



Contents lists available at ScienceDirect

Analytica Chimica Acta

journal homepage: [www.elsevier.com/locate/aca](http://www.elsevier.com/locate/aca)



# Simultaneous determination of bromine and chlorine in coal using electrothermal vaporization inductively coupled plasma mass spectrometry and direct solid sample analysis

Jefferson S. de Gois<sup>a</sup>, Éderson R. Pereira<sup>a</sup>, Bernhard Welz<sup>a,b,1</sup>, Daniel L.G. Borges<sup>a,b,1,\*</sup>

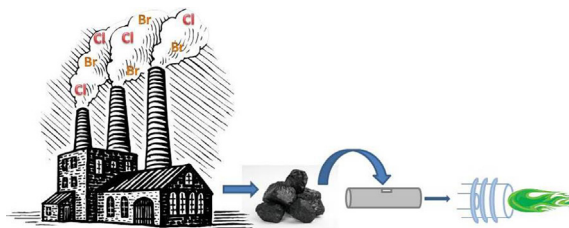
<sup>a</sup>Departamento de Química, Universidade Federal de Santa Catarina, 88040-970, Florianópolis, SC, Brazil

<sup>b</sup>INCT de Energia e Ambiente do CNPq, Brazil

## HIGHLIGHTS

- Direct analysis of coal samples is proposed for the first time for halogens determination using ICP-MS.
- Simultaneous determination of Br and Cl can be carried out.
- Sample treatment protocols are avoided, adding simplicity to the analytical procedure.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 22 July 2014

Received in revised form 11 September 2014

Accepted 15 September 2014

Available online xxx

### Keywords:

Direct solid sample analysis

Electrothermal vaporization

Halogen determination

Coal analysis

## ABSTRACT

A new method for the direct analysis of coal using electrothermal vaporization inductively coupled plasma mass spectrometry and direct solid sample analysis was developed, aiming at the determination of Br and Cl. The procedure does not require any significant sample pretreatment and allows simultaneous determination of both elements to be carried out, requiring small mass aliquots of sample (about 0.5 mg). All operating parameters, including carrier gas flow-rate and RF power, were optimized for maximum sensitivity. The use of modifiers/aerosol carriers (Pd, Pd + Al and Pd + Ca) was evaluated, and the mixture of Pd and Ca was chosen, allowing pyrolysis and vaporization temperatures of 700 °C and 1900 °C, respectively. Chlorine was accurately determined using calibration against solid standards, whereas Br could also be determined using calibration against aqueous standard solutions. The limits of quantification were 0.03  $\mu\text{g g}^{-1}$  for Br and 7  $\mu\text{g g}^{-1}$  for Cl, and no spectral interferences were observed.

© 2014 Elsevier B.V. All rights reserved.

## 1. Introduction

Chlorine is essential for humans, animals and plants, and is a precious commercial article since ancient times, as it was used, among other things, for the conservation of food. Bromine, in

contrast, has no known physiological function. Both elements, however, can also be highly toxic, depending on the compound in which they are present and their concentration [1]. These elements can be released to the environment by anthropogenic and natural processes, and they can be found in nature as polycyclic aromatic hydrocarbons (PAHs) [2], in a variety of organic compounds [3], in the molecular homoatomic form [4], as hydrogen halides and as oxides and salts [5,6]. Their presence in the atmosphere is normally regarded as hazardous due to their ability to react with  $\text{O}_3$  molecules [7]. In biological systems, halogens exert toxic effects that are similar to those of hazardous metals and metalloids, such as Hg and As [8].

\* Corresponding author at: Universidade Federal de Santa Catarina, CFM - Chemistry Department, Campus Universitario Trindade, 88040-970 Florianópolis, SC, Brazil. Tel.: +55 4837213611.

E-mail addresses: [daniel.borges@ufsc.br](mailto:daniel.borges@ufsc.br), [danqmc@yahoo.com](mailto:danqmc@yahoo.com) (D.L.G. Borges).

<sup>1</sup> [www.inct.cienam.ufba.br](http://www.inct.cienam.ufba.br).

Coal is a potential source of halogens due to the release of these elements to the atmosphere during combustion. The release of Br and Cl from coal is a serious concern, mainly because coal is, and probably will remain for quite some time, employed as a major source of energy in many countries [9]. The presence of these elements in coal, considering the increasing consumption of coal in the last decades, may represent a risk to the environment and consequently for living organisms [10,11].

Despite of the importance in monitoring halogens in coal, the determination of Br and Cl in these samples at trace levels is regarded as a complex analytical. There are only a few techniques available and the sample pre-treatment process that must be carefully carried out in order to avoid contamination and analyte loss [12]. Techniques such as ion chromatography and potentiometry using ion selective electrodes might be used in order to determine these elements, but these techniques require sample pretreatment before the analysis in order to release Br and Cl to an aqueous medium. Sample preparation introduces the risk of analyte loss by volatilization and the potential for sample contamination [13].

In general, the sample pretreatment for halogen determination can be carried out employing equipment such as pyrohydrolysis devices [14], microwave induced combustion [15], alkaline treatment [16] and digestion using pressurized vessels [17]. These techniques do not completely prevent problems related to contamination arising from impurities in the reagents, and the overall analytical process suffers from time-consuming steps that are inherent to these procedures. In addition, special apparatus and reagents are frequently required, and the preparation procedure typically dilutes the elements in the samples below the detection limits of many analytical instruments.

In order to avoid the problems related to sample pretreatment and also to determine trace levels of Br and Cl, direct solid sample (SS) analysis may be used with techniques that include high-resolution continuum source graphite furnace molecular absorption spectrometry (HR-CS GF MAS) [18], neutron activation analysis [19], X-ray fluorescence [20] and laser ablation coupled to inductively coupled plasma mass spectrometry (LA-ICP-MS) [21]. Direct solid sample analysis may also be carried out using electrothermal vaporization (ETV) coupled to ICP-MS, which leads to advantages such as reduced risk of interference due to matrix elimination in the pyrolysis step, greatly reduced risk of contamination as much less reagents are used, increased sensitivity and suitability as a simultaneous trace elemental analytical procedure [22].

Despite the potential use of SS-ETV-ICP-MS for halogen determination, this remains an unexploited area. The works related to SS-ETV-ICP-MS are limited to the determination of Cl in petroleum coke by Antes *et al.* [23] using a custom-made solid sampling device and the determination of I in botanical and biological samples by Resano *et al.* [24]. Both works demonstrated the feasibility of the determination of halogens with this technique. Given the high importance of Br and Cl determination in coal samples and the feasibility of its determination using SS-ETV-ICP-MS, the aim of this work was to develop an analytical method for Br and Cl determination in coal samples using direct solid sample analysis.

## 2. Experimental

### 2.1. Instrumentation

All experiments were carried out using an Elan 6000 inductively coupled plasma mass spectrometer equipped with an HGA-600 MS electrothermal vaporizer coupled to an auto sampler model AS-60 from PerkinElmer SCIEX (Thornhill, Canada). The cup-in-tube

technique described by Vollkopf *et al.* [25] was used for solid sampling experiments. The samples were weighed directly into a solid sampling glass capillary using a micro-balance model M2P (Sartorius, Göttingen, Germany) and transferred to pyrolytically-coated graphite cups from PerkinElmer (Norwalk, USA). The operating parameters of the ICP-MS instrument are listed in Table 1. Argon with a purity of 99.996% from White Martins (São Paulo, Brazil) was used as plasma, carrier and internal gas of the ETV.

A model ContraAA 600 high-resolution continuum source atomic absorption spectrometer (Analytik Jena AG, Jena, Germany) with a transversely heated graphite tube atomizer was employed for comparison. Pyrolytically-coated graphite tubes (Analytik Jena) were used in all experiments. The solid samples were weighed directly onto solid sampling platforms (Analytik Jena) using the M2P micro-balance. A manual solid sampling system SSA 6 (Analytik Jena) was used to insert the SS platforms into the graphite tube. For the determination of Br, the optimized pyrolysis and vaporization temperatures were 800 and 2200 °C, respectively, while for Cl determination the pyrolysis and vaporization temperatures were 600 °C and 2300 °C, respectively. The molecular absorption of CaBr molecule was measured at 625.315 nm, and the SrCl molecule was measured at 635.862 nm, both using integrated absorbance over three pixels (peak volume selected absorbance, PVSA,  $A_{\Sigma 3, \text{int}}$ ) [18].

### 2.2. Reagents, standards and samples

All reagents used were at least of analytical grade. Deionized water was obtained from a Milli-Q system (Millipore, Bedford, MA, USA) with a resistivity of 18.2 M $\Omega$  cm. Individual stock solutions containing each 1000 mg L<sup>-1</sup> Ca, Cl and Br were obtained from Quimilab (São Paulo, Brazil), Pd from Sigma-Aldrich (MO, USA) and Al, K, P, S and Sr from Spex (NJ, USA).

The coal certified reference materials (CRM) used were BCR-180 and BCR-182 from IRMM (Geel, Belgium), NIST 1630a and NIST 1632b from National Institute of Standards and Technology (Gaithersburg, MD, USA) and Sarm-19 from South Africa Bureau of Standards (Randburg, South Africa).

### 2.3. Procedures

Pyrolysis and vaporization temperatures of the ETV, the carrier gas flow rate and radio frequency power (RF) of the ICP-MS were optimized using the CRM BCR-182 and an aqueous solution containing Br and Cl. The modifiers studied were Pd and its corresponding mixtures with Ca and Al. In the latter cases, 200  $\mu$ g Pd was deposited into the sampling cups (10 injections of 20  $\mu$ L of a solution containing 1 g L<sup>-1</sup>) whereas Ca and Al were pre-reduced using 20  $\mu$ L of a solution containing 1 g L<sup>-1</sup> and applying the drying temperature of 100 °C and a pyrolysis temperature of 1000 °C before the addition of the samples [24]. The amount of deposited

**Table 1**  
Operating parameters of ICP-MS.

Sampling/skimmer cones	Pt	
Radio frequency power	1200 W	
Signal measurement	Peak hopping	
Autolens	On	
Detector voltage	Pulse 1500 V	Analogue: -2500
Dwell time	12 ms	
Readings/replicate	500	
Gas flow-rates		
	Main	15.0 L min <sup>-1</sup>
	Auxiliary	1.2 L min <sup>-1</sup>
	Carrier	1.1 L min <sup>-1</sup>

Download English Version:

<https://daneshyari.com/en/article/7555550>

Download Persian Version:

<https://daneshyari.com/article/7555550>

[Daneshyari.com](https://daneshyari.com)