yield quantitative bromide conversion. Thus, 40 mg L^{-1} $S_2O_8^{2-}$ was chosen for further experiments. Higher oxidant concentrations were not evaluated because they yield *ca.* 30% higher blank values that could hinder linear range.

3.3. Analytical features

Under the optimized conditions for bromate determination, a linear response was observed between 5.0 and 100 μg L^{-1} bromate (0.040–0.78 μmol L^{-1} BrO_3^-), described by equation $A=0.00288C_{Bromate}+0.314$ ($r=0.999$), in which A is absorbance and $C_{Bromate}$ is bromate concentration in μg L^{-1}. The difference between slopes obtained in different days was $<5.0\%$, indicating good reproducibility. The detection limit (99.7% confidence level), coefficient of variation ($n=20$; 0.39 μmol L^{-1}) and sampling rate (obtained from the time interval required for 20 measurements) were estimated at 2.0 μg L^{-1} (0.016 μmol L^{-1}), 1.0% and 40 determinations per hour, respectively. Reagent consumption per determination was estimated at 0.17 μg of 5-Br-PADAP and 230 μg of NaSCN, generating 6.0 mL of waste.

For bromide determination, linear range was observed between 20 and 400 μg L^{-1} Br^- (0.025–5.0 μmol L^{-1}), described by the equation $A=0.000931C_{Bromide}+0.334$ ($r=0.996$), in which $C_{Bromide}$ is bromide concentration in μg L^{-1}. The detection limit (99.7% confidence level; $n=10$) was estimated as 7.5 μg L^{-1} Br^-. By considering 5-fold dilution and bromide conversion into bromate, the equation slope was estimated at 0.00274 L μg^{-1}. The ratio between the estimated bromide and bromate slopes was 0.95, indicating bromide quantitative conversion. This is important because the concomitant determination of both species is allowed due to the additive absorbance. The comparison of the analytical features of the proposed procedure with some procedures in the literature is presented in Table 2.

Compared to HPLC procedures [6–8], the proposed flow system showed a noticeably higher sample throughput and comparable sensitivity. Chloride interference was not observed for bromate determination in the proposed procedure, which eliminates the need for additional sample treatment prior to analysis. Moreover, the acquisition and maintenance of the multi-pumping flow system is cheaper and simpler due to the easy replacement of equipment.

A general disadvantage of spectrophotometric procedures is the lack of alternatives for bromine speciation analysis since the bromide content can be indicative of the potential for bromate yield during ozonation. The methylene blue method [9] showed suitable quantification limit for drinking water analysis. Nevertheless, a 10 min delay time is needed for reaching chemical equilibrium, which hinders sample throughput. Furthermore, the measurements must be taken before 20 min have elapsed after the addition of reagents to avoid the degradation of the formed product.

The exploitation of mechanized bromate determination, as in the proposed procedure, brought inherent advantages of flow-based procedures, such as high precision and the yield of unstable

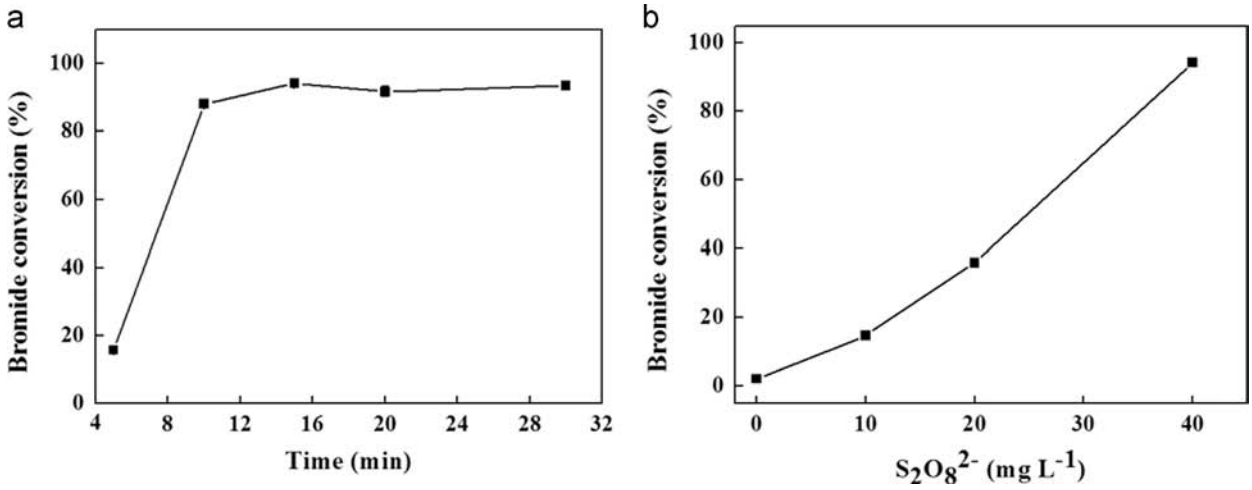

Fig. 4. Effect of time for photoconversion (a) and persulfate concentration (b) on bromide conversion efficiency to bromate.

Table 2
Analytical features of some procedures for inorganic bromine species determination.

Procedure	Principle	Linear range ($\mu g\ L^{-1}$)	LD[a] ($\mu g\ L^{-1}$)	Sampling throughput (h^{-1})	Reference
Ion-exchange chromatography	Separation and conductivity detection; Post-column derivatization and fluorimetric detection	1.0–40[b]; 5.0–500[c]	–	2	[6]
		Up to 15[b]	0.12[b]	2	[7]
		Up to 15[b]	0.28[b]	5	[8]
X-ray fluorescence	Bromate adsorption onto membranes	Up to 25[b]	1.0[b]	–	[12]
Chemiluminescence	Sulphite oxidation by bromate and hydrocortisone as sensitizer	45–64,000[b]	10[b]	120	[13]
Batch spectrophotometry	Methylene blue bromination and discoloration	4–50[b]	1.5[b]	–	[9]
	Phenol red bromination yielding bromophenol blue	100–1000[c]	40[c]	–	[18]
Flow-based spectrophotometry	5-Br-PADAP bromination and discoloration	250–2700[b]	100[b]	90	[10]
		180–3000[b]	150[b]	45	[10]
UV micro-digestion and flow-based spectrophotometry	5-Br-PADAP bromination and discoloration in a multi-pumping flow system; Batch bromide photoconversion into bromate	5.0–100[b]; 20–400[c]	2.7[b]; 8.0[c]	40	This work

[a] Detection limit.
[b] Bromate concentration.
[c] Bromide concentration.

species. In both FIA [10] and SIA [11] systems, comparable sampling rates were achieved, but the detection limits were 100 and 150 $\mu g\ L^{-1}$, respectively. These limits did not enable the quantification of bromate in drinking water [5]. The proposed multi-pumping flow system showed inherent advantages, such as miniaturization and minimization of reagent consumption of *ca.* 15 and 1000-fold compared to the FIA and SIA systems, respectively.

The main advantage of the proposed procedure is the possibility to exploit inorganic bromine speciation analysis without employing a separation technique that hinders sample throughput and the cost of the analysis. The use of UV photoconversion required simple and cheap devices that bring advantages for routine analysis.

3.4. Effect of concomitant species and applications

The effect of potentially interfering species on bromate determination was evaluated by adding 1.0 mg L^{-1} ClO^- or 5.0 mg L^{-1} Fe^{3+} to 50 $\mu g\ L^{-1}$ bromate solutions, yielding signal variations of *ca.* 300 and 20%, respectively. For bromide determination, a 30 $\mu g\ L^{-1}$ Br^- solution containing 200 mg L^{-1} Cl^- was evaluated after sample treatment and significant signal variation was not observed ($< 6.3\%$).

The interferences of ClO^- and Fe^{3+} were, respectively, due to the chlorination of 5-Br-PADAP in acidic media and formation of $[Fe(SCN)_6]^{3-}$. The addition of $NH_2OH \cdot HCl$ was evaluated to convert hypochlorite to chloride ions and Fe^{3+} to Fe^{2+}. It was observed that concentrations of up to 23 mmol L^{-1} (1.6 g L^{-1}) $NH_2OH \cdot HCl$ did not cause significant variations on bromate signals. Higher concentrations caused signal suppression due to bromate reduction to bromide. Thus, 12 mmol L^{-1} (0.4 g L^{-1}) hydroxylamine hydrochloride was employed, allowing the prompt elimination of up to 1.0 mg L^{-1} ClO^- and, after 10 min, of 5.0 mg L^{-1} Fe^{3+}. These values are *ca.* 2-fold higher than the maximum hypochlorite concentration required for water disinfection and 15-fold higher than the established threshold limits by EPA [7] for Fe^{3+}.

Chloride was evaluated in the sample preparation process because it could compete with bromide ions during photo-oxidation [22], thus affecting the analyte conversion. Significant signal variation was not observed with concentrations up to 200 mg L^{-1} Cl^-. In this work, 40 mg L^{-1} $K_2S_2O_8$ was employed for bromide conversion, which was *ca.* 500-fold smaller than in the flow-based procedure for chloride determination using photo-oxidation [23]. Higher chloride concentrations caused positive interference due to the conversion into chlorine that caused reagent discoloration due to chlorination.

Table 3
Mean values and uncertainties ($n=3$) for speciation analysis of inorganic bromine by proposed and reference procedures.

Sample	Bromate ($\mu g\ L^{-1}$)			Bromide ($\mu g\ L^{-1}$)		
	Added	Proposed	Reference [9]	Added	Proposed	Reference [18]
1[a]	20.0	(20.1 ± 0.5)	(20.0 ± 1.2)	250	(248 ± 7)	(260 ± 5)
	50.0	(47.0 ± 1.0)	(49.0 ± 1.0)	550	(551 ± 12)	(536 ± 6)
2[a]	20.0	(20.0 ± 0.2)	(18.3 ± 3.4)	250	(257 ± 8)	(262 ± 3)
	50.0	(48.8 ± 0.3)	(47.7 ± 2.0)	550	(557 ± 11)	(575 ± 3)
3[a]	20.0	(20.9 ± 0.3)	(16.9 ± 9.0)	250	(242 ± 8)	(255 ± 4)
	50.0	(49.7 ± 0.7)	(48.3 ± 1.0)	550	(558 ± 9)	(554 ± 9)
4[a]	20.0	(19.7 ± 0.3)	(17.9 ± 2.3)	250	(254 ± 7)	(262 ± 3)
	50.0	(48.4 ± 1.0)	(50.9 ± 1.0)	550	(547 ± 5)	(575 ± 17)
5[b]	20.0	(21.3 ± 0.3)	(18.4 ± 1.1)	250	(252 ± 4)	(233 ± 3)
	50.0	(50.0 ± 0.9)	(51.0 ± 2.0)	550	(559 ± 7)	(604 ± 3)
6[b]	20.0	(19.7 ± 0.2)	(18.8 ± 1.0)	250	(247 ± 2)	(254 ± 3)
	50.0	(52.3 ± 0.5)	(51.8 ± 2.0)	550	(547 ± 6)	(567 ± 26)
7[b]	20.0	(20.9 ± 0.2)	(19.0 ± 1.5)	250	(248 ± 4)	(248 ± 5)
	50.0	(50.0 ± 0.6)	(56.0 ± 3.0)	550	(554 ± 3)	(563 ± 4)

[a] Tap water.
[b] Commercial mineral water.

Three commercial and four tap water samples showed bromate and bromide concentrations lower than the detection limits. Therefore, the samples were spiked with 20 and 50 $\mu g\ L^{-1}$ bromate and 250 and 550 $\mu g\ L^{-1}$ bromide and analyzed by the proposed procedure. The results (Table 3) agreed with those obtained with the reference spectrophotometric procedures [9,18] at the 95% confidence level. Additionally, bromate and bromide recoveries were estimated at in the range 95–102%.

4. Conclusions

A flow-based procedure with solenoid micro-pumps aiming at inorganic bromine speciation in drinking water was developed based on the spectrophotometric determination of bromate with improved sensitivity and detection limit with long path-length spectrophotometry. Bromide determinations were carried out after conversion into bromate ions.

The mechanization of bromate determination in a flow-based procedure was advantageous due to the low stability of the formed brominated product. The detection was carried out before reactions reached chemical equilibrium, which increased the sampling rate compared to reference procedures. Waste generation was also reduced compared to the batch spectrophotometric and chromatographic procedures. The interference of a few concomitants was circumvented by simple addition of $NH_2OH \cdot HCl$ prior to the analysis.

For the first time, bromide photo-oxidation was carried out for sample preparation prior to spectrophotometric determinations aiming at inorganic bromine speciation analysis. This step required simple and low-cost instrumentation, estimated at US$ 40.00. Additionally, further separation steps were avoided, such as chloride elimination prior to chromatographic procedures. The exploitation of small sample volumes was also advantageous because the process became faster due to the higher irradiation efficiency, requiring 15 min irradiation per sample (7.5 min per replicate). The proposed procedure is thus a reliable and sensitive alternative for inorganic bromine speciation analysis with special advantages for routine analysis.

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