# SPECTROPHOTOMETRIC DETERMINATION OF BROMATE IN WATER USING MULTISYRINGE FLOW INJECTION ANALYSIS

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***A multisyringe flow injection system for the spectrophotometric determination of bromate in water is proposed, based on the oxidation of phenothiazine compounds by bromate in acidic medium. Several phenothiazines were tested, including chlorpromazine, trifluoperazine, and thioridazine. Higher sensitivity and lower LOD were attained for chlorpromazine. Interference from nitrite, hypochlorite, and chlorite was eliminated in-line, without any changes in the manifold. The automatic methodology using chlorpromazine allowed the determination of bromate between 25 and 750 $\mu g\ L^{-1}$, with LOD of 6 $\mu g\ L^{-1}$, good precision (RSD < 1.6%, n = 10), and determination frequency of 35 $h^{-1}$.***

***Keywords***: Bromate; Multisyringe flow injection analysis; Phenothiazines; Spectrophotometry; Water

## INTRODUCTION

Bromate is a by-product formed during the disinfection processes of waters containing bromide. The most exploited disinfection techniques used in water treatment supplies employ ozone or sodium hypochlorite as antiseptic agents. In both techniques, bromate formation was observed after treatment (Walters, Gordon,

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and Bubnis 1997; Weinberg, Delcomyn, and Unnam 2003). Due to the genotoxic (Nawrocki and Bilozor 1997) and carcinogenic (Kurokawa et al. 1990) properties of bromate, the US EPA (EPA 1998) and the European Community (EC 1998) established a concentration of $10\,\mu g\,L^{-1}$ as the maximum contaminant level (MCL), with a target concentration of $25\,\mu g\,L^{-1}$ during the transition period after legislation enforcement. For this reason, the development of fast and simple methodologies for bromate screening in water is mandatory.

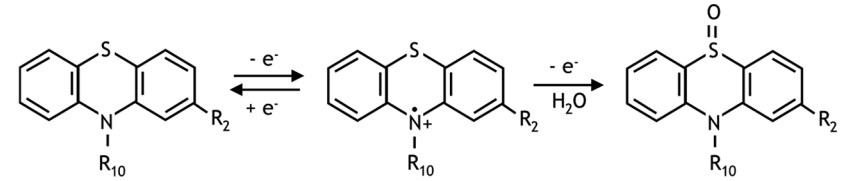
Among the analytical techniques for bromate determination, ion chromatography is the most common. However, it is time-consuming, requires highly skilled analysts, involves the use of expensive instrumentation, and, therefore, inappropriate for screening analysis. In response to the increasing demand of simple and inexpensive methods for bromate determination in water for human consumption, non-chromatographic methodologies based on flow injection analysis (FIA) were reported. These methods resorted to detection systems based on fluorescence (Almendral-Parra, Alonso-Mateos, and Fuentes-Prieto 2008), chemiluminescence (da Silva, Dias, and Magalhães 2001), mass spectrometry (Elwaer, McLeod, and Thompson 2000), potentiometry (Ohura et al. 2004; Ohura et al. 1986) or molecular absorption spectrophotometry (Almendral, Alonso, and Fuentes 2009; Alonso-Mateos, Almendral-Parra, and Fuentes-Prieto 2008; Chen et al. 1990; Gordon and Bubnis 1995; Gordon et al. 1994; Isawa and Yamane 2007; Uraisin et al. 2006). However, FIA systems are associated with high reagent consumption and effluent generation, which are prohibitive characteristics due to higher costs and increased human intervention required for daily monitoring on a large scale. Multisyringe flow injection analysis (MSFIA), proposed by Cerdà et al. (1999) constitutes a novel strategy for automating analytical determinations. This technique combines the multi-channel operation of FIA with the possibility of selecting exact sample and reagent volumes, a feature of sequential injection analysis (SIA) (Segundo and Magalhães 2006). In MSFIA systems, solutions are propelled into the flow network only when the determination occurs, or they are sent back to the respective flasks during the remaining time of the analytical cycle. Hence, the main objective of the present work was the development of a simple methodology based on MSFIA for bromate determination in drinking waters, with in-line elimination of interferences that would be found in drinking waters.

The spectrophotometric determination was based on the oxidation of phenothiazines, which originate colored compounds upon reaction with oxidizing agents in acidic medium (Puzanowska-Tarasiewicz et al. 1998). Considering that the absorption spectra and respective intensity are established by the substituents present in positions 2 and 10 of the tricyclic aromatic ring (Karpinska, Starczewska, and Puzanowska-Tarasiewicz 1996; Kojlo et al. 2001), the evaluation of different phenothiazine compounds was also performed (See Fig. 1).

## EXPERIMENTAL

### Reagents and Solutions

All solutions were prepared using Milli-Q water (resistivity $> 18\,M\Omega$ cm) and analytical grade quality reagents. A $1000\,mg\,L^{-1}$ stock standard solution of bromate



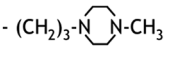
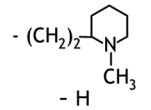

| Compound | $R_2$ | $R_{10}$ |
|---|---|---|
| Chlorpromazine | - Cl | $-(CH_2)_3N(CH_3)_2$ |
| Trifluoperazine | $-CF_3$ |  |
| Thioridazine | $-SCH_3$ |  |
| Phenothiazine | - H | - H |
| 2-Trifluoromethyl(phenothiazine) | $-CF_3$ | - H |

**Figure 1.** Schematic representation of the oxidative process of phenothiazine derivatives and structures of compounds studied.

was prepared by dissolving 0.3265 g of potassium bromate (Merck, Darmstadt, Germany) in 250 mL of water. Working standard solutions were prepared daily by appropriate dilution of the stock solution.

Each phenothiazine colorimetric reagent was daily obtained by dissolving the respective solids (Sigma-Aldrich, St Louis, MO, USA) in water, resulting in solutions of chlorpromazine 750 mg $L^{-1}$ (2.11 mmol $L^{-1}$), trifluoperazine 500 mg $L^{-1}$ (1.05 mmol $L^{-1}$) and thioridazine 500 mg $L^{-1}$ (1.23 mmol $L^{-1}$).

For the dissolution of phenothiazine and 2-(trifluoromethyl)phenothiazine, solutions were prepared using glacial acetic acid (d = 1.05, Merck), ethanol (d = 0.79, Merck), and N,N-dimethylformamide (d = 0.95, Promega, Mannheim, Germany).

Sulfuric acid (d = 1.84, Merck) and hydrochloric acid (d = 1.18, 37% (m/m), Pronalab, Lisbon, Portugal) were diluted in water. Sulfamic acid stock solution was obtained by dissolution of 20.0 g of the respective solid (Merck) in 200.0 mL of water. Sulfite stock solution was prepared by dissolving 15.8 g of sodium sulfite (Riedel-de Haën, Seelze, Germany) in 100.0 mL of water, resulting in a sulfite concentration of 100 g $L^{-1}$.

For the interference study, standard solutions containing bromate 0.250 mg $L^{-1}$ plus variable volumes of solutions containing the possible interfering species in a concentration of 1000 mg $L^{-1}$ were prepared using KCl, $K_2SO_4$, NaF, $CaCl_2$, $MgCl_2$, KBr, KI, $KNO_2$, $KNO_3$, NaClO, $NaClO_2$, $KClO_3$, and $Na_2SO_3$.

For accuracy assessment, tap water from Porto public supply was fortified with certified reference standard (U-ICC-010) from LGC Promochem (Teddington, UK).

## Apparatus

A schematic representation of the flow manifold is given in Fig. 2. The solutions were propelled through the flow system by means of a multisyringe burette (Crison Instruments, model BU 4S, Allela, Spain), equipped with four glass syringes (Microliter, Hamilton, Colorado, USA) with capacities of 2.50, 5.00, and 10.00 mL. All pistons were driven by a single motor controlled by computer software through a serial port. A three-way commutation valve (NResearch, 161T031, Caldwell, NJ, USA) was connected to the head of each syringe. Sample introduction in the flow system was carried out by including two additional commutation valves in the module. For all valves, the exchange options were classified by "on" or "off" lines. In the valves placed at the multisyringe module, the "on" line was assigned to the solution flasks and the "off" line was reserved for the flow network. For the other valves, the "on/off" positions were chosen to minimize the time when "on" position was activated in order to avoid over-heating problems. All tubing connecting the different components was made of PTFE with 0.8 mm inner diameter (Omnifit, Cambridge, UK). Gilson (Villiers-le-Bell, France) end-fittings and connectors were also used. Acrylic lab-made Y-shaped joints were used as confluences.

A 486 personal computer, running lab-made software written in QuickBasic 4.5 (Microsoft, USA), controlled the position of all solenoid valves, the number of steps, and the direction of piston displacement. A UV/Vis spectrophotometer (Helios $\gamma$, ThermoUnicam, Cambridge, UK), equipped with a flow-through cell (Starna Brand 75.3Q), with an internal volume of 140 µL and a flow path of 20 mm was used as

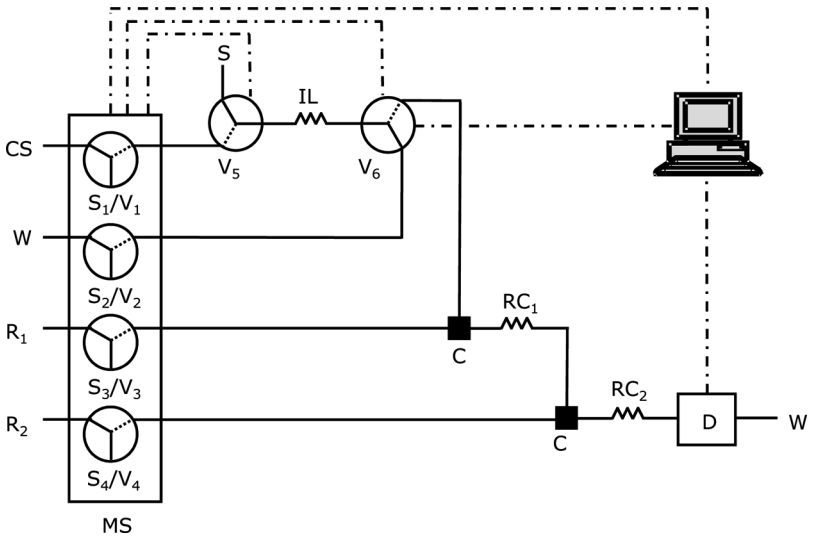



**Figure 2.** Schematic representation of multisyringe flow injection system for determination of bromate. MS: multisyringe piston burette; $S_i$: syringes ($S_1 = S_2 = 10.00$ mL, $S_3 = 2.50$ mL, $S_4 = 5.00$ mL); $V_i$: solenoid valves; C: confluences; IL: injection loop (1000 µL); $RC_i$: reaction coils ($RC_1 = 60$ cm; $RC_2 = 160$ cm); S: sample; CS: carrier ($H_2O$); $R_1$: phenothiazine compound solution; $R_2$: HCl solution; W: waste; D: spectrophotometer. In the solenoid valves, the position "on" is represented by a solid line and the position "off" is represented by a dotted line.

**Table 1.** Protocol sequence for the determination of bromate in waters

| Step | Description | Position of commutation valves[a] | | | | | | Time (s) | Volume (μL)[b] | Flow rate (mL $min^{-1}$)[b] |
|---|---|---|---|---|---|---|---|---|---|---|
| | | $V_1$ | $V_2$ | $V_3$ | $V_4$ | $V_5$ | $V_6$ | | | |
| 1 | Injection loop is filled with sample while syringes are filled with respective solutions | N | F | N | N | N | N | 24 | 4000 | 10.00 |
| 2 | Sample is injected and mixed with reagents; reaction product is detected | F | N | F | F | F | F | 69 | 4000 | 3.50 |

[a]N and F represent positions "on" and "off," respectively.
[b]Volumes and flow rates correspond to syringe 1 (10 mL).

detection system. Analytical signals were recorded using a chart recorder (Kipp & Zonen BD111, Delft, Holland), and data acquisition was performed using a PCL-711B interface card (Advantech, Taipei, Taiwan) at 3 Hz, using the same software developed for the flow system control. The data was analyzed using Microsoft Excel 2002 software.

### Flow Procedure

The developed flow protocol and timing sequence is given in Table 1. In the first step, syringes were partially filled with the respective reagents, and sample was aspirated into the injection loop through valves $V_5$ and $V_6$ (Fig. 2). Then, after flow reversal and commutation of the valves $V_5$ and $V_6$, solutions were propelled through the flow network, where the reagents were sequentially added to the sample. Sample was initially mixed with the phenothiazine reagent in reaction coil $RC_1$, which was subsequently merged with HCl in reaction coil $RC_2$. From this coil, the colored reaction product formed was further propelled towards the detector where the analytical signal was acquired.

## RESULTS AND DISCUSSION

### Development of the Multisyringe Flow Injection System

The MSFIA system comprises four syringes accommodated in the same propulsion unit (Fig. 2). Considering that phenothiazines are not stable at acidic pH, the color forming reagent and the acid required for pH adjustment were placed in different syringes (S3 and S4, respectively). Further, for sample introduction, a fixed volume scheme was assembled using two commutation valves (V5 and V6) and placing an injection loop between them, connected to their fixed port. Syringe S2 was connected to valve V6 in order to fill the injection loop while syringe S1 was connected to valve V5 in order to dispense sample into the flow network. After defining this initial configuration, several parameters (divided here as physical and chemical) were studied by a univariate approach.

**Physical parameters.** Initial studies were performed using 1000 μL of bromate standards (25–750 μg $L^{-1}$), 1.41 mmol $L^{-1}$ chlorpromazine solution and 6.0 mol $L^{-1}$ HCl solution. Temperature influence was assessed by introducing reaction coil $RC_2$ in a thermostatic bath and varying temperature between 20 and 60°C. As similar sensitivity was attained, room temperature (20°C) was chosen. Furthermore, aiming to decrease the detection limit and increase sensitivity of the reaction, flow cells with optical paths of 1 and 2 cm were compared. As the 2 cm flow cell provided an increase of 100% on the sensitivity, it was adopted in the following experiments.

The order of reagent addition has a strong influence on the reaction development and sample dispersion (Magalhães et al. 2006). Moreover, according to previous works, the formation of oxidation product was affected by the order of reagent addition, even in batch studies (Farrell, Joa, and Pacey 1995; Gordon et al. 1994). The sequence of reagent addition was evaluated by establishing calibration curves using bromate standards with concentrations ranging from 25 to 750 μg $L^{-1}$, using 2.11 mmol $L^{-1}$ chlorpromazine solution and 7.0 mol $L^{-1}$ HCl solution. Four possible sequences were studied, designated I to IV. For each addition sequence, modifications on the manifold were performed, resulting in four different configurations, represented in Fig. 3.

In scheme I, chlorpromazine was first mixed with the sample in reaction coil $RC_1$, followed by addition of the hydrochloric acid and development of the final reaction product in reaction coil $RC_2$. The sequence II consisted of mixing the sample with HCl, then adding the chlorpromazine. In scheme III, the chlorpromazine was added to the HCl, subsequently, adding the sample with the mixture in $RC_2$. Finally, sequence IV consisted of simultaneously mixing sample, HCl, and chlorpromazine.

Higher sensitivity (about 0.5 AU $mg^{-1}$ L) was attained with sequences I and III. Moreover, the signal due to the Schlieren effect (Dias et al. 2006) was minimized when sequence I was applied. Schemes II and IV gave rise to sensitivity values of 10

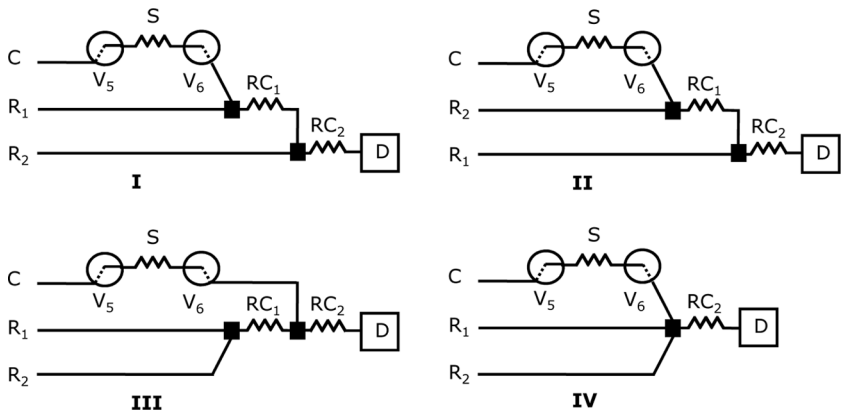



**Figure 3.** Schematic representation of manifold configurations enabling different sequences of reagent addition to sample. $V_i$: solenoid valves at "off" position; S: sample or standard (1000 μL); $RC_i$: reaction coils ($RC_1 = 60$ cm; $RC_2 = 160$ cm); C: $H_2O$; $R_1$: 2.11 mmol $L^{-1}$ chlorpromazine solution; $R_2$: 7.0 mol $L^{-1}$ HCl solution; D: spectrophotometer.

and 58% of the sensitivity achieved with sequence I and, consequently, narrower dynamic linear ranges. The pronounced decrease of the sensitivity observed when hydrochloric acid was added to the sample before chlorpromazine addition (scheme II) or simultaneously (scheme IV) may be due to bromate reduction by chloride (Uraisin et al. 2006) or traces of bromide or other oxidizers in the solutions (Farrell et al. 1995). To avoid this, the phenothiazine compound must be added to bromate before the reaction with HCl. Hence, scheme I was chosen for further work.

To increase the determination throughput, the flow rates of the reagents involved in the determination step were evaluated. Total flow rates within a range of 3.5–7.0 mL $min^{-1}$ were tested, corresponding to flow rates ranging from 2.0 to 4.0 for syringe 1 ($H_2O$), 1.0 to 2.0 for syringe 3 (chlorpromazine) and 0.50 to 1.0 for syringe 4 (HCl). The sensitivity was similar for all flow rates tested, allowing the increase of the determination rate by increasing the flow rates, without compromising the sensitivity. Nevertheless, high flow rates may cause backpressure in the flow system, which may lead to the damage of the solenoid valves. Thus, a total flow rate of 6.1 mL $min^{-1}$ was selected for the following experiments.

The length of the reaction coils was also studied by varying it from 40 to 100 cm for $RC_1$, and from 80 to 400 cm for $RC_2$. The sensitivity of the reaction was not affected by $RC_1$ length and it was fixed at 60 cm. On the other side, a decrease on the sensitivity was observed with the increase of $RC_2$. This decline, more prominent for the highest length (sensitivity decreased $> 7\%$), may be explained by the higher dispersion attained with longer reaction coils. $RC_2$ with 80 and 120 cm provided analytical signals with deformations corresponding to Schlieren effect, indicating poor mixing conditions. With a length of 160 cm, the Schlieren effect was smoothed; hence, this value was selected for further experiments.

Finally, the influence of the sample volume was evaluated in a range between 400 and 2000 μL. The sensitivity increased approximately 13% by increasing the sample volume from 400 to 600 μL, and 5% more to 800 μL, maintaining stable for higher volumes. A sample volume of 1000 μL was selected in order to ensure the minimal sample dispersion in the carrier solution and the achievement of the maximum sensitivity.

**Chemical parameters.** Phenothiazines have been applied to photometric determination of bromate but no comparison about their analytical performance or selectivity towards interfering species has been established under the kinetic control offered by flow injection analysis systems. Therefore, five phenothiazine compounds were considered as they were commercially available and presented a suitable cost for utilization on flow based systems: chlorpromazine, trifluoperazine, thioridazine, phenothiazine, and 2-(trifluoromethyl)phenothiazine. From these compounds, chlorpromazine, trifluoperazine, and thioridazine were soluble in acidic media (0.50 mmol $L^{-1}$ of each compound in 2.0 mol $L^{-1}$ HCl). They provided absorption spectra with maximum at 525, 505, and 635 nm in the presence of 100 μg $L^{-1}$ of bromate. Phenothiazine and 2-(trifluoromethyl)phenothiazine were not soluble in water. In fact, high concentrations of acetic acid or ethanol were required for dissolution of phenothiazine, whereas 2-(trifluoromethyl)phenothiazine was soluble in acetic acid and N,N-dimethylformamide. Therefore, the implementation of these compounds in the flow system was not possible and further studies were performed with the three

water soluble phenothiazines. Considering that the oxidation of phenothiazines takes place at high acidic conditions, hydrochloric acid was applied instead of other acids (namely $HNO_3$ and $H_2SO_4$) as it provided enhanced sensitivity in previous studies, probably due to the catalytic role of chloride ion (Uraisin et al. 2006).

Using the manifold depicted in Fig. 2, the influence of HCl concentration was carried out through establishment of calibration curves using bromate concentrations of 25–750 $\mu g\,L^{-1}$, maintaining fixed the concentrations of chlorpromazine (1.41 $mmol\,L^{-1}$), trifluoperazine (1.05 $mmol\,L^{-1}$), and thioridazine (1.24 $mmol\,L^{-1}$). The results, presented in Fig. 4a, revealed that HCl concentration has a strong influence on the sensitivity of the reaction as a significant increase on sensitivity up to 4.0 $mol\,L^{-1}$ was verified, with a further enhancement, less accentuated, for increasing concentrations. Hence, HCl concentrations of 7.0, 6.0, and 6.0 $mol\,L^{-1}$ were selected for further studies with chlorpromazine, trifluoperazine, and thioridazine, respectively.

Chlorpromazine, trifluoperazine, and thioridazine concentrations varied within the ranges of 0.563–2.11, 0.567–2.61 and 0.616–3.09 $mmol\,L^{-1}$, respectively (Fig. 4b). Chlorpromazine provided sensitivity values of 82, 87, 90, 94, and 97% of the obtained value with 2.11 $mmol\,L^{-1}$, remaining constant for upper values. Thus, the concentration of 2.11 $mmol\,L^{-1}$ was selected as the minimal concentration to achieve the highest sensitivity (0.518 $AU\,mg^{-1}$ L). Intending to enhance the sensitivity of the method by minimizing the sample dilution inside the manifold, the use of chlorpromazine as the carrier solution was also tested but sensitivity was not enhanced.

Regarding trifluoperazine, better sensitivity was achieved, using 1.05 $mmol\,L^{-1}$ of colorimetric reagent (0.321 $AU\,mg^{-1}$ L) but not as high as that observed for chlorpromazine. Nevertheless, this phenothiazine has been described previously as providing better sensitivity than chlorpromazine in batch studies (Farrell et al. 1995). In order to assess if a kinetic factor, e.g., lower reaction time, is the reason for this incongruity, the flow rate of the detection step was lowered to 6.1 mL $min^{-1}$, allowing more time for reaction to take place at $RC_2$. Nevertheless, similar

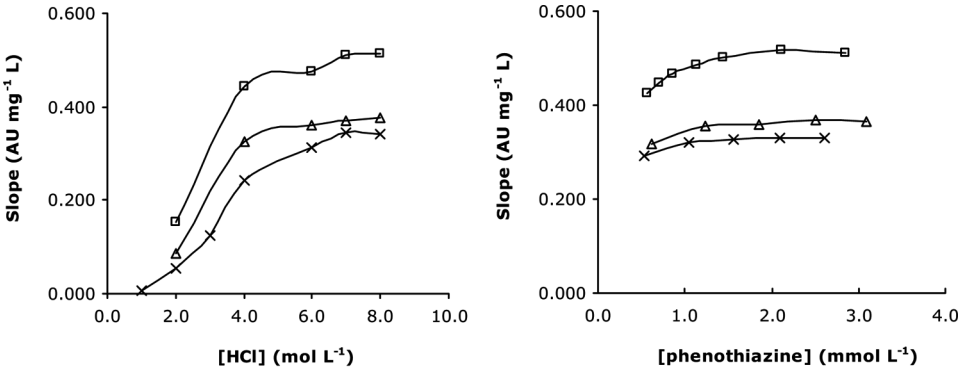



**Figure 4.** Influence of reagent concentration on sensitivity. (a) effect of HCl concentration using 1.41 $mmol\,L^{-1}$ chlorpromazine (□), 1.05 $mmol\,L^{-1}$ trifluoperazine (x), and 1.24 $mmol\,L^{-1}$ thioridazine (Δ); (b) effect of phenothiazine compound concentration (chlorpromazine (□), trifluoperazine (x), and thioridazine (Δ) using 6.0 or 7.0 $mol\,L^{-1}$ HCl.

slope values were attained (0.355 and 0.356 AU $mg^{-1}$ L for 3.5 and 6.1 mL $min^{-1}$, respectively), indicating that reaction time was not an issue. Further, a ten times higher concentration (21.3 mmol $L^{-1}$) of trifluoperazine was also tested, providing a slope of 0.351 AU $mg^{-1}$ L, indicating that the quantity of this reagent is not the limiting factor. Hence, trifluoperazine 1.05 mmol $L^{-1}$ was used in succeeding experiments.

For thioridazine an increase of 11% on the sensitivity was observed when increasing thioridazine concentration from 0.616 to 1.24 mmol $L^{-1}$. As similar sensitivity was attained for higher concentrations, the thioridazine concentration was fixed at 1.24 mmol $L^{-1}$, providing a sensitivity of 0.357 AU $mg^{-1}$ L.

Using the aforementioned conditions, the sensitivity was definitely higher for chlorpromazine ($0.518 \pm 0.003$ AU $mg^{-1}$ L) when compared to trifluoperazine ($0.346 \pm 0.002$ AU $mg^{-1}$ L) or thioridazine ($0.351 \pm 0.002$ AU $mg^{-1}$ L). Similar values for limits of detection (between 8 and 10 μg $L^{-1}$) were found for the three compounds. Reagent consumption was also similar, comprising 12 to 14 mmol of HCl, and 500 μg of trifluoperazine/thioridazine or 750 μg of chlorpromazine per determination.

**Interfering species.** The study of potential interfering species was performed by adding known concentrations of the possible interfering species to a standard solution containing 250 μg $L^{-1}$ of bromate. The apparent bromate content was then calculated by interpolation of the obtained analytical signal on calibration curves previously established with bromate standard solutions. Relative deviations between the apparent and real bromate concentration are given in Table 2. Considering RD > 5% for interfering species, nitrite, hypochlorite, and chlorite ions interfered in the methodology for all phenothiazines tested. According to Kojlo et al. (2001), these ions have the ability of oxidizing chlorpromazine and here the same effect was also observed for trifluoperazine and thioridazine.

**Table 2.** Relative deviation[a] (%) found on evaluating interfering species using chlorpromazine, trifluoperazine, and thioridazine as colorimetric reagents

| Species studied | Concentration tested ( mg $L^{-1}$) | Chlorpromazine | Trifluoperazine | Thioridazine |
|---|---|---|---|---|
| $Cl^-$ | 250 | 4.4 | 0.0 | 1.1 |
| $F^-$ | 1.50 | 1.5 | 1.2 | 2.2 |
| $SO_4^{2-}$ | 250 | 0.0 | 1.2 | 2.2 |
| $Ca^{2+}$ | 100 | 1.5 | −2.6 | 1.1 |
| $Mg^{2+}$ | 50.0 | 1.5 | 0.0 | 2.2 |
| $I^-$ | 0.0500 | 0.8 | −3.8 | 2.2 |
| $Br^-$ | 6.00 | 3.7 | 2.4 | 0.0 |
| $NO_2^-$ | 0.50 | 61.6 | 51.6 | 61.3 |
| $NO_3^-$ | 50.0 | 1.5 | 1.1 | −3.3 |
| $ClO^-$ | 2.00 | 71.1 | 50.8 | 37.9 |
| $ClO_2^-$ | 3.00 | 74.6 | 64.2 | 65.8 |
| $ClO_3^-$ | 0.500 | 0.8 | 1.1 | −2.2 |
| $SO_3^{2-}$ | 300 | −4.0 | n.d.[b] | n.d.[b] |

[a]Relative deviation between the apparent (250 μg $L^{-1}$ + interfering species) and real bromate concentration (250 μg $L^{-1}$).

[b]n.d. – not determined.

For each interfering ion, calibration curves were established employing the same conditions previously applied for bromate (Table 3). The extension of interference was evaluated through the ratio between the slopes of these calibration curves and the slope obtained for bromate standards. Nitrite interferes more than the other two anions, showing relative slopes of 0.73–0.93, which are higher compared to values of 0.05–0.31 obtained for hypochlorite and chlorite. For these two anions, interference was less pronounced when trifluoperazine was applied.

Considering that interfering species were similar and a better sensitivity was attained for chlorpromazine (about 1.5 times higher), this reagent was chosen to proceed for implementation of in-line interference removal.

### In-line elimination of interferences.

*Elimination of interferences caused by hypochlorite and chlorite ions.* Previous reports indicated that chlorite ion is removed after treatment of the samples with iron(II) or with a solution containing 10 mg $L^{-1}$ of sulfite (Gordon and Bubnis 1995; Gordon et al. 1994). Hence, iron(II) (6.0 mg $L^{-1}$) was added to standard bromate solutions (25 and 250 μg $L^{-1}$) prepared using tap water. After processing through the MSFIA system, apparent bromate concentrations above 890 μg $L^{-1}$ were obtained, for all assays, indicating that Fe(II) was not efficient in the elimination of the interference.

Subsequently, solutions containing 2.00 mg $L^{-1}$ of hypochlorite, bromate (25 and 250 μg $L^{-1}$), and sulfite concentrations of 5.00, 10.0, and 20.0 were also processed by the flow system. Recovery values of 95–100% were achieved, indicating that interference caused by hypochlorite was eliminated, possibly through reduction of $ClO^-$ to $Cl^-$, which does not interfere in the methodology. These results were independent of the sulfite concentration.

After the successful results attained with previous sample treatment, the implementation of sulfite in the flow system to eliminate this interference in-line was tested. This was performed by adding sulfite 300 mg $L^{-1}$ to the carrier solution (syringe 1). After analysis of a standard solution of hypochlorite, a signal correspondent to a bromate concentration of 516 μg $L^{-1}$ was obtained. The sulfite concentration increase to 3000 mg $L^{-1}$ led to a decrease of only 15% of the analytical signal, indicating that this strategy was not adequate to remove chlorite interference, probably to the inefficient mixture of the carrier solution with the central part of the sample plug.

Aiming to allow sulfite addition to all sample segments, this species was introduced in the chlorpromazine solution (syringe 3), since this reagent was added to the sample through confluence. However, precipitation was observed when a solution

**Table 3.** Assessment of methodology response to interfering species based on relative sensitivity[a] values

| Interfering species | Calibration range (μ g $L^{-1}$) | Chlorpromazine | Trifluoperazine | Thioridazine |
|---|---|---|---|---|
| Nitrite | 25–750 | 0.840 | 0.727 | 0.931 |
| Hypoclorite | 25–2500 | 0.310 | 0.053 | 0.165 |
| Clorite | 25–3600 | 0.233 | 0.137 | 0.164 |

[a]Relative sensitivity calculated as the ratio between the slope obtained for calibration curves using standards of interfering species and the slope obtained for bromate standards.

containing sulfite 70.0 mg $L^{-1}$ and chlorpromazine 2.11 mmol $L^{-1}$ was prepared. This was overcome by adding a few drops of HCl 2.0 mol $L^{-1}$. Using this solution in syringe S3, the analysis of a hypochlorite ion standard with a concentration of 2.00 mg $L^{-1}$ gave rise to an apparent concentration of 543 μg $L^{-1}$. This experiment was repeated using a sulfite concentration of 2.00 g $L^{-1}$ (30 times higher than the preceding), which originated an analytical signal below the detection limit, indicating the elimination of the interference. Recovery assays using tap water fortified with bromate certified reference standard (25, 100, and 250 μg $L^{-1}$, added concentration) and with hypochlorite (2.00 mg $L^{-1}$) and chlorite (3.00 mg $L^{-1}$) were performed. Recovery values between $90 \pm 2$ and $108 \pm 5\%$ were found.

*Elimination of the interference caused by nitrite ion.* Previous work reported the use of sulfamic acid to eliminate the interference caused by nitrite ion (Gordon et al. 1994; Uraisin et al. 2006) by addition of this reagent to the sample 10 min prior to flow analysis. Here, in-line removal of the interference caused by nitrite ion was tried by adding sulfamic acid to the chlorpromazine reagent, which was further mixed with the sample in $RC_1$. Sulfamic acid concentrations were evaluated within a range of 7.0–21 g $L^{-1}$, using solutions containing 25 μg $L^{-1}$ of bromate and 500 μg $L^{-1}$ of nitrite. Recovery values comprised between 94 and 98% were achieved, thus indicating the in-line elimination of interference originated by nitrite.

*Simultaneous elimination of the interferences.* Based on the results obtained in the preceding experiments for individual interferences removal, the simultaneous inclusion of sulfite (2.0 g $L^{-1}$) and sulfamic acid (21 g $L^{-1}$) in the chlorpromazine reagent was tested. However, these conditions yielded a decrease on the sensitivity of 83%, and also a shortening of the dynamic linear range. This occurrence may be explained by results obtained when the sequence of reagent addition was examined. When sulfamic acid is added simultaneously with chlorpromazine, the bromate present in the sample reacts with chlorpromazine and is simultaneously acidified, originating a pronounced decrease on the sensitivity as observed previously in Scheme IV (Fig. 3).

Hence, sulfite 2.0 g $L^{-1}$ was added to chlorpromazine solution and sulfamic acid was added to the HCl 7.0 mol $L^{-1}$, in a concentration of 10.5 g $L^{-1}$ (as syringe S4 introduces the double of reagent compared to syringe S3). Recovery tests with tap water with and without addition of interfering ions were carried out (Table 4), showing that no significant difference was found.

*Analytical figures of merit.* Applying the conditions set previously, the analytical features of the flow system (calibration curve, LOD, LOQ, precision, accuracy, and determination throughput) were established. The method provided a typical calibration curve represented by the equation $AU = 0.471\ (\pm 0.002) \times [BrO_3^-] + 0.0004\ (\pm 0.0008)$, (bromate concentrations expressed in mg $L^{-1}$). Detection and quantification limits of 6 and 21 μg $L^{-1}$ of bromate, respectively, were calculated as the concentration corresponding to the intercept value plus three (LOD) or ten (LOQ) times the statistic $s_{y/x}$ (Miller and Miller 2005).

The precision of the methodology was assessed from 10 consecutive injections of tap water fortified with 100 or 250 μg $L^{-1}$ of bromate. Relative standard deviations <1.6% were achieved ($n = 10$). Good recoveries (89–96%) were attained for

**Table 4.** Results obtained in recovery assays using tap water, with in-line elimination of interferences caused by nitrite, hypochlorite, and chlorite ions

| Bromate concentration ($\mu g\,L^{-1}$) | | | | |
|---|---|---|---|---|
| Added | Found[a] | Found[b] | Recovery[a] (%) | Recovery[b] (%) |
| 0 | <LOD | <LOD | — | — |
| 25 | LOQ ($21 \pm 2$) | $24 \pm 2$ | — | $96 \pm 3$ |
| 100 | $93 \pm 2$ | $89 \pm 3$ | $93 \pm 3$ | $89 \pm 3$ |
| 250 | $240 \pm 2$ | $237 \pm 3$ | $96 \pm 1$ | $95 \pm 1$ |

[a]Tap water fortified with bromate.

[b]Tap water fortified with bromate and with addition of nitrite ($500\,\mu g\,L^{-1}$), hypochlorite ($2.00\,mg\,L^{-1}$), and chlorite ($3.00\,mg\,L^{-1}$).

tap water fortified with 25, 100, or $250\,\mu g\,L^{-1}$ of bromate (Table 4). Finally, the determination frequency was $35\,h^{-1}$.

## CONCLUSION

The proposed method allowed the determination of bromate in tap water, within a concentration range of 25–$750\,\mu g\,L^{-1}$, with good precision. Furthermore, the detection limit was $6\,\mu g\,L^{-1}$, which is below the parametric value established by European and American legislation. Therefore, the proposed MSFIA system can be regarded as a suitable screening tool with potential application for monitoring the ozone treatment process for water disinfection. In this regard, more expensive techniques, such as chromatography and/or mass spectrometry, would only be required when LOD signal was surpassed. Compared to automatic, flow-based systems proposed for determination of bromate, the MSFIA system presented here offers some advantages, namely an enhanced throughput (about 3 times higher, except for the FIA system proposed by Uraisin et al. 2006). The most important feature accomplished by the new automatic system is the in-line elimination of interferences, attained by in-line addition of chemicals that prevent the interference of hypochlorite, chlorite, and nitrite, also presenting the possibility for application to on-line monitoring of water treatment.

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