



High purity polyimide analysis by solid sampling graphite furnace atomic absorption spectrometry



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ABSTRACT

In this work, Cr, Cu, Mn, Na and Ni were determined in high purity polyimides (99.5%) by solid sampling graphite furnace atomic absorption spectrometry (SS-GFAAS) using Zeeman effect background correction system with variable magnetic field, making possible the simultaneous measurement at high or low sensitivity. The following analytical parameters were evaluated: pyrolysis and atomization temperatures, feasibility of calibration with aqueous solution, linear calibration range, sample mass range and the use of chemical modifier. Calibration with aqueous standard solutions was feasible for all analytes. No under or overestimated results were observed and up to 10 mg sample could be introduced on the platform for the determination of Cr, Cu, Mn, Na and Ni. The relative standard deviation ranged from 3 to 20%. The limits of detection (LODs) achieved using the high sensitivity mode were as low as 7.0, 2.5, 1.7, 17 and 0.12 ng g⁻¹ for Cr, Cu, Mn, Na and Ni, respectively. No addition of chemical modifier was necessary, except for Mn determination where Pd was required. The accuracy was evaluated by analyte spike and by comparison of the results with those obtained by inductively coupled plasma optical emission spectrometry and inductively coupled plasma mass spectrometry after microwave-assisted digestion in a single reaction chamber system and also by neutron activation analysis. No difference among the results obtained by SS-GFAAS and those obtained by alternative analytical methods using independent techniques. SS-GFAAS method showed some advantages, such as the determination of metallic contaminants in high purity polyimides with practically no sample preparation, very low LODs, calibration with aqueous standards and determination in a wide range of concentration.

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1. Introduction

Polyimide (PI) is a polymeric material that presents important characteristics, such as thermo-oxidative stability, high mechanical strength, resistance to solvents and electrical properties [1–3]. This polymer has been widely employed for applications at high temperature [4] as dielectric for electronic components [5], frameworks [6], membranes for gas separation [7], composites [8], crystal liquid displays [9], electroluminescent diodes [10], encapsulating implant devices [11], among others.

Some works have shown the influence of elemental impurities (e.g., Cr, Cu, Mn, Na and Ni) in polymers that even at trace levels can catalyze oxidation processes causing irreversible decomposition, affecting the technological and thermal properties as well as the performance of the final product [12,13]. For PI coatings, Bellucci et al. [14] studied the corrosion of this polymer due to the presence of elemental impurities. In addition to the oxidation process, the presence of metallic ions may

modify the electrical properties of PI that is undesirable to further application as semiconductor and dielectric material [13,15,16].

According to the association of Semiconductor Equipment and Materials International (SEMI), a well defined control of elemental impurities in polymers used for semiconductor manufacturing as PI is required. In this sense, SEMI recommends a protocol (SEMI F48-0600) with several steps for sample preparation and further elemental determination by spectrometric techniques [17]. Inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS) are recommended by SEMI F48-0600, but these techniques require an efficient sample preparation step in order to avoid/minimize interferences [18]. However, most sample preparation methods have some disadvantages, such as prolonged total analysis times and risk of contamination or analyte losses, mainly for open systems [18–20]. In addition, the requirement of high amounts of concentrated acids can increase the limits of detection (LODs) [18,19]. It is important to mention that the method described by SEMI F48-0600 for the determination of Cr, Cu, Mn, Na and Ni is not recommended for polymers where LODs lower than 1 µg g⁻¹ are required as in the case for PI [17].

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Alternatively to analytical techniques that requires a sample preparation step, methods based on solid sampling (SS) are considered as a powerful and reliable approach for trace elements determination due to the possibility of achieving low LODs, low reagent consumption, relatively low sample preparation and small sample mass required for the analysis [21–23]. Some techniques based on the direct determination such as neutron activation analysis (NAA) [24], slurry sampling graphite furnace atomic absorption spectrometry [25], particle-induced X-ray emission and Rutherford backscattering spectrometry [26], have been used for elements determination in PI samples. In addition, several works have shown the feasibility of solid sampling graphite furnace atomic absorption spectrometry (SS-GFAAS) as one of the most powerful analytical technique for elemental determination in solid samples due to its simplicity, low LODs and low time consumption [27–31]. Recent publications have demonstrated the feasibility of SS-GFAAS for the determination of Cr, Cu, Mn, Na and Ni in various advanced materials, such as raw material for polyurethane [30], fluoropolymers [31], aluminum nitride [32], pharmaceutical grade barium sulfate [33], and yttrium oxyorthosilicate [34]. However, the use of this technique for the determination of these analytes in PI samples, has not yet been described in literature, although it is the most simple and low cost technique comparing to those cited above.

Due to the low elements concentration in PI, it is evident that there is still a need for accurate methods for its analysis. However, PI is very hard to digest, due its chemical inertness, being SS-GFAAS an efficient alternative for the analysis of this polymer. In this sense, SS-GFAAS with background correction system based on Zeeman effect was applied in the present work for the determination of Cr, Cu, Mn, Na and Ni. This background correction system allows the simultaneous monitoring of different sensitivities conditions (high and low sensitivity), being possible to determine elements at high or low concentration, without changing the wavelength or gas flow-rate during atomization. Therefore, the suitability of low or high sensitivity, as well as the pyrolysis and atomization curves for sample and aqueous standard solution, the linear calibration range, the influence of sample mass and the use of chemical modifier was investigated. The accuracy was evaluated by results comparison with those obtained by spike recovery tests and determination by ICP-OES and ICP-MS after sample digestion and also by NAA.

2. Experimental

2.1. Instrumentation and operating conditions

The determination of Cr, Cu, Mn, Na and Ni was carried out using a graphite furnace atomic absorption spectrometer (model AAS ZENIT 60, Analytik Jena, Jena, Germany) equipped with a transversely heated graphite tube atomizer and a background correction system based on Zeeman effect. This correction system allows changing the magnetic field strength from 0 to 1.0 T. The spectrometer was operated with the main analytical lines of the analytes for high and low sensitivity modes. Hollow cathode lamps (Narva, Berlin, Germany) were used as specific radiation sources. The spectrometer was equipped with a solid sample introduction device for the insertion of the graphite platform into the graphite tube (manual solid sampling system, model SSA-5, Analytik Jena). The instrumental parameters used for determinations by SS-GFAAS, ICP-OES and ICP-MS are described in Table 1. The minimum and maximum (min/max) magnetic field strength corresponding to high sensitivity mode were 0 and 0.8 T, while to low sensitivity mode they were 0.6 and 0.8 T, respectively. The background correction system employed in this work provides a special dynamic mode, allowing the extension of linear calibration range [35–38]. The use of dynamic mode presents some advantages due to the possibility of simultaneous analyte determination at low and high concentration, without using any alternative analytical line or applying furnace gas flow-rates [35–38]. For low analytes concentration, the high sensitivity mode was used and the absorbance was obtained by the difference on absorbance

Table 1

Instrumental parameters applied for the determination by SS-GFAAS, ICP-OES and ICP-MS.

Analyte	SS-GFAAS			ICP-OES (nm)	ICP-MS (m/z)
	Wavelength (nm)	Spectral bandpass (nm)	HCL current (mA)		
Cr	357.9	0.8	4.0	205.552	⁵² Cr
Cu	324.8	0.8	2.0	327.396	⁶³ Cu
Mn	279.5	0.2	7.0	257.610	⁵⁵ Mn
Na	589.0	0.5	3.0	589.592	ND
Ni	232.0	0.2	5.0	232.003	⁵⁸ Ni

ND = not determined.

between zero (switched off) and maximum magnetic field applied (0.8 T) [38]. For samples with high analyte content, the absorbance was measured applying a variable magnetic field between 0.6 T and 0.8 T, providing a reduction on the sensitivity [38].

Pyrolytically coated graphite tubes and platforms (Analytik Jena) were used throughout. A microbalance (model M2P, Sartorius, Göttingen, Germany) with resolution of 1 µg was used for sample weighing. The optimized heating programs for all analytes determined by SS-GFAAS are shown in Table 2.

Polyimide residues obtained after pyrolysis step were analyzed in an infrared spectrometer (model Spectrum 400 FT-IR/FT-NIR, PerkinElmer-SCIEX, Waltham, EUA) with deuterated triglycine sulfate (DTGS) detector and KBr beam splitter. Spectra were collected from 4000 to 650 cm⁻¹, with 16 scans. This instrument is equipped with an attenuated total reflection (ATR) universal sampling accessory supplied with a top plate of ZnSe crystal.

For results comparison, PI samples were digested in an ultra-high pressure single reaction chamber (SRC) system (model UltraWave™, Milestone, Sorisole, Italy) equipped with five quartz vessels (maximum volume, pressure and temperature of 40 mL, 199 bar and 300 °C, respectively).

An ICP-OES instrument (model Spectro Cirrus CCD, Spectro Analytical Instruments, Kleve, Germany) with a cross-flow nebulizer coupled to a double pass Scott type spray chamber was used for determination of analytes in digested samples. The radiofrequency (RF) power was set at 1400 W and the argon flow-rate was set at 12, 1.0 and 1.00 L min⁻¹ for principal, auxiliary and nebulizer gas, respectively. Chromium, Cu, Mn and Ni were also determined by ICP-MS using a model Elan DRC II™ spectrometer (PerkinElmer-SCIEX, Thornhill, Canada) equipped with a concentric nebulizer (Meinhard Associates, Golden, USA), a cyclonic spray chamber (Glass Expansion, Inc., West Melbourne, Australia) and a quartz torch with a quartz injector tube (2 mm i.d.). The RF power was set at 1300 W and the argon flow-rate was set at 15, 1.2 and 1.08 L min⁻¹ for principal, auxiliary and nebulizer gas, respectively.

Results for Cr, Mn and Na were also compared with those obtained by NAA analysis performed by the Nuclear and Energy Research Institute (IPEN, São Paulo, Brazil). Sample masses from 40 to 450 mg were irradiated using a neutron flow of 3×10^{12} N cm² s⁻¹. Gamma activity

Table 2

Heating program for the determination of Cr, Cu, Mn, Na and Ni in polyimide by SS-GFAAS.

Step	Cr	Cu	Mn	Na	Ni
<i>Pyrolysis</i>					
Temperature (°C)	1400	900	1300	1000	1100
<i>Atomization</i>					
Temperature (°C)	2500	2200	2400	1900	2500
Heating rate (°C s ⁻¹)	3000	3000	2000	2000	3000
Hold time (s)	10	10	8	10	8

Drying: 110 °C, ramp of 5 °C s⁻¹, hold time 30 s, Ar flow-rate 2.0 L min⁻¹.

Pyrolysis: hold time 40 s, Ar flow-rate 2.0 L min⁻¹.

Atomization: Argon flow-rate 0 L min⁻¹.

Clean out: 2500 °C, ramp of 3000 °C s⁻¹, hold time 5 s, Ar flow-rate 2.0 L min⁻¹.

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