Strategies for the determination of trace and toxic elements in pitch: Evaluation of combustion and wet digestion methods for sample preparation

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HIGHLIGHTS

- Metals determination in pitch by inductively coupled plasma optical emission spectrometry.
- Sample preparation methods based on combustion and wet digestion were evaluated.
- Diluted acid solutions were required for analytes absorption using MIC method.

GRAPHICAL ABSTRACT

ABSTRACT

Pitch is a complex matrix and hard to be digested. In this way, some sample preparation methods (wet digestion and combustion) were investigated for subsequent determination of Ba, Ca, Cd, Fe, Mg, Pb, Sr, V and Zn using plasma-based techniques as well as direct analysis by X-ray fluorescence (XRF). Among the investigated sample preparation methods, dry ashing and microwave-induced combustion (MIC) shown similar results for some analytes, but significant losses for Cd, Pb and Zn were observed when dry ashing was used. Thus, MIC was chosen once a diluted solution ($3\ mol\ L^{-1}\ HNO_3$) was suitable for analytes absorption, up to 400 mg of pitch could be digested and no analyte losses were observed. Accuracy of MIC was evaluated by analysis of a standard reference material of Green Petroleum Coke (NIST 2718). In addition, a comparison with results obtained by XRF and MIC was performed and no statistical difference was observed. Thus, the proposed MIC method can be considered as suitable for the digestion and further elements determination in pitch.

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1. Introduction

Pitch from crude oil has been widely used for the manufacture of industrial products in several fields [1]. In this sense, pitch has been used as a binder agent during the carbon anode production in aluminum industry (because of their excellent binding properties) and also for several applications such as the production of graphene nanosheets, the preparation of activated carbon fibers and poligranular graphite [2–6].

Pitch and its smoke are considered hazardous by-products commonly generated in industrial processes. Additionally, these

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compounds are toxic for human and animals on the aspects of carcinogenesis, teratogenesis and mutagenesis [7,8]. Taking into account that pitch smoke can be formed during heating process (including mainly paving process), toxic compounds (e.g., Cd and Pb) can be volatilized and directly absorbed through the respiratory tract affecting human health and also causing contamination of water and soil [9,10]. Moreover, acid products generated during the processing of coal, petroleum and petrochemicals, are considered hazardous for human and ecological receptors [11]. Thus, the knowledge of pitch composition is important for the development of effective remediation methods for their toxic effects [8,11]. Taking into account the requirements for pitch characterization concerning to the structural and chemical composition, several analytical techniques such as matrix-assisted laser desorption ionization time-of-flight mass spectrometry, supercritical fluid extraction and fractionation, thermogravimetric analysis and elemental analysis have been proposed [6,12–15]. However, information about metals content in this type of material is scarce in the literature. In the same way, the knowledge of impurities concentration in pitch is important due to the reactivity of carbon anodes be highly influenced by metals content. In this sense, there are some specifications for concentration of Ca and Fe (100 and 250 $\mu g\,g^{-1}$, respectively) for further use of pitch in the manufacture of carbon anodes used in the aluminum production. These limits consider the requirements regarding to environment and anode fabrication aspects, as well as the efficiency of reduction cells of aluminum oxide [13,16].

Considering that pitch is a complex matrix, some difficulties can be found for its digestion and further elemental determination by spectrometric techniques. In this sense, powerful digestion methods (generally applying high temperature and pressure) are required in order to bring the analytes into the final solution [17]. Some of sample preparation methods include these requirements and the classical dry ashing method theoretically achieves these objectives, providing high digestion efficiency (low residual carbon), using high sample mass and with high throughput. However, the main disadvantage of dry ashing is the risk analyte losses (e.g., Cd, Pb and others) [18]. Then, digestion in closed systems should be the option to avoid these problems.

In this way, microwave-induced combustion (MIC) in closed vessels has been proposed for digestion of many kinds of samples, especially those considered as "hard to digest" (e.g., crude oil, graphite, carbon nanotubes and coal), allowing further determination of metals, non-metals, halogens and rare earth elements [18–21]. Among the advantages of MIC, the digestion of relatively high amounts of sample (generally from 500 to 700 mg) using diluted solutions, the low generation of effluents and lower risks of analyte losses and contamination can be highlighted [22–28]. Moreover, this method could be considered as safe for the analyst since pitch digestion is carried out in a closed system avoiding direct contact of the analyst with released toxic products.

Considering that no official method is available for elements determination in pitch, the feasibility of sample preparation methods was investigated for pitch digestion and further determination of Ba, Ca, Cd, Fe, Mg, Pb, Sr, V and Zn by inductively coupled plasma optical emission spectrometry (ICP-OES). For MIC method, some important parameters such as the concentration of absorbing solution (1–14.4 mol L^{-1} HNO$_3$) were evaluated. Other sample preparation methods such as microwave-assisted digestion (MAD) and dry ashing were also investigated. Residual carbon was determined in order to evaluate the efficiency of all digestion methods for pitch. Accuracy was evaluated by analysis of a standard reference material (SRM) by ICP-OES after MIC as well as by analysis of pitch by XRF.

2. Materials and methods

2.1. Instrumentation

A Multiwave 3000 (Anton Paar, Austria) microwave sample preparation system equipped with a rotor for eight high-pressure closed quartz vessels (capacity of 80 mL, maximum pressure and temperature of 80 bar and 280 °C, respectively) was used for pitch digestion by MIC and MAD. A commercial quartz holder (Anton Paar) was used to insert the filter paper and sample inside the quartz vessels for MIC method.

A muffle furnace (model LF0913, Jung, Brazil) was used for pitch digestion using dry ashing method. The cavity of furnace has an internal volume of 9 L and this system was equipped with temperature and time controller (maximum operation temperature of 1300 °C). Platinum crucibles (capacity of 50 mL) were used for sample digestion.

An inductively coupled plasma optical emission spectrometer (model Optima 4300 DV, Perkin Elmer, USA) using axial view mode, equipped with a cyclonic spray chamber and a GemCone™ nebulizer was used for elements determination. This instrument was also used for carbon determination in all digests. For plasma generation, nebulization and auxiliary gas, argon with a purity of 99.996% (White Martins, Brazil) was used. The operational conditions for ICP-OES instrument are described in Table 1.

An XRF instrument (model S8 Tiger wavelength dispersive, Bruker, Germany) was used for comparison of results. XRF instrument was equipped with a 4 kW Rh X-ray tube, scintillation counter, flow proportional counter with P10 gas flow, automatic mask, collimator, filter and crystal changers, and robotic sample loader.

2.2. Reagents, standards and samples

Ultrapure water was distilled, deionized and further submitted to a Milli-Q system (18.2 MΩ cm, Millipore Corp., USA) and was used to prepare all standard solutions and reagents as well as for sample dilution. All solutions were prepared with analytical grade reagents (Merck, Germany). Concentrated nitric acid (65%, Merck) was previously purified in a quartz sub-boiling system (model DuoPur, Milestone, Italy). Hydrogen peroxide (30%, Merck) was also used for pitch digestion by MAD. Nitric acid was also used for cleaning procedures.

A multielement stock reference solution (SCP33MS, SCP Science, Canada) containing 10 mg L^{-1} of all analytes was used to prepare the calibration solutions for ICP-OES were diluted in 5% HNO$_3$

Table 1
Operational conditions for determination of elements by ICP-OES.

Parameter	ICP-OES
RF power, W	1400
Plasma gas flow rate, L min^{-1}	15.0
Auxiliary gas flow rate, L min^{-1}	0.2
Nebulizer gas flow rate, L min^{-1}	0.70
Sample flow rate, mL min^{-1}	2.1
Spray chamber	Cyclonic
Nebulizer	GemCone™
Observation view	Axial
Wavelength, nm	Ba (455.403), Ca (317.933), Cd (214.440), Fe (238.204), Mg (285.213), Pb (220.353), Sr (421.552), V (290.880), Zn (213.857), C (193.030)[a] and Y (371.029)[a]

[a] Used for carbon determination.