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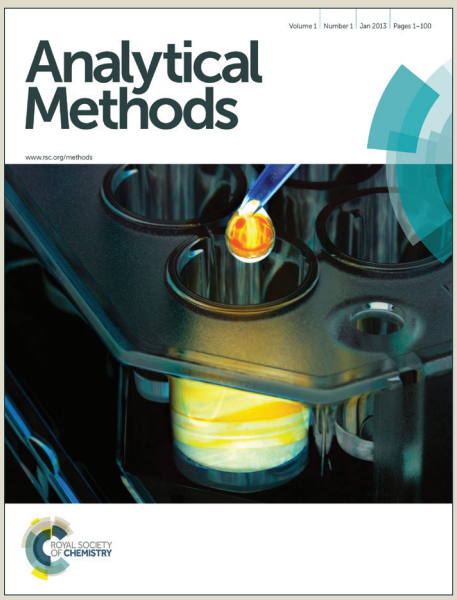

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Spectrophotometric determination of bromide in waters using the Multisyringe Flow Injection Analysis technique coupled to a gas-diffusion unit

Kaewta Danchana[a,b,c], Fernando Maya[a], Prapin Wilairat[b,d], Kanchana Uraisin[b,c], Víctor Cerdà[a]*

[a] Department of Chemistry, University of the Balearic Islands, Cra de Valldemossa km 7.5, 07122 Palma de Mallorca, Spain

[b] Flow Innovation-Research for Science and Technology Laboratories (FIRST Labs.)

[c] Department of Chemistry and Center of Excellence for Innovation in Chemistry, Faculty of Science, Mahidol University, Rama VI Rd, Bangkok 10400, Thailand

[d] National Doping Control Centre, Mahidol University, Bangkok 10400, Thailand

***Corresponding author.** Tel.: +34 971 173261; Email address: victor.cerda@uib.es

Abstract

A novel spectrophotometric method for the determination of bromide has been developed using the Multisyringe Flow Injection Analysis technique (MSFIA). This method is based on the decolorization of methylene blue by the bromine released from the oxidation of bromide by bromate in acidic condition. By incorporating a gas-diffusion unit to the MSFIA system the transferred bromine reacts with methylene blue in the acceptor stream. The decrease of the methylene blue absorbance is monitored at 745 nm. The oxidation conditions are not strong enough to oxidize chloride to chlorine, which is a major component of both natural and seawater.

The proposed method provides linearity for the determination of bromide over the range $1x10^{-5}$ mol L^{-1} to $6x10^{-5}$ mol L^{-1} in $5x10^{-2}$ mol L^{-1} of chloride, with a correlation coefficient

(r^2) of 0.9939, and a precision of 3.1% (%RSD for 3 x10^{-5} mol L^{-1} Br^- in 5x10^{-2} mol L^{-1} Cl^-, n=10). The limit of detection (3σ) is 0.5x10^{-5} mol L^{-1}. The proposed method has been applied to the determination of Br^- in water samples, obtaining recoveries in the analysis of spiked tap, natural, and seawater samples in the range of 90 - 106 %.

Keywords: Bromide Determination, Multisyringe Flow Injection Analysis, Gas-diffusion, Methylene Blue, Spectrophotometric Detection.

1. Introduction

Bromide (Br^-) is a trace element present in food, medicines, biological fluids and environmental samples. Br^- is a natural trace element commonly presented in waters like natural water, drinking water and seawater. The typical concentration of Br^- in waters is approximately 100 µg L^{-1} [1]. Higher Br^- concentrations are found in seawater, approximately 60-70 mg L^{-1} [2]. Br^- in fresh water typically range from trace amounts to about 0.5 mg L^{-1}, and in desalinated waters is around 1 mg L^{-1} [3]. According to the Environmental Protection Agency (EPA), a high dose of Br^- might cause adverse effects on human health [4]. In addition, Br^- is a potential source of bromine (Br_2), which is reactive with the natural organic matter [5].

The determination of Br^- in environmental samples have been reported using high performance liquid chromatography [6], ion chromatography [7,8], inductively coupled plasma-mass spectrometry [9], gas chromatography [10,11], capillary electrophoresis [12] and using a Br^- ion-selective electrode [13]. UV-vis spectrophotometric methods are a simple and cost-effective alternative for the determination of Br^-, and usually involve

the use of an indicator reaction [14-18]. The main drawback of these approaches is the lack of selectivity, being chloride (Cl^-) and iodide (I^-) the major interferences. A typical example for this kind of reactions is the methylene blue (MB) reaction [2, 19]. MB is a thiazine type dye used for dyeing fabrics and as a stain in medicine, bacteriology, and microscopy [20]. The MB reaction for the determination of Br^- is based on the oxidation of Br^- to Br_2 and the subsequent decolorization of the MB, which is monitored at 745 nm. However, this reaction lacks of selectivity for the determination of Br^- in real samples. In this case, the use of solid-phase extraction or other similar sample pretreatments based on the use of functional solid supports are not useful, since the interference from other anions still persist. A useful approach to overcome this drawback is the gas-diffusion (GD) separation [21], since the oxidation product of Br^- is volatile [22]. GD separation requires laboratory automation tools to be properly performed. In this sense, the multisyringe flow injection analysis (MSFIA) [23-25] is a versatile and robust technique for the automation of multiple sample pretreatments [26-30], including GD separation procedures [31-35].

In this work, we developed a MSFIA-GD approach with spectrophotometric detection for the determination of Br^- in water samples. The oxidation of Br^- using bromate (BrO_3^-) and the subsequent membrane-based separation enabled the application of the proposed method to the determination of Br^- to water matrices with different saline contents.

2. Experimental

2.1. Reagents and solutions

All chemicals used are of analytical reagent grade or higher. All reagents are prepared by using deionized water (resistivity > 18 MΩ cm). The stock solution of Br^- (10^{-2} mol L^{-1}) is obtained by dissolving 0.119 g of KBr crystals (Sigma-Aldrich, USA) in 100 ml water. The stock solution of Cl^- (1 mol L^{-1}) is obtained by dissolving 2.9220 g of NaCl crystal (Fluka, Switzerland) in 50 mL of water. Standard solutions of Br^- are prepared by stepwise dilution of the bromide stock solution using $5x10^{-2}$ mol L^{-1} of NaCl.

As oxidizing agent a 0.01 mol L^{-1} potassium bromate solution is used. It is prepared by dissolving 0.7545 g of $KBrO_3$ crystals (Sigma-Aldrich, USA) in 500 mL of a 1 mol L^{-1} H_2SO_4 (Sigma-Aldrich, USA) solution. The stock solution of MB (10^{-2} mol L^{-1}) is prepared by dissolving 0.0015 g of MB crystals in 50 mL of water. A working solution of $4x10^{-5}$ mol L^{-1} MB is prepared by dilution from the stock MB solution in 1 mol L^{-1} H_2SO_4.

For the interference studies, working standard solutions are prepared from stock solutions of NaF (0.5 mol L^{-1}), NaI (1 mol L^{-1}), KSCN (1 mol L^{-1}), $NaNO_3$ (1 mol L^{-1}) and $NaNO_2$ (1 mol L^{-1}), all of them obtained from Sigma-Aldrich.

2.2. Sample preparation

The proposed method has been applied to water samples such as tap water, groundwater and seawater. Seawater samples were diluted 50-fold before analysis. For comparison purposes, Br^- content in the samples was measured by ion chromatography (IC). Samples were filtered through a 0.45 μm nylon filter prior to IC analysis.

2.3. Manifold and software

The scheme of the MSFIA system incorporating a gas-diffusion unit is shown in **Figure 1**. The developed instrumental set-up consists of a multisyringe module (Burette 4S model, Crison instruments, Barcelona, Spain). The multisyringe module is equipped with three glass syringes (Hamilton, Bonaduz, Switzerland) with a volume of 5 mL each. A three-way solenoid valve (V1, V2, and V3, N-Research, West Caldwell) is placed on the head of each syringe. We define as *OFF* position, when the syringes are connected to their respective reservoirs containing the carrier or the reagents. *ON* position is used to load or inject a fluid towards the flow network containing the gas-diffusion unit and the detector. Syringe 1 (S1) contains milli-Q water, syringe 2 (S2) contains the MB reagent, and syringe 3 (S3) contains the BrO_3^- reagent.

All tubing is polytetrafluoroethylene (PTFE) tubing 0.8 mm i.d. The volume of the holding coil (HC) is 3 mL. All confluence points are made from polymethylmethacrylate (PMMA). Three external solenoid valves (V4, V5 and V6) from Takasago (STV-3 1/4UKG, Nagoya, Japan) are connected to the auxiliary ports of the multisyringe module. V4 is used for the loading of the samples into the system. V5 is connected to a waste reservoir and is used for the washing of the sample tube between samples, in order to avoid carry-over. V6 is placed between the GD chamber and the detector, in order to close the acceptor stream when Br_2 is transferred through the membrane, minimizing the dispersion of Br^- in the acceptor phase prior its quantification.

The reaction coil (RC, 65 cm) is used to mix the sample with the BrO_3^- reagent in order to generate Br_2.

A lab-made gas-diffusion (GD) chamber is constructed from two rectangular PMMA blocks (30 x 100 mm), each one with a semi-circular U-shaped channel [25]. A strip of semipermeable PTFE membrane (LACHAT, Loveland, USA) is placed in between the two halves separating the donor and the acceptor channels.

The multisyringe module is controlled by the lab-made software software Autoanalysis 5.0 (Sciware Systems SL, Bunyola, Spain). A USB2000 Miniature Fiber Optic Spectrophotometer (Ocean Optics Inc., Dunedin, FL, USA) is used as detector. The decolorization of MB is detected at 745 nm.

3. Results and discussions

3.1. Methodology for the determination of Br^- using the MSFIA-GD technique

The analytical procedure for the MSFIA-GD system is detailed in **Table 1**. Steps 1-4 comprise the steps required for the proper loading of the sample into the MSFIA system avoiding carry-over between different samples. In step 7, a controlled sample volume is introduced into the system. In step 8, Br^- is oxidized by BrO_3^- in H_2SO_4 in the donor stream generating Br^-. Due to the fast kinetics of the reaction Br_2 is immediately generated transferred through the membrane to the acceptor channel. The solution contained in the acceptor channel, which is MB in H_2SO_4 in a stop flow mode is gradually preconcentrating the transferred Br^-. In step 10, the product of the decolorization of the MB due to the transferred Br^- is measured spectrophotometrically at 745 nm.

3.2. Study of the composition of the donor stream

In order to ensure an efficient conversion of Br^- to Br_2 and its subsequent transference through the GD membrane, the study of the concentration of both BrO_3^- and H_2SO_4 present in S3 is a critical step.

The effect of the concentration of BrO_3^- on the measured absorbance is shown in **Figure 2A**. The concentration of BrO_3^- has been studied in a range of 0-0.05 mol L^{-1} using a $3x10^{-4}$ mol L^{-1} Br^- standard in a $5x10^{-2}$ mol L^{-1} Cl^- solution. The absorbance of the Br^- standard increased gradually with the concentration of BrO_3^-, and a similar trend was observed with the blank. The increase in the measured absorbance was more accentuated from 0 to 0.01 mol L^{-1} BrO_3^-, getting stabilized for higher concentration values. In order to obtain the highest ratio between the absorbance measured for the Br^- standard and the blank, a concentration of BrO_3^- of 0.01 mol L^{-1} was selected for further experiments.

The reaction between Br^- and BrO_3^- in the donor stream requires a strong acid medium in order to be accomplished. We studied the concentration of H_2SO_4 added to the BrO_3^- reagent in order to maximize the transfer of Br^- through the GD membrane. The H_2SO_4 concentration was studied in the range of 0-2.5 mol L^{-1}. In order to obtain the best signal to blank ratio, we selected a concentration of H_2SO_4 of 1 mol L^{-1}. The effect of the H_2SO_4 in the BrO_3^- reagent on the measured absorbance is shown in **Figure 2B**.

3.3. Study of the composition of the acceptor stream

The acceptor stream of the GD is composed by an aqueous solution of the MB dye in H_2SO_4, which is under stopped-flow conditions in the Br^- transfer step. Since we are measuring the decolorization product of the MB, the baseline of our method will be established by the concentration of MB. We obtained a stable baseline with an appropriate intensity by using a MB concentration of $4x10^{-5}$ mol L^{-1}. We modulated the concentration of H_2SO_4 added to the MB reagent (**Figure 3A**). The effect of H_2SO_4 was studied in the range within 0.5-2.5 mol L^{-1}. The presence of H_2SO_4 in the MB is required in order to detect the MB at 745 nm. Without the presence of H_2SO_4 in the acceptor stream the wavelength of the maximum absorbance for MB shifts to 680 nm. Performing this measurement in acidic conditions we obtain a higher reaction rate, and simultaneously avoid the potential interference from colored material present in the matrix of the samples. The net absorbance increases gradually with the H_2SO_4 concentration. In order to avoid the excessive use of H_2SO_4, we select the minimum H_2SO_4 concentration that provide us with a good net absorbance, enabling a wider linear dynamic working range possible, thus selecting a 1 mol L^{-1} H_2SO_4 for further experiments.

3.4. Effect of flow rates

The flow rate of both the donor and the acceptor chamber solutions in the GD unit are critical parameters in order to ensure an efficient transference of the analyte through the GD membrane. When GD separation is performed in order to separate an analyte from the matrix of the sample, the sensitivity of the method decrease in comparison with the direct measurement. This is the general trend when both donor and acceptor solutions

flow through the GD chamber at an identical flow rate. In order to minimize this effect, the acceptor solution stream is stopped, and the transferred Br^- is preconcentrated in the volume of acceptor solution hold in the acceptor channel.

Once the analyte has been transferred through the GD membrane, the flow rate of the injection of the acceptor reaction plug containing the decolorization product is a relevant parameter, since the sensitivity gained in the GD process can be partially lost due to the dispersion of the decolorization product within the acidic MB carrier. As is shown in **Figure 3B**, this parameter was studied from 1-5 mL min^{-1}. Results showed that the dispersion in the acceptor channel is not significant in the studied range, selecting a value of 3 mL min^{-1} for further experiments.

Once the experimental conditions of the acceptor channel have been optimized, the flow rate of the donor channel was studied. The contact time between the analyte and the GD membrane decreases while increasing the flow rate, having an influence in the yield of transferred Br^-. The minimum flow rate enabled by the multisyringe pump used in this experiment is 0.3 mL min^{-1} (when a 5 mL syringe is used). The flow rate of the sample through the membrane chamber was studied between 0.3-3 mL min^{-1} (note that the total flow rate in the GD chamber is 2-fold higher, since the sample is mixed with the BrO_3^- also injected using a 5 mL syringe). As is shown in **Figure 3C**, the maximum signal was observed using the lowest flow rate enabled, decreasing this one gradually while increasing the flow rate. However, in a compromise in order to obtain a high signal and a concomitant high analysis throughput, a flow rate for the preconcentration step of 1 mL min^{-1} was selected.

3.5. Effect of the sample volume

The sample volume is an important parameter in the MSFIA-GD system developed, potentially increasing the sensitivity of the methodology by increasing the sample volume, since we work using stop-flow conditions in the acceptor stream.

The effect of the sample volume was studied between 0.25-3 mL. As is shown in **Figure 3D**, an increase in the sample volume provided an increase on the sensitivity of the method. However, increasing the sample volume causes a decrease of the analysis throughput. In a compromise between sensitivity and a high analysis throughput we selected a sample volume of 1 mL for further studies.

3.6. Analytical features on the MSFIA-GD-UV-Vis

Once the relevant physical and chemical parameters have been studied and selected (**Table 2**). The analytical features of the MSFIA-GD system were calculated. A linear response of Br^- was obtained (y = 0.0194x + 0.0159, net absorbance vs. Br^- concentration $x10^{-5}$ mol L^{-1}). The linear dynamic range for the determination of Br^- is from $1x10^{-5}$ mol L^{-1} to $6x10^{-5}$ mol L^{-1} Br^- in $5x10^{-2}$ mol L^{-1} of Cl^- with a correlation coefficient (r^2) of 0.9939. The repeatability for 10 consecutive measurements was 3.1% (RSD for $3x10^{-5}$ mol L^{-1} Br^- in $5x10^{-2}$ mol L^{-1} of Cl^- , n=10). The limit of detection (LOD, 3σ) and the limit of quantification (LOQ, 10σ) were $0.5x10^{-5}$ mol L^{-1} Br^- and $1.0x10^{-5}$ mol L^{-1} Br^-, respectively. The reagent consumption for the analysis of one sample including three replicates is 78 µg MB, 10 mg $KBrO_3$ and 1.17 g H_2SO_4. The total aqueous waste generation per sample (n=3) is 19.5 mL. The analysis throughput of the MSFIA-GD

system for the determination of Br^- is 12 h^{-1}. The sampling rate (n=3) including conditioning steps to avoid carry-over between samples is 3 h^{-1}.

3.7. Interference study

The effect of potentially interfering ions on the developed methodology for the determination of Br^- in waters was evaluated using a $3x10^{-4}$ mol L^{-1} Br^- in $5x10^{-2}$ mol L^{-1} Cl^-. We assumed that a given ion interfere in our method when its concentration modified the measured absorbance ±5%. A good selectivity of the developed method was obtained for most of the common ions present in waters. Na^+, F^-, NO_3^- or SO_4^{2-} did not interfere even when they are added to the Br^- standard in a concentration 500-fold higher. The selectivity against Cl^- was also remarkable, and no Cl^- interference was observed up to the addition of 250-fold Br^-. However, lower tolerance ratios were observed for several ions typically absent in non-polluted waters such as I^-, SCN^- or NO_2^- providing an interference higher than the 5% when they are present at the same concentration level as Br^-.

3.8. Application of the MSFIA-GD-UV-vis system

The developed MSFIA-GD system was applied to the determination of Br^- in different types of water samples. Tap water, well water and seawater samples were tested (**Table 3**). All samples were analyzed directly using the MSFIA-GD system, except seawater that was diluted 50-fold prior analysis. Tap water and well water Br^- concentration was below the established LOD. Br^- in seawater was detected at a concentration of 91 mg L^{-1}, which is in accordance with the typical levels of Br^- in seawater (65-155 mg L^{-1}) [36]. The different water samples were spiked with Br^- at two

different levels, and the Br^- recovery values were obtained. In this case, satisfactory recoveries ranging from 90-106 % were obtained in all instances. Furthermore, we measured the amount of Br^- present in the samples by ion chromatography (IC). In this case, the results obtained for all three samples are in agreement with those obtained with the MSFIA-GD technique. While the levels of Br^- in tap water and well water samples were also below the LOD, Br^- was detected in seawater. The relative error between both methods was just a 4%, reinforcing the validation of our method besides the standard addition measurements performed.

3.9. Comparison with similar automated systems for the determination of Br-.

In comparison with other spectrophotometric methods for the determination of Br^-. The proposed MSFIA-GD method provided a more selective alternative, minimizing the effect of interfering ions when direct spectrophotometric measurements are performed. Using stopped-flow conditions the loss of sensitivity due to the non-transferred Br^- is minimized obtaining similar limits of detection and linear working ranges than other direct spectrophotometric methods (**Table 4**), enabling the selective determination of Br^- in water samples.

4. Conclusion

In this work, we have developed an improved automatic approach for the selective determination of Br^- present in waters based on their conversion to volatile species prior to spectrophotometric detection. Br^- in water samples is converted to Br_2 and its

subsequently separated by membrane-based gas-diffusion, prior its quantification based on the decolorization of the MB dye.

Automation based on the MSFIA technique enabled the versatile use of the gas-diffusion technique for the reproducible transfer of Br^- through the membrane, by using stopped-flow conditions in the acceptor stream, minimizing the loss of performance inherent to GD membrane-based separations. The developed method was successfully applied to the determination of Br^- in different kinds of water samples, as measured by calculating the recoveries of spiked samples, or by validation using ion chromatography.

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Figure captions

Figure 1. Schematic representation for the MSFIA-GD system for the spectrophotometric determination of Bromide. S: syringe (S1, S2, S3: 5 mL), V: solenoid valve, HC: holding coil, RC: reaction coil, GD: gas-diffusion unit, Carrier: H_2O, R1: $4x10^{-5}$ mol L^{-1} MB in 1 mol L^{-1} H_2SO_4, R2: 0.01 mol L^{-1} $NaBrO_3$ in 1 mol L^{-1} H_2SO_4.

Figure 2. Effect on the measured absorbance of the **A)** bromate concentration and the **B)** sulfuric acid concentration in syringe 3. Studies performed using using $3x10^{-4}$ mol L^{-1} Br^- in $5x10^{-2}$ mol L^{-1} NaCl.

Figure 3. Effect on the measured absorbance of the **A)** Concentration of H_2SO_4 in the MB reagent. **B)** Flow rate of the reaction between MB and the transferred Br^- in the acceptor channel of the GD chamber. **C)** Flow rate of the donor stream of the GD chamber for the transfer of Br^- through the membrane. **D)** Sample volume. Studies performed using $3x10^{-4}$ mol L^{-1} Br^- in $5x10^{-2}$ mol L^{-1} NaCl.

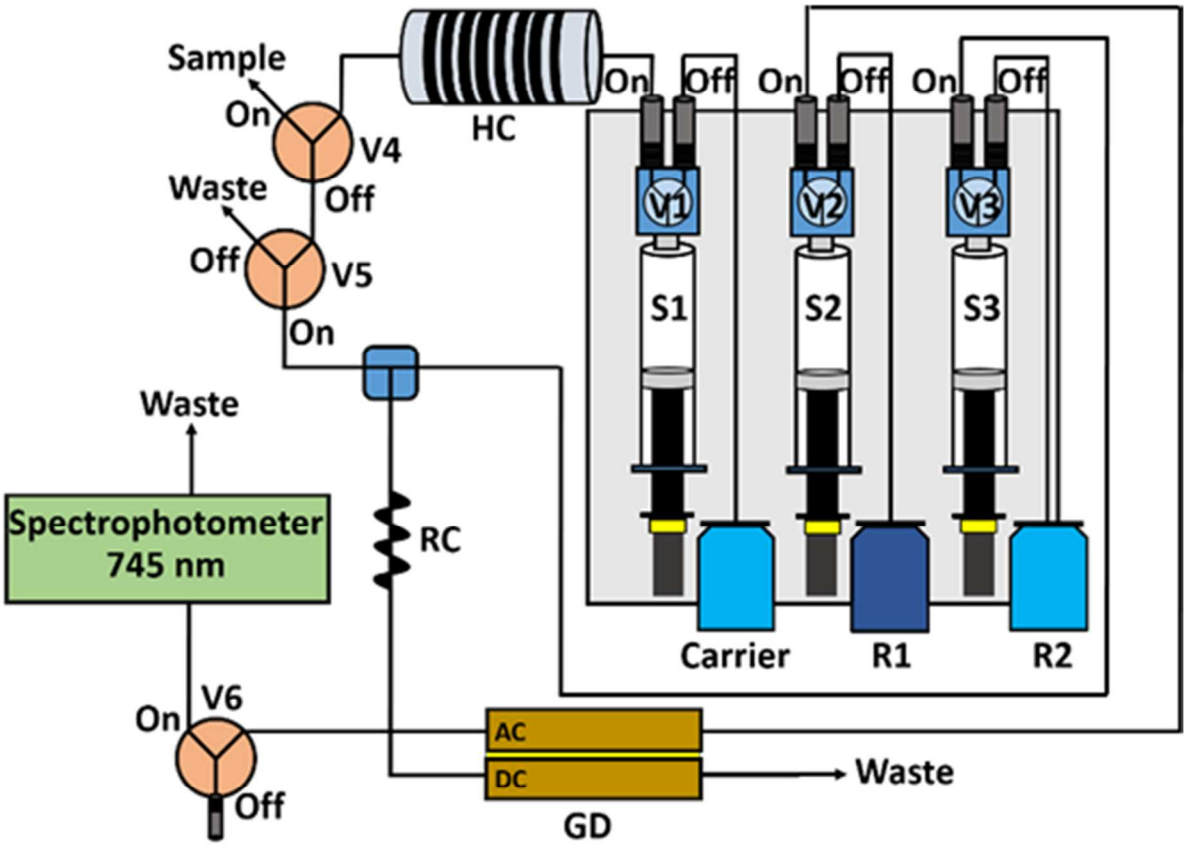

Figure 1

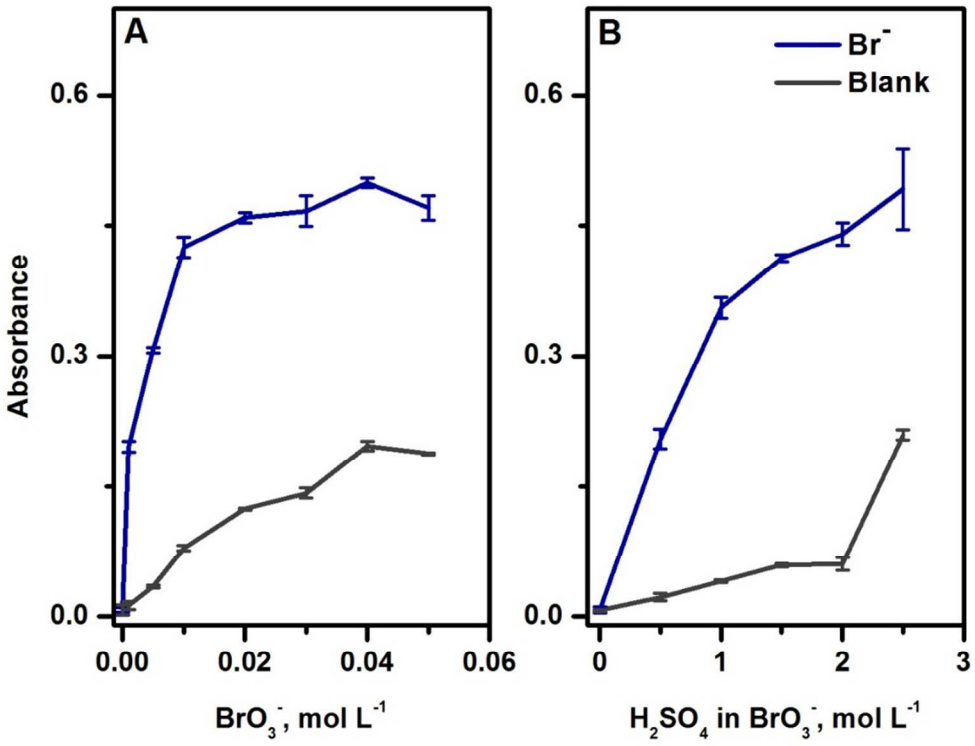

Figure 2

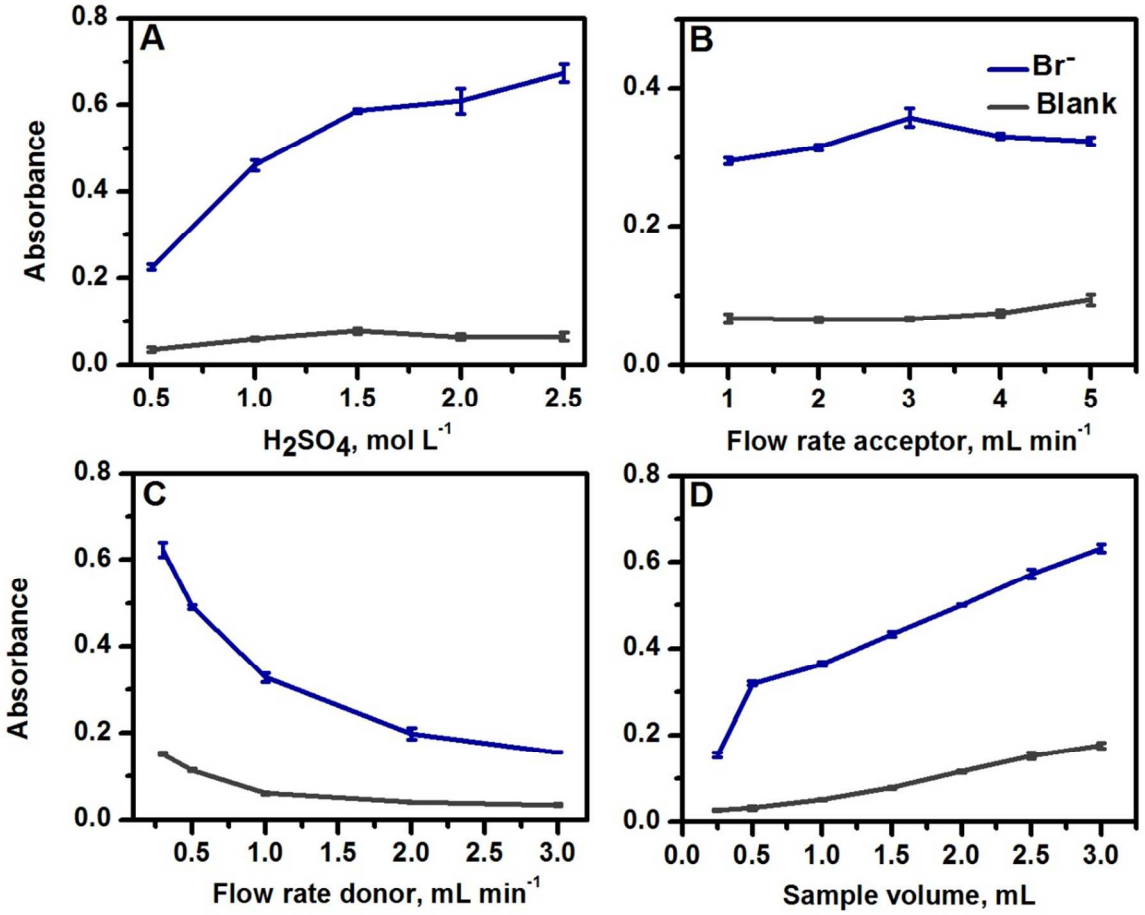

Figure 3

Table 1. Automatic procedure for the determination of Br^-.

Step	Description	Volume (mL)	Flow rate (mL min^{-1})	Operation	Valve position					
					V1	V2	V3	V4	V5	V6
1	Multisyringe	1.00	5	Dispense	Off	Off	Off	Off	Off	Off
2	Multisyringe	1.00	5	Pick up	On	Off	Off	On	Off	Off
3	Multisyringe	1.50	5	Dispense	On	Off	Off	Off	On	Off
4	Multisyringe	Fill	5	Priming Pick up	Off	Off	Off	Off	Off	Off
5	AutoAnalysis			Start Loop						
6	Multisyringe	1.00	3	Dispense	Off	On	Off	Off	Off	On
7	Multisyringe	1.00	3	Pick up	On	Off	Off	On	Off	Off
8	Multisyringe	2.00	1	Dispense	On	Off	On	Off	On	Off
9	Detector			Start acquisition						
10	Multisyringe	2.00	3	Dispense	Off	On	Off	Off	Off	On
11	Detector			Stop acquisition						
12	Multisyringe	Fill	5	Priming pick up	Off	Off	Off	Off	Off	Off
13	Autoanalysis			End Loop[a]						

[a]Finish analysis, or return to position 5 to make a replicate.

Table 2.

Optimized experimental conditions for Br^- determination.

Parameter	Selected value
Sample volume	1 ml
Flow rate donor stream, step 8	1 ml min^{-1}
Flow rate acceptor stream, step 10	3 ml min^{-1}
BrO_3^- concentration	0.01 mol L^{-1}
MB concentration	$4x10^{-5}$ mol L^{-1}
H_2SO_4 concentration in BrO_3^- solution	1 mol L^{-1}
H_2SO_4 concentration in MB solution	1 mol L^{-1}
Holding coil volume	3 ml
Reaction coil volume	65 cm

Table 3

Analysis of Br^- in water samples by using the proposed MSFIA-GD method and using ion chromatography (IC).

Sample	Bromide added ($x10^{-5}$ mol L^{-1})	Found ($x10^{-5}$ mol L^{-1})	Recovery (%)	Ion chromatography ($x10^{-5}$ mol L^{-1})
Tap water	0	<LOD	-	<LOD
	1	0.96±0.05	96	
	2	2.13±0.03	106	
Well water	0	<LOD	-	<LOD
	1	1.00±0.08	100	
	2	2.11±0.07	105	
Seawater*	0	1.82±0.03	-	1.90±0.02
	1	2.72±0.09	90	
	2	3.65±0.03	92	

*Seawater has been diluted 50-fold prior analysis with the MSFIA-GD system and IC.

Table 4. Comparison of spectrophotometric methods for the determination of Br^-.

Method	Reagents	LOD (mol L^{-1})	Linear range (mol L^{-1})	Ref.
Phenol red method	Phenol red, chloramine-T, acetate buffer	$1.25x10^{-7}$	$3.1x10^{-7}$ - $1.9x10^{-5}$	15
Methylene blue Method	Methylene blue, sodium chloride, sulfuric acid and hydrogen peroxide	$1.25x10^{-6}$	$4x10^{-5}$ - $1.25x10^{-4}$	37
m-cresolsulfonephthalein method	m-cresolsulfonephthalein, sodium periodate	$1.87x10^{-6}$	$2x10^{-6}$ - $2.5x10^{-4}$	38
MSFIA-GD MB method	Methylene blue, sodium bromate and sulfuric acid	$0.5x10^{-5}$	$1x10^{-5}$ - $6x10^{-5}$	This work

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