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Talanta

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Simultaneous determination of iron and nickel in fluoropolymers by solid sampling high-resolution continuum source graphite furnace atomic absorption spectrometry



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ARTICLE INFO

Article history:

Received 15 May 2016

Received in revised form

18 July 2016

Accepted 21 July 2016

Available online 22 July 2016

Keywords:

Fluoropolymer

HR-CS GF AAS

Solid sampling

Iron

Nickel

Simultaneous determination

ABSTRACT

This paper reports the development of a method of simultaneous determination of iron and nickel in fluoropolymers by high-resolution continuum source graphite furnace atomic absorption spectrometry (HR-CS GF AAS) with direct solid sampling. In order to carry out simultaneous measurements, both the main resonance line of nickel (232.003 nm) and the adjacent secondary line of iron (232.036 nm) were monitored in the same spectral window. The proposed method was optimized with a perfluoroalkoxy (PFA) sample and was applied to the determination of iron and nickel in fluorinated ethylene propylene (FEP) and modified polytetrafluoroethylene (PTFE-TFM) samples. Pyrolysis and atomization temperatures, as well as the use of Pd and H₂ (during pyrolysis) as chemical modifiers, were carefully investigated. Compromise temperatures for pyrolysis and atomization of both analytes were achieved at 800 and 2300 °C, respectively, using only 0.5 L min⁻¹ H₂ as chemical modifier during pyrolysis. Calibration curves were performed with aqueous standards by using a single solution which contained both analytes. Limits of detection were 221 and 9.6 ng g⁻¹ for iron and nickel, respectively. Analyte concentrations in all samples ranged from 3.53 to 12.4 μg g⁻¹ for iron and from 37 to 78 ng g⁻¹ for nickel, with relative standard deviation less than 19%. Accuracy was evaluated by comparing these results with those obtained by inductively coupled plasma mass spectrometry after sample digestion by microwave-induced combustion and no significant statistical difference was observed.

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1. Introduction

Fluoropolymers have been considered a special group among polymeric materials due to their specific characteristics. Polytetrafluoroethylene (PTFE), the first fluoropolymer with significant industrial applications, was synthesized by Planket in 1938 [1]. Thenceforward, several perfluorinated materials derived from PTFE, such as fluorinated ethylene propylene (FEP), polyvinylidene fluoride (PVDF), modified polytetrafluoroethylene (PTFE-TFM) and perfluoroalkoxy (PFA), have been developed [2]. The main advantages of fluoropolymers comprise their inertness, high resistance to solvents and aggressive chemicals, ability to be molded in several shapes, thermal stability and excellent dielectric constants. All characteristics allow their application to several fields of industry, such as chemical, automotive, communication, electrical,

electronic and medical ones. In addition, fluoropolymers have also been characterized by providing high levels of purity, a fact that, combined with the previously described properties, makes them interesting for different industrial applications. A well-known application of fluoropolymers for analytical chemists is its use in the production of digestion flasks for conventional or microwave heating. However, careful monitoring of inorganic contaminants (e.g., iron and nickel) in this raw material is mandatory to avoid contamination during sample digestion for analytical purposes [2,3].

The Semiconductor Equipment and Materials International (SEMI) has established guidelines for the control of metallic impurities in different polymeric materials, including PTFE, PVDF and PFA. According to the SEMI F48-0600 protocol [4], the determination of trace elements should be carried out preferably by inductively coupled plasma mass spectrometry (ICP-MS) due to their high sensitivity and multielemental capability. However, due to chemical inertness and low levels of contaminants (ng g⁻¹ range

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or lower), elemental determination in fluoropolymers has still been a challenge.

A few studies of sample preparation of fluoropolymers for subsequent determination of trace elements have been published [5–8]. According to the literature, sample preparation for fluoropolymers can be carried out by dry ashing, microwave-assisted digestion (MAD) and combustion in closed vessels. In the method of dry ashing, the sample is placed in a platinum or quartz crucible and heated by a muffle furnace. However, the use of high temperatures in open systems leads to poor recoveries, mainly of volatile elements and by in situ formation of volatile halogenides [6]. Likewise, digestion in closed vessels (e.g., MAD) cannot provide efficient digestion, especially of fluoropolymers, due to the previously described properties, mainly their inertness [8].

As an alternative for fluoropolymer digestion, combustion methods have been developed and resulted in efficient digestion, mainly due to the high temperatures achieved (up to 1400 °C) during combustion [5,6]. Different combustion systems, such as a commercial system of microwave-induced combustion (MIC), have been proposed [6,8] and applied to fluoropolymer digestion, as well as other matrices [5,9–11]. Taking into account the inertness of fluoropolymers and the high temperatures reached by combustion methods, they are considered more efficient when a solution is required for analyte detection [5]. However, considering the high purity of fluoropolymers, even high sensitivity techniques (e.g., ICP-MS) do not provide suitable limits of detection (LOD) for the analysis of digests. Therefore, a solid sampling (SS) approach is an excellent option for the determination of impurity at low levels and avoids sample preparation [12].

Atomic spectrometry techniques combined with solid sampling has some advantages, such as low risk of contamination and analyte losses, low LOD (avoiding sample dilution), low sample mass, high speed of analysis and the avoidance of corrosive and hazardous reagents [13,14]. Considering the possibility of coupling SS systems, some detectors, such as ICP-MS, inductively coupled plasma optical emission spectrometry (ICP OES) and graphite furnace atomic absorption spectrometry (GF AAS) are the preferred ones and, in most cases, the commercially available ones [7,13]. The main advantage of plasma-based techniques over AAS techniques is the multielemental capability. However, detectors based on AAS are less prone to interferences and more robust [13]. The analysis of polymeric materials by SS-GF AAS [12,15] and by solid sampling high-resolution continuum source graphite furnace atomic absorption spectrometry (SS-HR-CS GF AAS) [16–19] has been widely described for many types of polymers. However, the determination of trace elements in fluoropolymers by using AAS techniques is scarce in the literature. Other solid sampling techniques, such as laser ablation inductively plasma mass spectrometry (LA-ICP-MS) [20] and X-ray fluorescence spectrometry (XRF), have been used for the direct analysis of polymers [21]. However, calibration of LA-ICP-MS has been a challenge and there are no studies of fluoropolymer analysis. Although spectral interferences in AAS techniques are less pronounced than plasma-based ones, the employment of HR-CS GF AAS has been useful to the direct analysis of solid samples [22]. One of the well-known advantages of HR-CS AAS instruments is that the charge-coupled device (CCD) array detector (with 200 pixels) allows the simultaneous measurement of more than one element per run. In multielemental analysis, the analytes need to have absorption lines (main and/or secondary) within the monitored spectral interval. The main requirements for simultaneous determination by HR-CS GF AAS are two suitable lines in the same spectral window, suitable sensitivity of all analytes and similar temperatures for pyrolysis and atomization of analytes [23–25]. Among the potential inorganic contaminants to be investigated in fluoropolymers, iron and nickel have similar volatilities (boiling temperature are 2861

and 2913 °C, respectively). In this case, the main resonance line for nickel (232.003 nm) can be monitored close to the secondary line of iron (232.036 nm). Thus, this study reports the development of a simple and fast method for simultaneous determination of iron and nickel in fluoropolymer samples by SS-HR-CS GF AAS. Results were compared with those obtained by ICP-MS and ICP OES after MIC digestion.

2. Experimental

2.1. Instrumentation

The determination of iron and nickel was carried out by a high-resolution continuum source atomic absorption spectrometer (model ContrAA 700, Analytik Jena, Jena, Germany), equipped with a manual solid sampling system (model SSA 6, Analytik Jena) and a transversely heated graphite tube atomizer. Pyrolytic graphite tubes (without dosing hole) and platforms for solid sampling were used. A Xe short-arc lamp (GLE, Berlin, Germany) in “hot-spot” mode was used as radiation source. A linear CCD array detector with 588 pixels (200 used for analytical purposes and the remaining, for internal functions) was also used. Samples were weighed by a microbalance (model M2P, Sartorius, Göttingen, Germany) with precision of 0.001 mg.

In order to compare results, samples were digested by MIC [5] with a microwave sample preparation system (model Multiwave 3000[®], Anton Paar, Graz, Austria), equipped with up to eight high-pressure quartz vessels with 80 mL of internal volume (maximum pressure and temperature were 80 bar and 280 °C, respectively). Samples were ground by a cryogenic mill (model 6750, Spex CertiPrep, Metuchen, USA) and pressed as pellets by a hydraulic press (Specac, Orpington, UK).

After digestion by MIC, iron and nickel were determined by an inductively coupled plasma mass spectrometer (model Elan DRC II, Perkin-Elmer Sciex, Thornhill, Canada) equipped with an ultrasonic nebulizer (model U6000AT+, CETAC Technologies, USA). Instrumental conditions for iron and nickel determination by ICP-MS were adjusted according to the manufacturer's recommendations whereas the radiofrequency (RF) power was set at 1300 W. Besides, plasma, auxiliary and nebulizer gas flow rates were set at 15, 1.2 and 1.15 L min⁻¹, respectively. Although ⁵⁷Fe and ⁶⁰Ni are not the most abundant isotopes of iron and nickel, the use of an ultrasonic nebulizer yielded good results for these elements, since it was operated in the following conditions: heating temperature was 140 °C, cooling temperature was –5 °C and sample flow rate was 2.0 mL min⁻¹.

Analytes were also determined by ICP OES (model Spectro Ciros CCD, Spectro Analytical Instruments, Kleve, Germany), which was equipped with a cross-flow nebulizer and a Scott double-pass spray chamber. Iron and nickel were determined at 238.204 and 231.604 nm, respectively. The RF power was set at 1400 W and plasma gas flow rates were set at 12, 1.0 and 1.00 L min⁻¹ for main, auxiliary and nebulizer gases, respectively. Digestion efficiency (expressed as residual carbon content - RCC) was calculated after carbon determination by the same ICP OES instrument in conditions described by a previous study [26]. Argon (99.996%, White Martins, São Paulo, Brazil) was used for plasma generation.

2.2. Reagents and samples

All reagents used in this study were of analytical grade. Water used for preparing all reagents and reference solutions was distilled, deionized and further purified by a Milli-Q system (Millipore Corp., Bedford, USA). Concentrated HNO₃ (65%, Merck, Darmstadt, Germany) was purified by a sub-boiling distillation system (model

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