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Research Note

Surface studies on graphite furnace platforms covered with Pd, Rh and Ir as modifiers in graphite furnace atomic absorption spectrometry of tellurium

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ABSTRACT

The main objective of this work is the study of correlations between the efficiency of the distribution of the permanent platinum group modifiers Pd, Rh and Ir over the graphite surface with the aim of improving analytical signal of tellurium.

Modifier solution was deposited onto the platform and pyrolysed after drying. In the case of Pd, the physical vaporization/deposition technique was also tested.

In order to analyze the differences amongst coverings (morphology, topology and distribution), the graphite surfaces were studied with scanning electron microscopy and energy dispersive X-ray microscopy.

Micrographs for physical vaporization and pyrolytic deposition of Pd were also analyzed in order to explain the lack of signal obtained for tellurium with the first alternative. Similar micrographs were obtained for pyrolytic deposition of Ir and Rh and then, compared to those of Pd. Ir showed the most homogeneous distribution on the graphite surface and the tallest and sharpest transient.

With the aim of improving the analytical signal of tellurium, the correlation between the surface studies and the tellurium transient signal (height, area and shape) is discussed.

1. Introduction

The employment of chemical modifiers [1,2] has earned a place of privilege in graphite furnace atomic absorption spectrometry (GFAAS). Consequently, chemical modification has evolved from the classic matrix modifiers described by Ediger [3], towards the permanent modification introduced by Shuttler in 1992 [4]. Up to date, the permanent modification has been considered a versatile and efficient “in situ” chemistry with an important presence in the literature [5–9].

Amongst the chemical modifiers, the noble metals of high melting point (Ir, Pd, Pt, Rh and Ru) [10–13] and the carbide forming elements (Hf, Mo, Nb, Ta, Ti, V, W, Zr) [9,14–16] are the most employed either as mono-compound modifiers or combined [17–19].

Particularly in the case of the platinum group modifiers (PGMs), several studies have been published with the aim of explaining their mechanisms of action [20–22], in some cases through comparison with classic modification as reported recently by Borges et al. [23].

Regarding tellurium, recent studies have been devoted to the determination of traces by hydride trapping electrothermal atomization either onto platinum coated tungsten coils [24] or palladium or ruthenium electrothermally modified graphite tubes [25]. Also ultratrace amount speciation has been reported by different alternatives of microextraction followed by electrothermal atomization with electrodeposition of palladium [26,27].

In fact the permanent modification needs both: the choice of the chemical compound and a method for coating that is able to control the size and distribution of the particles of the modifier onto the graphite platform. On the knowledge that the characteristics of the coating are related to the mechanisms of action of the modifiers [4,15,20,28,29],

Table 1
Graphite furnace temperature program for conditioning graphite tubes with the permanent modifier.

Step	Temp./°C	Ramp time/s	Hold time/s	Ar flow/ml min^{-1}
1	100	30	10	250
2	130	20	10	250
3	1200	30	10	250
4	1200	–	10	250
5[a]	2000	–	5	250

[a] Pd: 1500 °C

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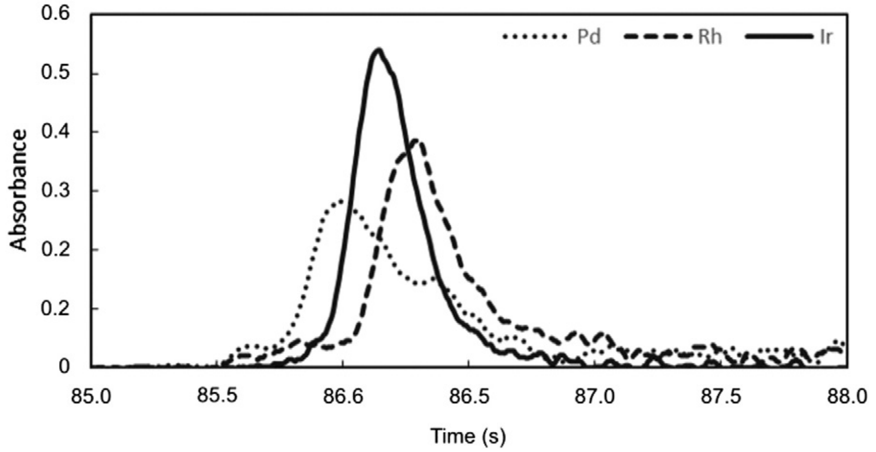

Fig. 1. Absorbance profiles for the atomization of 1 ng of Te (IV) in the presence of 20 μg of modifier.

different alternatives such as sputtering and electrodeposition, were presented in the literature and compared to the classical electrothermal cover [21,26,27,30].

In a previous work, we studied the use of permanent modifiers of platinum group in order to evaluate improvements on the determination of tellurium in sulfur by GFAAS [31]. Coatings of the graphite furnace with

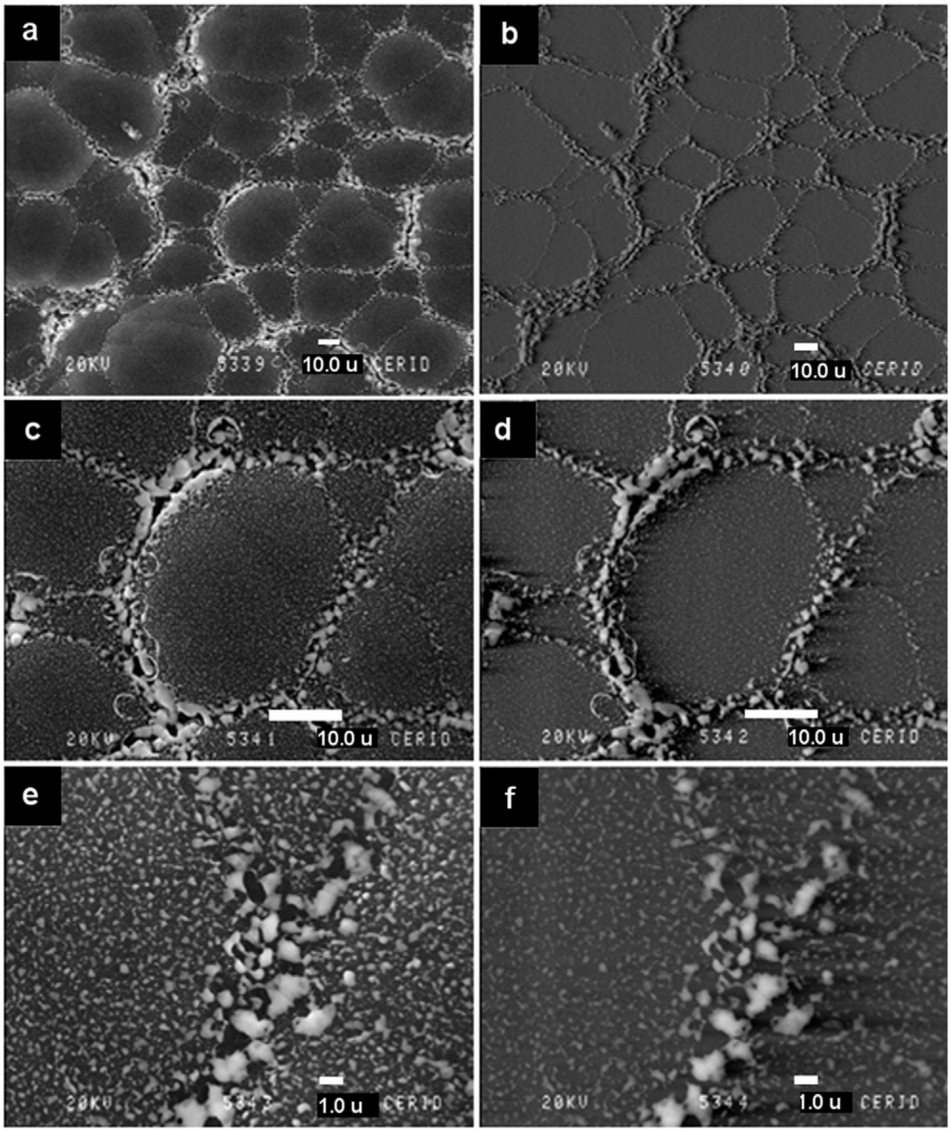

Fig. 2. SEM micrographs of graphite platforms covered with Pd (pyrolysed). (a), (c) and (e) SE images at magnification of 600; 2000 and 6000 respectively. (b), (d) and (f) BSE corresponding images.

Pd, Rh and Ir were assayed, giving Ir the best analytical results when experiments were performed with tellurium solutions in fairly concentrated nitric acid. Moreover, important differences on the shape of the analytical signal were observed which could be explained through the observation of the modified graphite surfaces.

This observation moved our curiosity towards explaining the differences mentioned above. Consequently, the modified surfaces were investigated by scanning electron microscopy (SEM) for morphologic and topographic studies and energy dispersive X-ray microscopy (EDX) to evaluate the distribution (surface and subsurface) of the PGMs.

For doing this, the different modifiers were thermally deposited on the graphite platforms and, in the case of Pd, the physical vaporization/deposition technique (PVD) was also tested.

The correlation between the results obtained with SEM and EDX and the transient signals of tellurium are discussed.

2. Experimental

2.1. Reagents

All reagents were analytical reagent grade. Doubly deionized water (DDW, 18 MΩ cm^{-1}) obtained from a Milli-Q water System (Millipore, Bedford, MA, USA) was used throughout the experiments. All operations were performed on a laminar flow clean bench. All laboratory ware were thoroughly cleaned with $(1 + 1)$ nitric acid and rinsed with DDW.

Te (IV) stock standard solution (0.1 g l^{-1}) in nitric acid was prepared by dissolving sodium tellurite (BDH) in HNO3 5% (v/v) (Merck). Working solutions of Te (IV) were prepared by appropriate dilution of the stock standard solution in HNO_3 5% (v/v).

Standard solutions of Pd (1.000 g l^{-1}) were prepared by dissolving $Pd(NO_3)_2$ (Merck, Darmstadt, Germany) in HNO_3 15% (v/v). Rh solutions (1.000 g l^{-1}) were obtained by dissolving $RhCl_3 \cdot 3H_2O$ (Alfa Aesar, Massachusetts, USA) in HCl 20% (v/v). Ir solutions (1.000 g l^{-1}) were prepared from metallic Ir (Merck) in HCl 10% (v/v). Metallic Pd (Merck) 99.9% was employed for thermal evaporation experiments.

2.2. Instrumentation

A Shimadzu 6700 Atomic Absorption Spectrometer (Kyoto, Japan) equipped with a graphite furnace accessory GFA 6000 and an autosampler ASC-6000 were used to obtain the analytical signals. A Hamamatsu hollow cathode lamp was employed as radiation source at 214.3 nm with a slit width of 2 nm and 8 mA lamp current. Background correction was performed using a deuterium lamp.

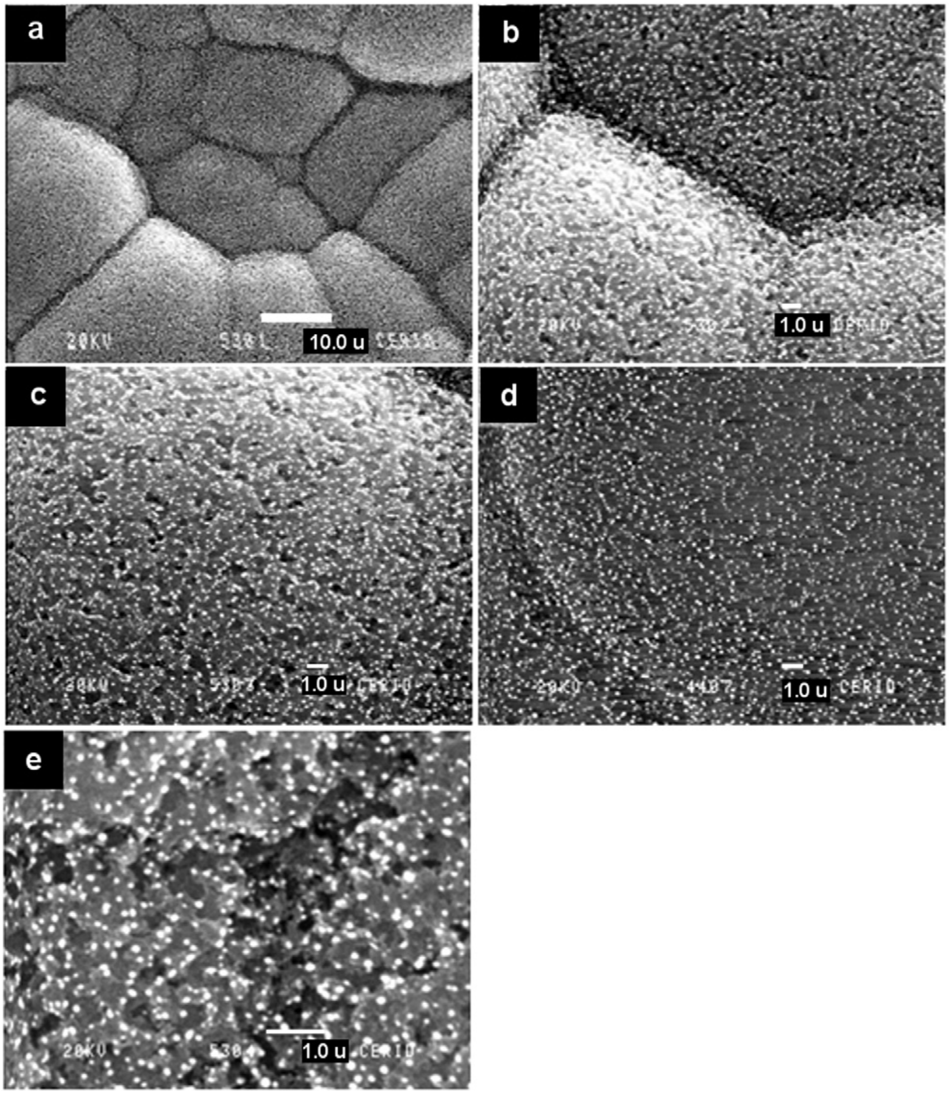

Fig. 3. SEM micrographs of graphite platforms covered with Ir (pyrolysed). (a) and (b) SE images at magnification of 2000 and 6000 respectively; (c) SE image ×6000 of another view of the surface; (d) BSE corresponding image; (e) detail of (d) at magnification of 18000.

Tubes with integrated graphite platform (Shimadzu) were used throughout the experiments. High purity argon (AGA, Argentina) was used as internal gas.

A thermal evaporator Model Auto 306 (Edwards, UK) was used for the physical deposition of Pd on the platform graphite.

The graphite surfaces were examined with a JEOL scanning electron microscope (Model JSM-35C) equipped with an energy-dispersive X-ray system.

2.3. Procedure

2.3.1. Permanent modification

In the electrothermal deposition technique, the permanent modification of the graphite surface was obtained by injecting 20 μl of 1.000 g l^{-1} solutions of the respective noble metals onto the tubes with graphite platforms. Tubes were dried and thermally treated (Table 1) in order to obtain the metals in their reduced form. This sequence was repeated five times before obtaining the micrographs.

In the PVD technique a wire of palladium was used that was sublimated and deposited on the graphite platform. Sublimation was carried out with a thermal evaporator at a pressure of 10.5 mB. The Pd film was deposited on the platform of graphite at a rate of 0.2 nm/s without heating the substrate. The coating thickness obtained was 80 nm.

A volume of 50 μl of 20 μg Te(IV) l^{-1} (equivalent to a mass of 1 ng of Te (IV)) was injected into the graphite platforms after PGM deposition.

2.3.2. Analysis of the modified surfaces

The graphite platforms prepared as described under 2.3.1 were held in the SEM instrument. SEM micrographs were made in the modes of secondary electron (SE) and backscattered electron (BSE) images using an accelerating voltage of 20 kV. The magnification used (×600, ×2000, ×6000 and ×18,000) is detailed in each one of the sequences presented. All micrographs were obtained over the whole platform.

X-ray spectra were acquired with an accelerating voltage of 20 kV and the qualitative elemental chemical analysis (X-ray microanalysis) was carried out by treating the spectra with EDX system software. Depth distribution of the noble metals was obtained at distances from the surface ranging between 0 and 6.5 μm at intervals of 1 μm. From doing this, platforms were manually cut into two halves and then, consecutively scanned.

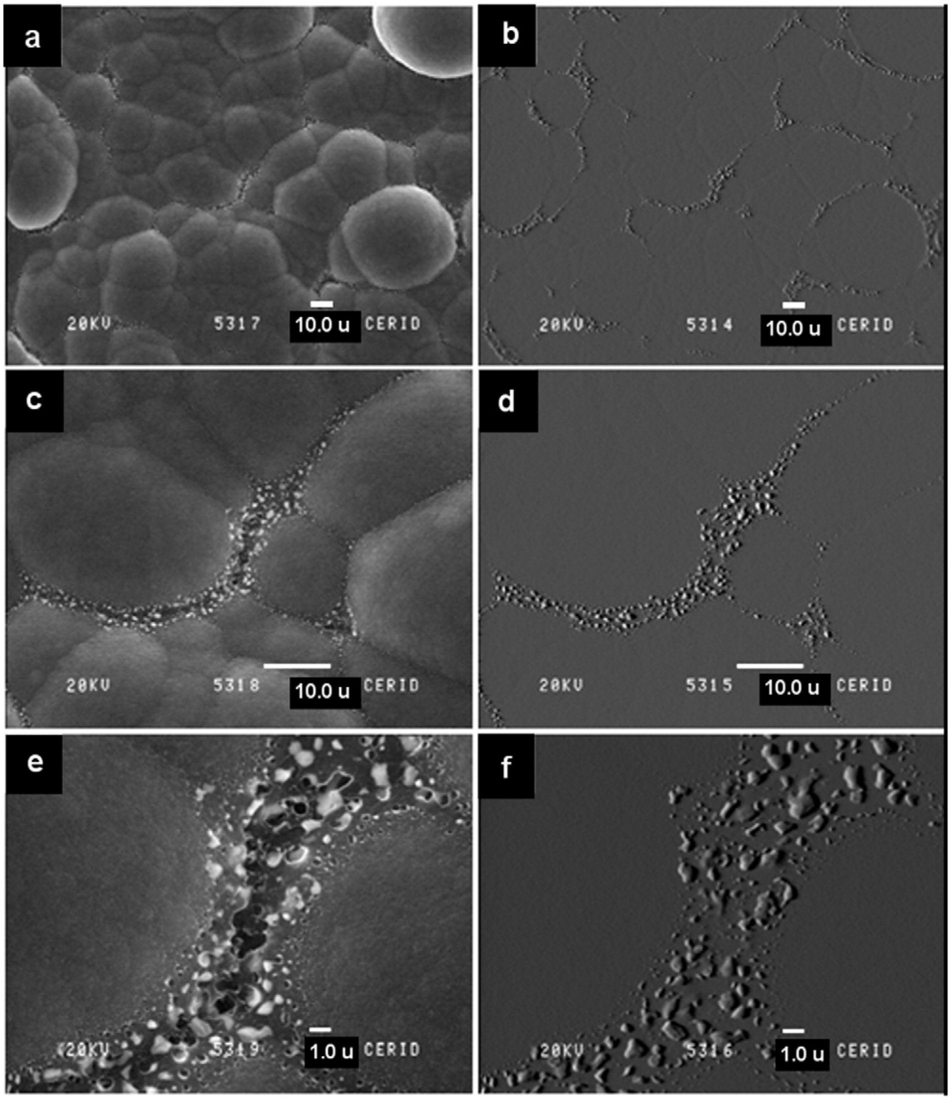

Fig. 4. SEM micrographs of graphite platforms covered with Rh (pyrolysed) (a), (c) and (e) SE images at magnification of 600; 2000 and 6000 respectively; (b), (d) and (f) BSE corresponding images.

3. Results and discussion

The influence of the pyrolysis temperature on the absorbance was studied [31] in the range from 600 to 1500 °C, with atomization temperature set for 2400 °C. The maximum pyrolysis temperatures obtained were 1200 °C in the presence of Pd, 1300 °C in the presence of Rh and 1400 °C in the presence of Ir.

Fig. 1 shows the absorbance profiles obtained from the atomization of 1 ng of Te (IV) in the presence of the different PGM modifiers.

As can be seen, in the Ir case a highly symmetrical and narrow peak with no tailing was obtained. Conversely, in the presence of rhodium the signal was broader and showed an important tailing similar. The same was observed with the employment of palladium.

3.1. Electrothermal deposition technique

Figs. 2, 3 and 4 show micrographs corresponding to surfaces modified with Pd, Ir and Rh respectively.

The palladium distribution on the graphite surface is poorly homogeneous (see Fig. 2). With the pyrolysis treatment, palladium is deposited forming numerous agglomerated islands as displayed in the SEM micrographs of the figure. The deposit is clearly not uniform and resembles a cauliflower shape.

As mentioned in the literature [11,20,32], the signal of the analyte may be impoverished or distorted in the presence of large amounts of modifier. In agreement, the formation of agglomerates — consistent with higher masses of Pd in certain areas of the platform — could explain the broadening of tellurium atomization signal. Tellurium would remain in the agglomerated islands of Pd until a sufficiently high temperature is reached, producing the migration of the analyte outside of the modifier. The limiting step of the atomization velocity would be controlled by the rate of migration of Te. This position is consistent with the results obtained by Shiue et al. [33].

Fig. 3 reproduces the topography of Ir deposition onto the graphite surface. A cauliflower shape relief is observed but in this case, the islands are smaller and more homogeneous when compared to Pd. This morphology and surface distribution of Ir could be responsible of a better contact between Te and this modifier, leading to a more efficient stabilization. This result is compatible with the characteristics of the tellurium atomic signal. In the presence of Ir, highly symmetrical and narrow peaks with no tailing were obtained (see Fig. 1).

On the other hand, Rh is deposited only on the valleys of the cauliflower-like surface structure of the pyrolytic graphite as shown in Fig. 4. The non-uniform distribution and the existence of large areas without modifier do not promote the contact between the analyte and the modifier. This is consistent with the characteristics of the tellurium atomization signal in the platform with Rh.

EDX spectra (Fig. 5) were performed as described under 2.3.2 but no signal was detected from 1.5 μm onwards for any of the PGM modifiers assayed. Unfortunately, the sensitivity was poor and our experiments were not conclusive about penetration.

3.2. Physical vaporization/deposition technique

Pd-PVD micrographs showed a uniform film of 100% Pd covering the whole surface of graphite (Fig. 6), which was not observed with pyrolysis.

In the first case, no signal was obtained which could be attributed to the lack of graphite. In the second case, graphite exposes on the superficial area yielding to an increment on the analytical signal. The PVD coating seems to avoid the participation of graphite in the stabilization of Te which is concurrent with the lack of signal in atomic absorption. According to our results, the action of Pd on Te stabilization should involve the participation of graphite in order to obtain an analytical signal.

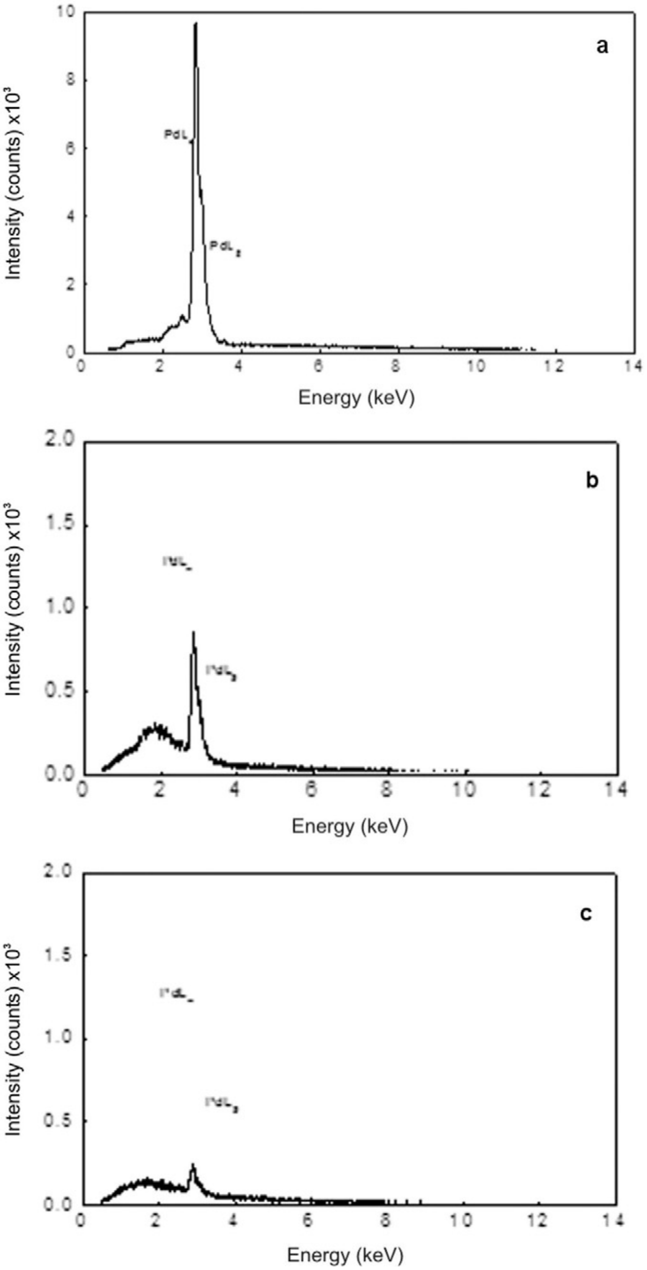

Fig. 5. EDX spectra for Pd taken in the cutting zone (a) on the surface; (b) and (c) below the surface between 0.5 at 1.5 μm and 1.5 at 2.5 μm, respectively.

4. Conclusions

The correlation between the transient signals obtained by GFAAS of Te and SEM micrographs and EDX spectra has been evaluated. SEM superficial results showed that the distribution of the modifier onto the graphite furnace could change the shape and area of the peaks. Depth experiments with EDX were not convincing about penetration of the modifiers.

Pd-PVD micrographs revealed that the presence of graphite contributes to the stabilization of Te in the furnace.

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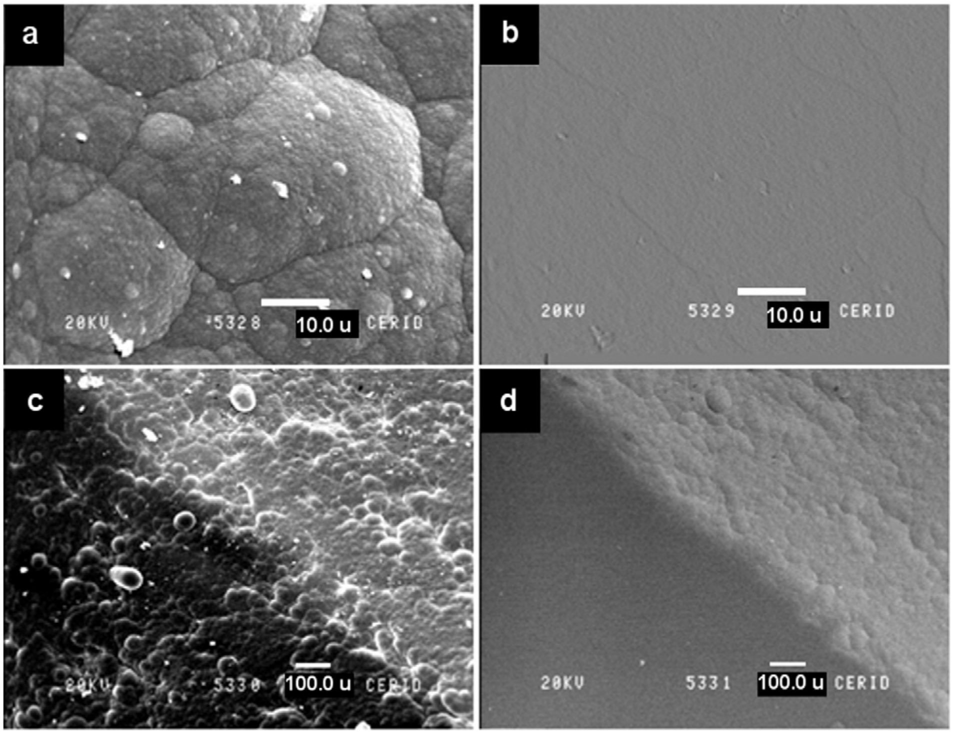

Fig. 6. SEM micrographs of graphite platforms covered with Pd (PVD). (a) and (c) SE images of interface area (×2000) and (×100), respectively. (b) and (d) BSE corresponding images.

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