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Determination of bromine by high resolution molecular absorption of strontium mono bromide generated in a graphite furnace

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ABSTRACT

The bromine concentration was determined by means of molecular absorption of strontium monobromide (SrBr) generated in the gas phase of the vaporizer of a high-resolution continuum source electrothermal atomic absorption spectrometer. For this purpose, the wine and drug samples were introduced into the graphite furnace together with Sr and the molecular absorption of SrBr at 651.0581 nm was measured. The effects of SrBr wavelength, graphite furnace program, and the amount of Sr on the accuracy, linearity and sensitivity were investigated and the experimental parameters were optimized. All quantifications were performed in zirconium coated tubes. The limit of detection and the characteristic mass for the method were 1.6 ng and 3.0 ng of Br, respectively. In order to check the risk of non-spectral interference, all quantifications were performed by both standard addition and external calibration techniques. In general, the results were not significantly different. Finally, the bromine was determined in wines and various drug samples obtained from markets and drugstores. The bromine quantity in the drug samples was in agreement with those given by the producers.

1. Introduction

Bromine intoxication (Bromism) has been shown to cause many problems such as delirium psychomotor reduction, mental confusion, halucinations, poor concentration, headaches, irritability and depression.

Brominated substances are used in the manufacture of several pharmaceuticals including analgesics, sedatives, and antihistamines. Bromine is also used as an antibacterial agent in pools and hot tubs. Bromine compounds are also effective pesticides, used both as soil fumigants in agriculture, particularly fruit-growing, and as a fumigant to prevent pests from attacking stored grain and other produce. Some perfumes and pharmeceuticals also contain bromine. Brominated compounds are used as a water purifier/disinfectant in swimming pools and hot tubs. They are also used to control algae and bacterial growth in industrial processes [1,2].

Bromine is commonly used as a component of flame retardants. The major brominated compounds involved in flame retardants are tetrabromobisphenol A, vinyl bromide, and decabromodiphenyl ether. Hydrobromic acid reduces the reactions that occur between the fire and oxygen. Some pesticides contain bromine; for example methyl bromide fumigates soil and kills pests. It was reported that 35,000 metric tonnes of pesticides containing bromine attacked weeds, fungi and soil-borne diseases in 1991 [3].

Bromine can be determined by different techniques. For this purpose, gravimetric [4], spectrophotometric analysis [5], mass spectrometry (MS) [6,7], X-ray fluorescence spectrometry (XFS) [8,9], neutron activation analysis (NAA) [10,11], laser induced plasma spectrometry (LIPS) [12,13], laser-excited fluorescence spectroscopy (LEFS) [14], and capillary electrophoresis (CE) have been used [15]. One of the most important methods for the determination of bromide is the ion chromatography (IC) [16]. In addition, inductively coupled plasma mass spectrometry (ICP-MS) has been used for the determination of bromine and iodine in active pharmaceutical ingredients [17].

Direct determination of bromine by atomic absorption spectrometer (AAS) cannot be established because its resonance absorption line is located in the vacuum ultraviolet region around 149 nm [18]. However, some attempts have been made to determine bromine using line source AAS (LS-AAS) [19–23]. All these methods were based on the formation of a diatomic molecule in the flame or graphite furnace between bromine and a metal added to the sample and determination of bromine using a hollow cathode lamp (HCL) having an appropriate emission line overlapping with one of the very narrow rotational lines of the molecule.

However, spectral interference may occur upon coincidence of the emission line of the selected HCL line with the absorption line of other sample concomitants, which cannot be observed directly by LS-AAS. In addition, since the emission intensity selected from HCL is mostly a non-resonance line, it is weak causing relatively high noise. Thus, an ideal HCL may not always be found and the wavelength cannot be selected freely. The analysis is limited with the available wavelength of

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Table 1
The graphite furnace temperature program optimized for the determination of Br from MAS of SrBr at 651.0581 nm.

Step	Temperature, °C	Ramp time, s^{-1}	Hold time, °C s^{-1}	Gas flow, L min^{-1}
Drying	80	6	20	2.0
Drying	90	3	20	2.0
Drying	110	5	20	2.0
Pyrolysis	400	300	20	2.0
Pyrolysis	400	0	5	Stop
Molecule formation	2200	2700	5	Stop
Cleaning	2650	500	4	2.0

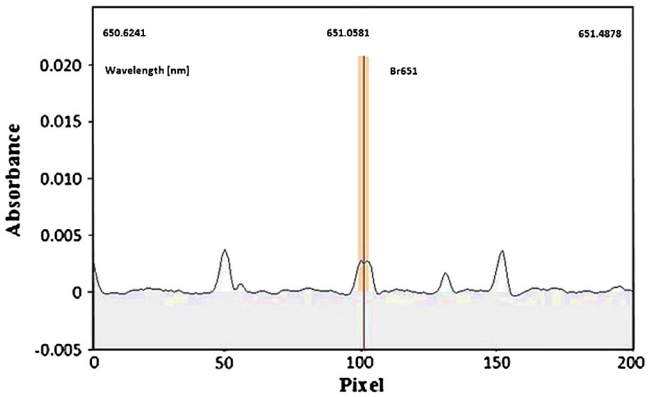

Fig. 1. The absorption spectrum obtained in the vicinity of 651.0581 nm molecular absorption line for SrBr (Sr: 60 μg; Br: 40 ng).

HCL. The concentration of bromine in real samples is generally low and consequently it is not effective in human life. In order to get low LOD, the sensitivity of diatomic molecules (i.e. absorption coefficients) should be high, the diatomic molecule formation yield should be high (bond dissociaton energy should be high) whereas the reproducibility should be reproducible (low standard deviation). The diatomic molecules formed between bromine and various metals are generally not stable enough, i.e. (bond dissociation energies are low). Therefore, the determination of bromine via diatomic molecules in LS AAS has not been successfully performed (at least as much as F and sulphur).

The drawbacks for HCL in LS-AAS do not occur with the use of high resolution continuum source AAS (HR-CS AAS). With this equipment, the absorption of any rotational line of diatomic molecules can be suitably measured exactly on the rotational line of the diatomic molecule to be used for quantification. Welz et al. extensively reviewed the determination of non-metals using high temperature by molecular absorption spectrometry in flames and furnaces [24,25].

There are only a few reports on bromine determination by HR-CS AAS using the molecular absorption of formed gaseous AlBr and CaBr [26,27]. Huang et al. [26] evaluated the molecular absorption of the metallic mono-bromides AlBr, CaBr, GaBr, InBr, MgBr, and SrBr, generated in a graphite furnace and AlBr, CaBr, and SrBr were found to be favorable. Huang succeeded in determining bromine levels in a graphite furnace, investigating the molecular absorption spectra of AlBr at 278.914 nm and of CaBr at 625.315 nm. Except for strong absorption bands of CaF around 625.3 nm, which interfered with the CaBr absorption, no spectral interference was observed for CaBr or AlBr measurements. Bromine was later successfully determined via CaBr again by high resolution continuum source electrothermal AAS (HR-CS-ET AAS) [27]. Both ionic and bonded concentration of the bromine in aqueous and organic solvents could be determined.

The aim of this study is to develop a new procedure for the determination of Br by HR-CS AAS using the molecular absorption line of SrBr formed in graphite furnace. The experimental parameters were optimized and the method was validated. The method was applied for the determination of bromine in wine and drug samples.

2. Experimental

2.1. Instrumentation

An Analytik Jena ContrAA 700 graphite furnace high resolution continuum source atomic absorption spectrophotometer equipped with MPE auto sampler (Analytik Jena, Jena, Germany) and a 300W xenon short-arc lamp (XBO 301, GLE, Berlin, Germany) was used for all measurements. The equipment has a double monochromator with a prism pre-monochromator and an echelle monochromator for high resolution. The resolution is about 1.5 pm per pixel at 200 nm. Measurements were carried out at 651.0581 nm of SrBr using integrated absorbance (peak volume selected absorbance, PVSA) summated over five pixels [28]. All measurements were performed using pyrolytically coated graphite tubes with integrated PIN platform (Analytik Jena Part No. 407-A81.025).

2.2. Reagents and solutions

In all dilutions a high-purity water (resistivity 18.2 MΩ cm) obtained by a TKA reverse osmosis and a TKA deionizer system (TKA Wasseraufbereitungsysteme GmbH, Niederelbert, Germany) was used. Inorganic acids and reagents were of analytical grade (HNO3, 65% (*w*/*w*), Merck, Darmstadt, Germany). The bromine standard was prepared from sodium bromide (Merck, Darmstadt, Germany). A stock solution of 10,000 mg L^{-1} strontium was prepared from strontium nitrate

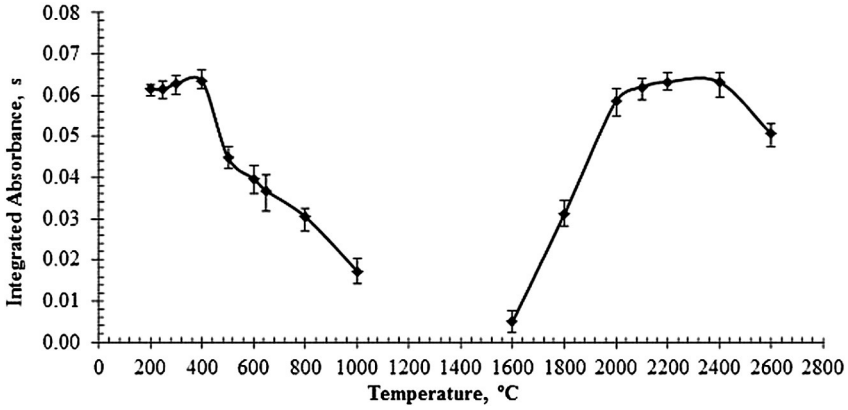

Fig. 2. Pyrolysis and vaporization curves for 40 ng of bromine in the presence of 60 μg of strontium according to the temperature program given in Table 1. Each point represents the mean of three measurements with standard deviations.