



Direct determination of bromine in plastic materials by means of solid sampling high-resolution continuum source graphite furnace molecular absorption spectrometry

M.R. Flórez, M. Resano *

Department of Analytical Chemistry, University of Zaragoza, Pedro Cerbuna 12, 50009 Zaragoza, Spain



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ABSTRACT

This work investigates the potential of high-resolution continuum source graphite furnace molecular absorption spectrometry for the direct determination of bromine in polymers, which could be interesting in view of the current regulations restricting the use of organobrominated compounds. The method developed is based on the addition of Ca (300 μg) and Pd (30 μg) to favor the formation of CaBr, which is monitored at the main molecular "lines" (rotational spectra) found in the vicinity of 625.315 nm.

It was found that accurate results could be obtained for all the samples investigated (polyethylene, polypropylene and acrylonitrile butadiene styrene certified reference materials) using any of the lines studied and constructing the calibration curve with aqueous standards. Furthermore, the combined use of the main four CaBr lines available in the spectral area simultaneously monitored permits to easily expand the linear range up to 2000 ng, provides a limit of detection of 1.8 ng (1.8 $\mu\text{g g}^{-1}$ for a mass of 1 mg) and further improves precision to values between 3–7% RSD. Overall, the method proposed seems suited for the fast and simple control of these types of samples (approximately 10 min for sample are required), circumventing the traditional problems associated with sample digestion (e.g., losses of volatile compounds), and providing sufficient sensitivity to easily comply with regulations.

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1. Introduction

The ubiquity of plastic materials and the huge amount of plastic waste generated in the modern world have led to a growing concern in terms of their environmental impact. In this context, special attention is being paid to a variety of different inorganic and organic additives incorporated to the structure of the polymers to enhance their qualities [1], and to their leakage to the environment [2].

Most polymeric materials, and particularly those aiming to be employed in the production of electronic devices, electrical appliances, clothing and furniture, are very often protected against ignition by the addition of the so-called brominated flame retardants (BFRs). The term BFRs encompass several organic compounds containing various atoms of bromine within their molecular structure, such as polybrominated diphenylethers (PBDEs), polybromobiphenyls (PBBs), tetrabromobisphenol A or hexabromocyclododecane. The function of all of these additives is to modify the behavior of the flammable host material against fire, inhibiting its combustion and significantly reducing the risk of fire-related damages. Their mechanism of action is based on the capability of the halogen to trap the oxidizing free radicals generated in the combustion, therefore, stopping the flame from propagating [3].

Unlike other types of polymer additives, flame-retardants are weakly bonded to the flammable materials, hence being highly prone to be released into the environment. Besides, two of the main characteristics of these organobrominated compounds, which make them suitable as BFRs for plastics, are their hydrophobic nature and their very long-term stability, both features being a serious problem when speaking about bioaccumulation in the ecosystem and the wildlife, categorizing them as persistent pollutants [3–5].

While new types of environmentally safe flame-retardants are investigated, regulations and restrictions on the use of BFRs are being implemented in order to lower their impact. Within the European Union, the 2002/95/EC directive on the "Restriction of the use of certain Hazardous Substances" (RoHS) restrains the use of PBBs and PBDEs in electrical and electronic equipment since July 2006 [6], and further regulations have set the maximum permitted limit for PBBs and PBDEs to 1000 mg kg^{-1} (0.1% w/w) [7]. It is essential then to have robust analytical methods for monitoring the presence of these compounds in raw plastic materials to ensure that this legal limit is met.

Several techniques have been employed to determine BFRs concentrations, either by means of speciation-based methods such as gas chromatography mass spectrometry [8] or liquid chromatography inductively coupled plasma mass spectrometry [9], or methods based in total Br determination such as X-Ray fluorescence spectrometry (XRF) [10], inductively coupled plasma mass spectrometry (ICP-MS) [11,12], ion exchange chromatography [13] and some others. However, most of the

* Corresponding author. Tel.: +34 976761634; fax: +34 976761290.
E-mail address: mresano@unizar.es (M. Resano).

applications found in the literature require extensive sample preparation in order to bring the sample into solution. These previous steps need to be thoroughly controlled in order to minimize the risk of Br losses due to its high volatility [14,15].

It can be mentioned that, owing to the large number of samples that need to be controlled on a daily basis due to the abovementioned regulations, the development of screening schemes becomes very appealing [16,17]. This means that analysis of all samples can be carried out first by means of a fast and simple method that is able to provide the total Br content, hopefully filtering out most samples, such that only in those cases in which the Br content is sufficiently high to be of concern, the application of a more time consuming method capable of providing information on the different Br species that are present in the sample becomes necessary [11].

In order to develop such fast and simple methodologies for total Br content in polymers, the use of solid sampling techniques seems promising, and it has also been demonstrated that they can be incorporated well into a screening scheme [17,18]. However, few approaches focusing on the direct determination of Br in polymers (or in solid materials in general) have been published to date.

Techniques that have been studied within this context are radio-frequency glow discharge-optical emission spectroscopy (rf-GD-OES) [19] or mass spectrometry (rf-GD-MS) [20,21], laser-induced plasma spectroscopy (LIPS) [22], laser ablation (LA)-ICP-MS [23], XRF [15,23,24], and neutron activation analysis (NAA) [25]. However, all of those techniques show some drawbacks to operate efficiently in the scheme proposed. High limits of detection (LOD) were reported in the cases of rf-GD-OES, rf-GD-MS and LIPS, while the main difficulty associated with XRF and LA-ICP-MS seems to be the limited number of reference materials available, which are typically required for calibration when using these (and most solid sampling) techniques [23,24,26]. Moreover, XRF results have been reported to be not only affected by the composition of the matrix but also by the form in which the sample is available (granulates or pucks) [24]. On the other hand, despite its detection power, NAA requires the availability of a nuclear reactor, and it is thus hardly accessible to routine and industrial laboratories.

A technique that has demonstrated potential for direct analysis of solid samples in general, and of polymers in particular, is graphite furnace atomic absorption spectrometry [27–29]. Several examples demonstrate the benefits of this technique for straightforward analysis of polymers using aqueous standards for calibration [30–33]. While traditionally this technique did not permit the direct monitoring of halogens, as their atomic lines were not accessible, the arrival of high-resolution continuum source instrumentation has opened new possibilities in this field making it possible to monitor not only atomic but also molecular “lines” [34,35]. In this regard, two recent articles by Huang et al. [36] and by Limburg and Einax [37] have demonstrated that it is feasible to determine Br using this approach, after sample dissolution. However, to the best of the authors’ knowledge, no report on the use of this technique for the direct determination of Br in solid samples has been published yet.

It is the goal of this paper to develop a simple, fast and sensitive enough to comply with regulation procedure for the direct determination of total Br content in plastic samples by means of high-resolution continuum source graphite furnace molecular absorption spectroscopy (HR CS GFMS). This method will be based in the formation of the diatomic molecule CaBr, which is stable in gas phase even at a relatively high temperature, and in the subsequent recording of its molecular spectra in the vicinity of 625.315 nm.

2. Experimental

2.1. Instrumentation

All the measurements in this work were carried out using a HR CS AAS instrument (ContrAA 700), which is commercially available from Analytik Jena AG (Jena, Germany). This instrument is equipped with

both flame and graphite furnace atomizers, in separate compartments, a Xenon short-arc lamp (GLE, Berlin, Germany) operating in “hot-spot” mode as the radiation source, a high-resolution double echelle monochromator (DEMON) and a linear CCD array detector with 588 pixels, 200 of which are used for monitoring the analytical signal and performing BG corrections, while the remainder are used for internal functions such as correcting for fluctuations in the lamp intensity. More details on this type of instrumentation can be found elsewhere [38,39].

The HR CS AAS instrument is equipped with a transversely heated graphite tube atomizer and an automated solid sampling accessory (SSA 600). This solid sampling device incorporates a microbalance with a readability of 1 µg. Pyrolytic graphite tubes and solid sampling graphite platforms were used in this work.

2.2. Samples and standards

2.2.1. Standards and reagents

Purified water was obtained from a Milli-Q system (Millipore, Billerica, USA). HNO₃ solutions were prepared from pro-analysis grade 14 mol L⁻¹ HNO₃ (Merck, Darmstadt, Germany).

Bromide aqueous solutions were prepared from commercially available 1 g L⁻¹ Br standard (CertiPUR Bromide standard solution traceable to SRM from NIST NaBr, Merck) by appropriate dilution with purified water. A 20 g L⁻¹ Ca solution was prepared from a solid CaCO₃ reagent (ACS reagent, ≥99.0%, powder, Sigma-Aldrich, St. Louis, USA) dissolved in 0.14 mol L⁻¹ HNO₃. Pd modifier was prepared from commercially available 10 g L⁻¹ single-element standard (as Pd(NO₃)₂, Merck) by appropriate dilution with 0.14 mol L⁻¹ HNO₃.

2.2.2. Samples

Six reference materials with a certified bromine content encompassing three different types of plastic materials were analyzed in order to validate the method developed. Polyethylene samples ERM-EC680 and ERM-EC681, as well as Polypropylene ERM-EC591, were purchased from the Institute for Reference Materials and Measurements (IRMM, Geel, Belgium), all of them being available in granules of approximately 10 mg weight. Polyethylene’s PE-H-11A and PE-L-11A were purchased from Modern Analytical Techniques (MAT) LLC (Hillsborough, USA), and were available as plastic discs with a diameter of approximately 31 mm and 13 mm thickness. Acrylonitrile butadiene styrene resin was purchased from the Federal Institute for Materials Research and Testing (BAM, Berlin, Germany) in a disc form with 40 mm diameter and 6 mm thickness. A list collecting details for each material tested can be found in Table 1.

2.3. Procedure for the determination of Br by SS HR CS GFMS

This method does not involve any sample pre-treatment beyond cutting each plastic material into fragments of appropriate mass (see Table 2) using a ceramic knife. The solid sampling device used allows for automatic weighing and transport of the samples to the furnace by means of a pair of tweezers. After first taring the empty sample platform, an appropriate amount of sample is deposited onto the platform to be weighed. Subsequently, all the required reagents – 10 µL of a Pd(NO₃)₂ solution (30 µg Pd), plus 15 µL of a CaCO₃ solution (300 µg Ca), both prepared in 0.14 mol L⁻¹ HNO₃ – are added, and the platform

Table 1
Certified reference materials (CRMs) analyzed in this work.

	Type of polymeric material	Certified Br content/mg kg ⁻¹
ERM-EC680	High density polyethylene	808 ± 19
ERM-EC681	High density polyethylene	98 ± 5
PE-H-11A	High density polyethylene	1100 ± 44
PE-L-11A	Low density polyethylene	500 ± 20
ERM-EC591	Polypropylene	2080 ± 70
BAM-H010	Acrylonitrile butadiene styrene	240 ± 21

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