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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

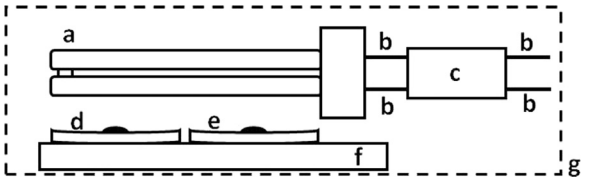

Fig. 1. Photo-reactor scheme for bromide conversion, constructed with a 13-W low-pressure mercury vapor lamp (a), powered through electrical contacts (b) by a lamp reactor (c). Sample aliquots (300 μL) were added onto glass watches at different distances (d and e) from the lamp filament. A metallic support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