Spectrochimica Acta Part B xxx (2014) xxx–xxx

Contents lists available at ScienceDirect

Spectrochimica Acta Part B

journal homepage: www.elsevier.com/locate/sab

Application of direct solid sample analysis for the determination of chlorine in biological materials using electrothermal vaporization inductively coupled plasma mass spectrometry

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ARTICLE INFO

Article history:
Received 15 May 2014
Accepted 6 September 2014
Available online xxxx

Keywords:
Chlorine determination
Direct solid sample analysis
ICP-MS
Electrothermal vaporization
High-resolution continuum source molecular absorption spectrometry

ABSTRACT

This work describes a methodology developed to carry out Cl determination in biological materials using electrothermal vaporization inductively coupled plasma mass spectrometry and direct solid sample analysis. The solid samples were directly weighed into graphite 'cups' and inserted into the graphite furnace. The RF power and the carrier gas flow rate were optimized at 1300 W and 0.7 L min^{-1}, respectively. Calibration could be carried out using aqueous standard solutions with pre-dried modifiers (Pd + Nd or Pd + Ca) or using solid certified reference materials with the same pre-dried modifiers or without the use of modifiers. The limit of quantification was determined as 5 μg g^{-1} under optimized conditions and the Cl concentration was determined in five certified reference materials with certified concentrations for Cl, in addition to three certified reference materials, for which certified values for Cl were unavailable; in the latter case, the results were compared with those obtained using high-resolution continuum source molecular absorption spectrometry. Good agreement at a 95% statistical confidence level was achieved between determined and certified or reference values.
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1. Introduction

Chlorine is regularly produced by industries worldwide and has applications that range from purification of drinking water to the production of bleached paper, plastics, solvents and pharmaceuticals [1]. Given the widespread use of Cl, exposition to the element occurs frequently due to manipulation of products, transportation or even due to environmental contamination [1,2]. According to the Agency for Toxic Substances & Disease Registry (ATSDR), exposure to Cl may affect the respiratory tract and eyes, causing acute irritation and triggering inflammatory processes [3].

Monitoring of Cl in biological and botanical materials is characterized by difficulties that extend from sample pretreatment until the final instrumental determination [4]. Sample preparation must be carefully conducted in order to avoid contamination and analyte loss; acid digestion, which is most frequently used as a sample pre-treatment procedure, is not recommended due to the formation of HCl, which can be lost by volatilization. Alternative strategies have been employed such as pyrohydrolysis and combustion techniques using customized combustion flasks, the Schöniger combustion flask, microwave-induced combustion and direct sample analysis [4–6].

Instrumental determination frequently requires techniques such as ion chromatography [7], potentiometric analysis using ion selective electrodes (ISE) [8], instrumental neutron activation analysis [9] or X-ray fluorescence spectrometry [4]. The main difficulty associated to instrumental Cl determination resides in the poor sensitivity that characterizes the majority of the aforementioned analytical techniques, in addition to considerable risk of interference, low analytical throughput and, on occasions, high analytical cost [7–9]. Spectrometric techniques such as inductively coupled plasma mass spectrometry (ICP-MS) [5,6] and high-resolution molecular absorption spectrometry (HR-CS MAS) [10] may also be employed to determine Cl in a variety of samples, although the application of these techniques to halogens determination is restricted to a few examples given in the literature.

Considering the inherently high sensitivity and extended linear range [11], ICP-MS appears as a suitable technique for the quantitative determination of halogens. However, the quantification of this group of elements may be negatively affected by their high ionization energies, as well as severe memory effect that is frequently associated to sample introduction using nebulizers [4–6]. In order to overcome these difficulties, alternative sample introduction devices, such as laser ablation [12,13] and other direct solid sample analysis systems using lab-made vaporization systems [6] have been employed.

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http://dx.doi.org/10.1016/j.sab.2014.09.005
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Please cite this article as: J.S. de Gois, et al., Application of direct solid sample analysis for the determination of chlorine in biological materials using electrothermal vaporiz..., Spectrochim. Acta Part B (2014), http://dx.doi.org/10.1016/j.sab.2014.09.005

Application of direct solid sample analysis using electrothermal vaporization (SS-ETV) ICP-MS for Cl determination has been described only twice, in a work by Yan et al. [5] in aqueous standards and by Antes et al. [6]. In the latter case, the authors applied standard addition calibration to determine Cl in petroleum coke samples using a lab-made SS-ETV device, based on enclosure of a high-power lamp in a glass chamber. Advantages such as minimum sample pretreatment and improved sensitivity and sample throughput are typically associated to SS-based procedures [14–16]. Nonetheless, it is apparent that application of SS-ETV-ICP-MS for halogen determination remains as an unexploited field, in spite of its potential to solve complex analytical situations.

Hence, the goal of this work is to describe the direct determination of Cl in biological materials using SS-ETV-ICP-MS, including a systematic investigation of calibration protocols.

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 and an AS-60 autosampler (Perkin-Elmer SCIEX, Thornhill, Canada). Platinum sampler and skimmer cones were used. The ICP was operated at a 1300 W RF power, and the gas flow rates were set at 0.7 L min^{-1} (carrier gas), 1.2 L min^{-1} (auxiliary gas) and 15.0 L min^{-1} (main gas). A dwell time of 50 ms was adopted, and measurements were carried out in 'peak hopping' mode with 'autolens'. The 'cup-in-tube' technique described by Völlkopf et al. [15] was used to insert solid samples directly into the graphite furnace. In this technique, the sampling hole of the pyrolytically coated graphite tube is enlarged so that the sampling 'cup' could be inserted. The solid sampling cup is made from high-density electrographite and coated with pyrolytic graphite with approximate dimensions of 7.0 × 4.5 × 6.8 mm, and it supports a maximum of 160 mg of sample [15]. The solid sampling cups, loaded with the sample, were inserted into the graphite tube and removed after completion of the analysis using a special tool. The temperature program adopted for SS-ETV-ICP-MS analysis is shown in Table 1. The monitored isotope was ^{35}Cl.

The solid samples were weighed using a micro-balance model M2P (Sartorius, Göttingen, Germany). Argon with a purity of 99.996% (White Martins, São Paulo, Brazil) was used as plasma, carrier and internal gas of the ETV.

In order to provide comparative results for samples with unknown Cl concentration, a ContrAA 600 high-resolution continuum source atomic absorption spectrometer (Analytik Jena AG, Jena, Germany) with a transversely heated graphite tube atomizer was used. The SrCl molecule was used for quantitative measurements of Cl at 635.863 nm, using integrated absorbance of three pixels (peak volume selected absorbance, PVSA, $A_{\sum 3,int}$). Pyrolytically coated graphite tubes (Analytik Jena) were used in all experiments. The solid samples were weighed directly onto solid sampling platforms (Analytik Jena) using an M2P micro balance. A manual solid sampling system, SSA 6 (Analytik Jena), was used to insert the SS platforms into the graphite tube. The pyrolysis and vaporization temperatures used for HR-CS MAS analysis were optimized as 600 °C and 2300 °C, respectively.

Table 1
Temperature program adopted for the determination of Cl in biological samples using direct solid analysis and ETV-ICP-MS.

Step	Temperature/°C	Ramp time/s	Hold time/s
Cleanout	2300	5	10
Cooling	20	5	15
Drying[a]	100	3	15
Pre-reduction of modifier	1000	5	10
Cooling[b]	20	10	60
Drying	100	3	10
Pyrolysis	200[c]/600[d]/700[e]	5	10
Cooling	20	2	5
Vaporization	2000[c]/1500[d]/1800[e]	2	18

[a] Modifier injected on this step.
[b] Sample inserted on this step.
[c] Temperatures adopted for analyses without modifier.
[d] Temperatures adopted upon the use of pre-dried Pd + Nd modifiers.
[e] Temperatures adopted upon the use of pre-dried Pd + Ca modifiers.

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 MΩ cm. Individual stock standard solutions containing 1000 mg L^{-1} each Ca or Cl were obtained from Quimilab (São Paulo, Brazil). A 1000 mg L^{-1} Pd stock standard solution from Sigma-Aldrich (Missouri, USA), a 1000 mg L^{-1} Nd solution (Spex, New Jersey, USA) and a 1000 mg L^{-1} Zr solution (Fluka, Buchs, Switzerland) were used as modifiers. Stock standard modifier solutions were prepared in 10% HNO_3. A 1000 mg L^{-1} Sr solution was prepared from high-purity $SrCO_3$ (Vetec, Duque de Caxias, Brazil). The sample solutions and modifiers were automatically inserted into the graphite furnace in 20 μL aliquots using the autosampler.

The following certified reference materials (CRM) were used: Corn Bran (NIST SRM 8433), Bovine Muscle Powder (NIST SRM 8414), Whole Egg Powder (NIST SRM 8415), Wheat Flour (NIST SRM 1567a), Bovine Liver (NIST SRM 1577b) and Non-Fat Milk Powder (NIST SRM 1549) all from the National Institute of Standards and Technology (Gaithersburg, USA); Pig Kidney (BCR 186) and Mussel Tissue (BCR 278R), both from IRMM (Geel, Belgium) and Beef Liver (NCS-ZC 71001) from NACIS (Beijing, China).

2.3. Analytical procedure

Carrier gas flow rate, radio frequency (RF) power and pyrolysis and vaporization temperatures (Tp and Tv, respectively) were optimized using the CRM NIST 8414 for direct solid analysis studies. This sample was chosen due to the fact that the certified Cl concentration is intermediate among those from the other CRM analyzed. A 50 mg L^{-1} Cl solution was also used to investigate the experimental parameters. The use of modifiers was evaluated by pipetting Pd and the mixture of Ca + Pd and Nd + Pd as acid aqueous solutions directly onto the solid samples. For comparison, the modifiers were also pre-dried in the sampling cup, prior to insertion of the solid samples or aqueous standards. For the studies involving aqueous solutions, 10 μL aliquots of each modifier were added together with the samples. Alternatively, the sampling cup was pre-treated with a total of 200 μg Pd as permanent modifier (10 injections of 20 μL of the stock solution). Calcium and Nd were then pre-reduced using a Tp of 1000 °C [18], before the addition of each sample. Chlorine quantification in CRM was carried out using calibration against aqueous or solid standards using Pd + Nd or Pd + Ca pre-dried as modifiers and also without modifier using a solid standard. The calibration range extended from 0.2 to 3.0 μg Cl. All measurements were carried out monitoring the ^{35}Cl isotope.

In order to establish a comparison of the results with those from an alternative technique, the biological samples were directly weighed (approximately 0.05 to 0.5 mg) onto SS platforms, previously treated with a total of 400 μg Zr (10 injections of 40 μL containing 40 μg of the modifier) as a permanent chemical modifier. Subsequently, 10 μL (2% *m*/*v*) of the molecule-forming Sr solution (as $SrCO_3$) was pipetted onto the biological samples and introduced into the graphite furnace to be submitted to the temperature program, aiming at the determination using high-resolution continuum source molecular absorption spectrometry (HR-CS GF MAS).

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