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Analytical note

Determination of bromide in aqueous solutions via the TlBr molecule using high-resolution continuum source graphite furnace molecular absorption spectrometry

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ABSTRACT

The paper describes the determination of bromide by evaluating the molecular absorption of thallium mono-bromide (TlBr) at the rotational line at 342.9815 nm by making use a high-resolution continuum source graphite furnace atomic absorption spectrometer. The effects of variables such as the wavelength, graphite furnace program, amount of Tl and the use of a modifier were investigated and optimized. Various chemical modifiers have been studied, such as Pd, Mg, Ag and a mixture of Pd/Mg. It was found that best results were obtained by using Ag which prevents losses of bromide during pyrolysis step through precipitation of bromide as AgBr. In this way, a maximum pyrolysis temperature of 400 °C could be used. The optimum molecule forming temperature was found to be 900 °C. Bromide concentrations in various water samples (CRM, bottled drinking water and tap water) were determined. The quantification was made by both linear calibration and standard addition techniques. The results were matched well those of the reference method. The calibration curve was linear in the range between 1 and 1000 ng Br with a correlation coefficient R = 0.999. The limit of detection and characteristic mass of the method were 0.3 ng and 4.4 ng of Br.

1. Introduction

Bromine is found naturally in the earth's crust (0.00078%) in various chemical forms, analogue to chlorine compounds. In small amounts, bromine is a natural constituent of all waters but it is more abundant in the oceans (65–80 mg L^{-1}), resulting from long-term leaching. Concentrations of bromide in fresh water typically range from trace amounts to about 0.5 mg L^{-1}. In the form of anion, bromine is present in small amounts in all living organisms. However, bromine has no known biological role for humans. In the 19th century, bromide compounds (e.g. LiBr, KBr) were widely used for their sedative effect. Long-term excess consumption of bromine can cause syndrome known as bromism [1]. Bromine is used in many areas such as agricultural chemicals, insecticides, pharmaceutical, dyestuffs and chemical intermediates. Bromine compounds are frequently used as flame retardants. They are added to furniture foam, plastic casings for electronics and textiles to make them less flammable.

For the determination of bromine, classical gravimetric, volumetric or colorimetric procedures could be used. Nowadays, instrumental techniques such as inductively coupled plasma mass spectrometry (ICP-MS) [2–4], X-ray fluorescence spectrometry (XFS) [5], laser induced plasma spectrometry (LIPS) [6,7], neutron activation analysis (NAA) [8] or capillary electrophoresis (CE) [9] are commonly used for the determination of trace concentration of bromine. For routine determination, ion chromatography (IC) is the most commonly used method as prescribed by DIN EN ISO 10304-1 [10].

Atomic absorption spectrometry (AAS) cannot be used for the direct determination of bromine because its resonance absorption line is located in the vacuum ultraviolet region around 154.07 nm [11]. Measurement in this region requires a vacuum chamber, which is expensive and complicated for routine use. However, several attempts have been made to avoid this obstacle using line source AAS (LS AAS). A few articles dealing with the usage of LS AAS for bromine determination are cited in recent review articles by Butcher [12], Resano et al. [13] and Welz et al. [11,14]. These methods are based on the formation of a diatomic molecule between bromine and metal in the gas phase at high temperatures. Absorption of very narrow structured rotational lines of these molecules was evaluated using a hollow cathode lamp (HCL) with a suitable emission line. Because of a low sensitivity, low spectral resolution and a high risk of spectral interferences caused by other atoms or molecules, this method did not found a practical application. This failure was overcome in the last decade with the development of high-resolution continuum source atomic absorption spectrometers (HR-CS AAS). This instrument uses a Xe short-arc lamp with high

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intensity as a continuum source, which allows access to any wavelength between 190 and 900 nm. Furthermore, the HR-CS AAS apparatus is equipped with a high-resolution double monochromator, consisting of a prism and the echelle grating and for signal detection is used a charge-coupled device (CCD) detector. This kind of equipment allows to the registration of spectrum of any rotational line of diatomic molecules at high resolution and for determination of non-metals, such as sulfur, nitrogen and the halogens. Because it is a relatively new technique, only few reports for bromine determination by HR-CS MAS using the molecular absorption of AlBr [15], CaBr [15–19] or SrBr [20] can be found in the literature so far.

The present work was motivated by the idea to use this technique for the determination of Br via molecular absorption of thallium mono bromine, which has not been described up to now. The TlBr molecule has bond dissociation energy of (334 ± 2) kJ mol^{-1} which is comparable to the energies of another diatomic molecules, such as CaBr and SrF that have dissociation energies of (311 ± 9) kJ mol^{-1} and (333 ± 9) kJ mol^{-1}, respectively [21]. The aim of this work was to develop a novel procedure for the determination of Br by HR-CS GFMAS using the molecular absorption of TlBr. The main experimental parameters, such as pyrolysis and vaporization temperatures or amount of modifier, were optimized and the method was validated. The elaborated method was applied for the determination of bromide in different water samples.

Thallium as an ionic salt reaches the +3 and + 1 oxidation states. Tl-compounds represent extremely toxic, carcinogenic and hazardous materials with potentially high solubility in water and extensive skin-penetration ability and should be handled with care. Thallium is a suspected human carcinogen. Soluble thallium salts were historically used in rat poisons and insecticides [22]. The estimated lethal dose for the average adult for thallium is 1 g (approximately 14–15 mg kg^{-1}) [23].

2. Experimental

2.1. Material and methods

Molecular absorption measurements were carried out by making use of a high-resolution continuum source atomic absorption spectrometer contrAA 700 (Analytik Jena AG, Jena, Germany) with a transversely heated graphite tube atomizer. This instrument is equipped with a Xe short-arc lamp operating in hot-spot mode, which emits a continuous spectrum from 190 to 900 nm; a high-resolution double echelle monochromator (DEMON) and a linear CCD array detector. Measurements were carried out at the 342.9815 nm using integrated absorbance summed over five pixels. All measurements were performed using pyrolytically coated graphite tubes with an integrated PIN platform (Analytik Jena Part No. 407-A81.026). The reference cathodic stripping chronopotentiometric measurements were carried out by an electrochemical flow-through analyzer EcaFlow model 150 GLP (Istran, Bratislava, Slovakia) with commercial electrochemical flow-through cell of type 353c with Pt auxiliary, Ag/AgCl reference and gold-amalgam wire working electrode [24].

2.2. Standards, reagents and samples

All reagents were of analytical grade or highest available purity. Throughout the experiments nano pure water from NANOpure system (Wilhelm Werner GmbH, Germany) was used. The bromide standard was prepared by dissolving high-purity sodium bromide (Centralchem, Banská Bystrica, Slovakia) in nano pure water. The molecule-forming reagent stock solution containing 10 g L^{-1} of thallium was prepared from thallium sulfate (Sigma Aldrich). For stabilization of bromide Ag modifier was prepared from $AgNO_3$. For the interference studies, solutions of Al, As, B, Ba, Ca, Cl, Cr, Cu, F, Fe, Ga, I, In, Mg, Pb, Sr and Zn were prepared in nano pure water from 1 g L^{-1} stock solutions (Czech Metrology Institute, Czech Republic) of the corresponding element. Argon was of the 99.998% purity. The certified reference material (CRM) QC 1060, Anions - WP (Sigma Aldrich), was used for method validation. Various types of waters samples obtained from market were also analyzed.

2.3. Procedure

Bromide was determined via the molecular absorption line of diatomic thallium mono bromine (TlBr) at 342.9815 nm. Throughout all measurements, 15 μL of the thallium solution, 10 μL of the Ag modifier, and 10 μL of the respective bromide solution were injected onto the integrated platform of the pyrolytically coated graphite tube. The optimized graphite furnace program used for the measurement is presented in Table 1. Argon flow rate was 2.0 L min^{-1} during all steps, except for the molecule formation process, during which the gas flow was interrupted. Water samples were injected into the graphite furnace directly without sample preparation.

For the reference method, standard solutions and samples were prepared by diluting them in the carrier electrolyte. Bromide ions were electrochemically deposited as Mercury(I) bromide at the surface of gold-amalgam wire working electrode at constant potential. The cell was rinsed with the carrier electrolyte and in the last step the deposit was stripped by a negative constant current to get elemental Au/Hg and bromide anions. During this last step, the stripping chronopotentiogram was recorded [25].

3. Results and discussion

3.1. Selection of the absorption line

Dittrich et al. proposed the TlBr molecular bands around 266.8 nm and 342.9 nm for the analytical purposes [26]. This bands are identified to be a line of electronic transition $C - X^1\Sigma^+$ and $A^3\Pi_0^+ - X^1\Sigma_0^+$ respectively, with a bond dissociation energy of approximately 334 kJ mol^{-1} [21]. Both wavelength ranges were checked for sensitivity and spectral interferences. In the vicinity of 266.8 nm there are atomic lines of Fe and Cr, which may lead to a spectral overlap. No spectral interference was observed at 342.9815 nm, moreover, this band exerts a much better sensitivity. The wavelength resolved and time-wavelength resolved (3D) absorption spectra obtained for certified water sample QC 1060 in the vicinity of the molecular absorption band of TlBr at 342.9818 nm is shown in Fig. 1.

3.2. Optimization of the procedure

The formation efficiency of TlBr molecules is highly dependent on the amount of thallium. Tl should be in a great excess over Br to ensure a quantitative reaction and to achieve the highest sensitivity. To optimize the influence of Tl amount, 15 μL of Tl from 10 to 5000 mg L^{-1}, corresponding to 0.15–75 μg, were injected to graphite furnace together with 10 μL of bromide solution. As Fig. 2 implies, the integrated absorbance of TlBr increased almost linearly up to 15 μg of Tl and did not significantly change up to 75 μg in the presence of 1.0 μg of Br. The same trend was observed for injection of 0.5 μg and 0.1 μg of Br. Due to

Table 1
The optimized graphite furnace program for the determination of bromide via MAS of TlBr.

	Temperature (°C)	Heating rate (°C s^{-1})	Hold time (s)
Drying	80	6	20
Drying	90	3	20
Drying	120	10	10
Pyrolysis	400	50	20
Autozero	400	0	5
Molecule formation	900	2000	5
Cleaning	2500	500	4