Talanta 147 (2016) 76–81

Contents lists available at ScienceDirect

Talanta

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

Feasibility of halogen determination in noncombustible inorganic matrices by ion chromatography after a novel volatilization method using microwave-induced combustion

Rodrigo M. Pereira [a], Vanize C. Costa [a], Carla A. Hartwig [a], Rochele S. Picoloto [b], Erico M.M. Flores [b], Fabio A. Duarte [b], Marcia F. Mesko [a,*]

[a] Centro de Ciências Químicas, Farmacêuticas e de Alimentos, Universidade Federal de Pelotas, 96160-000 Pelotas, RS, Brazil
[b] Departamento de Química, Universidade Federal de Santa Maria, 97105-900 Santa Maria, RS, Brazil

ARTICLE INFO

Article history:
Received 3 June 2015
Received in revised form
10 September 2015
Accepted 11 September 2015
Available online 13 September 2015

Keywords:
Chlorine determination
Fluorine determination
Cement analysis
Sample preparation
Volatilization
Microwave-induced combustion

ABSTRACT

A microwave-induced combustion (MIC) system based on the volatilization process was applied for subsequent halogen determination from noncombustible inorganic matrices. Portland cement samples were selected to demonstrate the feasibility of the proposed method, allowing the subsequent determination of Cl and F by ion chromatography (IC). Samples were mixed with high-purity microcrystalline cellulose, wrapped with a polyethylene film and combusted in quartz closed vessels pressurized with oxygen (20 bar). Water and NH_4OH (10, 25 or 50 mmol L^{-1}) were evaluated for Cl and F absorption, but water was selected, using 5 min of reflux after volatilization. Final solutions were also suitable for analysis by pontentiometry with ion-selective electrode (ISE) for both analytes, and no difference was found when comparing the results with IC. The accuracy of the proposed method for Cl was evaluated by analysis of certified reference materials (CRMs), and agreement with certified values ranged from 98% to 103%. Results were also compared to those using the procedure recommended by the American Society of Testing and Materials (ASTM) for the determination of total chlorides (C114-13), and no difference was found. Volatilization by MIC using a mixture of cement, cellulose and a biological CRM was carried out in order to evaluate the accuracy for F, and recovery was about 96%. The proposed method allowed suitable limits of detection for Cl and F by IC (99 and 18 mg kg^{-1}, respectively) for routine analysis of cement. Using the proposed method, a relatively low standard deviation (< 7%), high throughput (up to eight samples can be processed in less than 30 min) and lower generation of laboratory effluents, when compared to the ASTM method, were obtained. Therefore, the method for volatilization of Cl and F by MIC and subsequent determination by IC can be proposed as a suitable alternative for cement analysis.

1. Introduction

Trace element determination in inorganic matrices is still a challenge, especially because these samples are generally difficult to digest, even using concentrated acids and pressurized systems. Analytical techniques available for the determination of trace elements require analytes in a solution compatible with the analytical instrument. In this sense, a suitable sample preparation method is crucial to obtain reliable results. Furthermore, when the purpose is the determination of halogens, the difficulties increase, considering that these elements are prone to losses by volatilization. On the other hand, some halogens (such as Cl and F) are present as ubiquitous elements that can increase the risk of contamination, resulting in inaccurate results. Moreover, sample preparation methods can be time consuming as well as the major source of errors mainly for further halogen determination [1].

In spite of the difficulties in the sample preparation step for inorganic matrices, such as cement, and subsequent halogen determination, there are some methods described in the literature for this purpose, such as fusion [2,3], extraction [4,5], slurries [6,7] or even volatilization by pyrolysis [8] or pyrohydrolysis [9–11]. In general, these methods are time consuming and prone to contamination, considering the requirement of many reagents and a

Abbreviations: ANOVA, Analysis of variance; ASTM, American Society for Testing and Materials; CRM, certified reference material; FLX, Fluxana; LIBS, laser-induced breakdown spectroscopy; MIC, microwave-induced combustion; NIST, National Institute of Standards and Technology; NRCC, National Research Council Canada; PE, polyethylene; TISAB, total ionic strength adjustment buffer; TXRF, total reflection X-ray fluorescence

* Corresponding author.
E-mail address: marcia.mesko@pq.cnpq.br (M.F. Mesko).

http://dx.doi.org/10.1016/j.talanta.2015.09.031
0039-9140/

relatively high number of stages (e.g., fusion). In addition, losses of halogens by volatilization can be observed when acidic solutions are used, even working with closed systems [1]. It is important to note that, in some cases, sample preparation can not provide suitable solutions for analytical techniques that are often used for halogen determination, such as spectrophotometry [10], ion chromatography (IC) [11,12], potentiometry with ion-selective electrode (ISE) [13,14] and inductively coupled plasma mass spectrometry (ICP-MS) [12,15]. Moreover, most of the sample preparation methods for further halogen determination in inorganic matrices usually present low throughput, which is a crucial parameter for routine analysis.

Alternatively, the direct determination of halogens can be performed using techniques that allow solid analysis, such as total reflection X-ray fluorescence spectrometry (TXRF) [16,17] and laser-induced breakdown spectroscopy (LIBS) [18,19]. However, although these techniques present a good performance for some samples/analytes and do not require extensive sample preparation steps, the limit of detection (LOD) for some elements can not be suitable. In addition, these techniques also have some drawbacks, such as a lack of standards for calibration and requiring a very homogeneous sample, which can be considered their main limitation, affecting the precision and accuracy of results [10,20,21]. Therefore, the development of alternative strategies allowing the determination of halogens in inorganic samples is still important.

The analytes separation from the sample matrix by volatilization can be a feasible strategy for further halogen determination. Pyrolysis and pyrohydrolysis are examples of methods that allow the separation of volatile elements from matrices by using high temperature (500–1200 °C) [8–11]. However, these methods allow the treatment of one sample per run, which can be unfeasible if a high number of samples must be processed.

Microwave-induced combustion (MIC) is a method that is based on sample burning in oxygen-pressurized closed vessels, followed by analyte absorption in a suitable solution. This system also allows the application of a reflux step, which improves absorption and, consequently, ensures quantitative results. Due to these advantages, this method was applied for digestion of combustible samples for further halogen determination, such as bovine liver, corn starch, milk powder and wheat flour [22,23], shrimp [24], animal feed [25], carbon nanotubes [26], graphite [27], coal [28], fluoropolymers [29] and high-purity magnesium [30], among others. However, MIC has mainly been used for the digestion of samples containing considerable amounts of organic matter, i.e., only combustible samples can be directly and efficiently decomposed. In spite of this limitation, MIC has been recently applied for soil samples in order to determine volatile elements (As, Cd, Hg and Pb) [31,32], using microcrystalline cellulose as an aid for combustion. An important advantage is the possibility of analyte separation from the sample matrix, which result in lower interferences during the determination step.

In this sense, the aim of the present work was to demonstrate for the first time the feasibility of MIC for halogen volatilization from noncombustible inorganic matrices and further determination by IC. Portland cement was selected to demonstrate the applicability of this method, considering that cement is widely used in concrete preparation. Chlorine and F are examples of halogens that must be monitored in cement, taking into account that these elements at high concentration may increase the corrosion of steel structures of reinforced concrete. In this way, the control of these elements is essential to ensure the quality of cement and its related products. Ion chromatography with a conductivity detector was selected due to its multielement capability and suitable LODs for Cl and F. Microcrystalline cellulose and graphite were evaluated as volatilization aids, and the type and concentration of absorbing solutions were also studied. Accuracy was evaluated by analysis of certified reference materials (CRMs). Additionally, in order to compare the results obtained by IC, ISE was also used for the analytes determination. A comparison with official method C114-13 from the American Society for Testing and Materials (ASTM) for Cl determination in cement [33] was also performed.

2. Experimental

2.1. Instrumentation

Samples of Portland cement were submitted to the proposed volatilization method by MIC using a microwave oven (Multiwave 3000 microwave sample preparation system, Anton Paar, Austria) equipped with up to eight high-pressure quartz vessels with internal volume of 80 mL. The maximum values for operational temperature and pressure were 280 °C and 80 bar, respectively. Holders were manufactured in quartz and used to insert the sample inside the quartz vessel. Cement samples were dried using a conventional oven (model 400/2ND, De Leo, Brazil).

Chlorine and F determination was carried out using an ion chromatograph (model IC 2.861.0020, Metrohm, Switzerland). The parameters for Cl and F determination by IC are shown in Table 1, which were adapted from previous works [25,28]. Additionally, analytes determination was performed using a potentiometer (model HI 3221, Hanna Instruments, USA) equipped with electrods for Cl (model HI 4107, Hanna Instruments) and for F (model HI 4110, Hanna Instruments).

2.2. Reagents and samples

All solutions and dilutions were prepared in ultrapure water (18 MΩ cm) obtained from a purification system (Mega Up, Megapurity, South Korea), and all reagents used in this study were of analytical grade or higher purity.

Ammonium hydroxide solutions were evaluated as an absorption solution in the MIC method, and these solutions were prepared from 27% NH_4OH (Synth, Brazil). An ammonium nitrate solution (6 mol L^{-1}), which was used as a combustion igniter, was prepared by dissolving the solid reagent (Merck, Germany) in water. Pharmaceutical grade microcrystalline cellulose and ultrapure graphite fine powder (99.99%, Merck) were used as volatilization aids. Graphite was previously purified in a microwave oven (Multiwave 3000) with 10% (v/v) HNO_3 solution (1400 W of power for 30 min and 0 W for 20 min for cooling). The microcrystalline cellulose was purified by immersion in 10% (v/v) HNO_3 solution for 24 h, washed with ultrapure water and dried in a class 100 laminar flow-bench (CSLH-12, Veco, Brazil).

Small discs of filter paper (15 mm diameter, 12 mg) with low ash content (Black Ribbon Ashless, Schleicher & Schuell GmbH, Germany) were used as an aid for the combustion/volatilization

Table 1
Parameters used for the determination of chloride and fluoride by IC.

Parameters	Conditions
Column	Anion-exchange, Metrosep A Supp 5 (polyvinylalcohol with quaternary ammonium groups, 250 mm × 4 mm i.d.)
Guard column	Metrosep A Supp 4/5 Guard (polyvinylalcohol with quaternary ammonium groups, 5 mm × 4 mm i.d.)
Eluent	3.2 mmol L^{-1} Na_2CO_3 + 1.0 mmol L^{-1} $NaHCO_3$ (pH 10.5)
Eluent flow rate	0.7 mL min^{-1}
Injection volume	20 μL
Suppressor	Chemical type
Detection	Conductivity
Determination mode	Peak-area