

On-line preconcentration, ion chromatographic separation and spectrophotometric determination of palladium at trace level

M.C. Bruzzoniti^a, C. Mucchino^b, E. Tarasco^a, C. Sarzanini^{a,*}

^aDepartment of Analytical Chemistry, University of Turin, Via P. Giuria 5, 10125 Turin, Italy

^bDepartment of General and Inorganic Chemistry, Analytical Chemistry, Physical Chemistry, University of Parma, Parco Area delle Scienze 17/A, 43100 Parma, Italy

Received 20 February 2003; received in revised form 20 May 2003; accepted 22 May 2003

Abstract

A new method for the determination of Pd by ion chromatography and spectrophotometric detection has been developed. The technique is based on the separation of palladium as PdCl_4^{2-} by anion exchange and on the detection, at a wavelength of 407 nm, of metal as PdI_4^{2-} after a post-column reaction with KI. The column used was an IonPac AS4 with HCl and HClO_4 eluents. The eluent concentration and composition of post-column reagent were optimised in order to obtain the best separation and sensitivity for Pd. In order to reduce the detection limit, an on-line preconcentration step, has been optimised. The method, as developed, was suitable for palladium determination within a 300 ng/l D.L. value. The method applied to a BCR reference material (CRM 277, estuarine sediment) gave satisfactory results in agreement with the certified value within a D.L. value of 1.3 $\mu\text{g/l}$ for the real sample.

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Keywords: Trace analysis; Palladium

1. Introduction

Palladium can be found as a free metal associated with platinum and other platinum group metals (PGMs), as well as with nickel and copper deposits. The natural concentration of palladium in the continental earth crust is estimated, at today, to 15 $\mu\text{g/g}$ [1].

Good catalyst for hydrogenation and dehydrogenation reactions, palladium is alloyed for use in jewellery, in dentistry applications, in fine instruments

such as watches and some surgical tools, for electrical contacts and for the purification of hydrogen gas.

Palladium has no biological role. All palladium compounds should be regarded as highly toxic and as carcinogenic. However, palladium chloride was formerly prescribed as a treatment for tuberculosis without too many bad side effects. There is currently much discussion about its bioavailability and toxicology.

The largest application of palladium is in the catalytic field. The extended use of palladium in automotive catalytic converters and in the chemical industry has led to increasing concentrations of this metal in environmental compartments. PGMs may enter the environment and interact with complexing

*Corresponding author. Tel.: +39-11-670-7628; fax: +39-11-670-7615.

E-mail address: corrado.sarzanini@unito.it (C. Sarzanini).

materials, such as humic substances [2]. An increase in the palladium concentration in ambient air near frequently used roads is expected [3–6].

The complexity of matrix and low concentration levels of palladium in ambient air make a direct measurement of metal difficult. The application of highly sensitive techniques, ICP-MS [7–9], GFAAS [10], NAA [11], coupled with an enrichment procedure, is necessary. Separation and preconcentration procedures have been developed for several matrices. For this purpose, systems based on liquid–liquid extraction [12–14], ion-exchange [15–17], solid sorbent extraction [8,18–20] and electrochemical deposition [21] have been used. Recently, separation and preconcentration were achieved by ion-exchange using microcolumns packed with Cellex-T resin: selective palladium elution from the column was performed with 1.2 M thiourea (pH 0.5) or 4 M potassium thiocyanate (pH 1). The FAAS and GFAAS are implied as detection techniques [22]. The sensitivity of the electrochemical methods, particularly adsorptive stripping voltammetry, was studied for the determination of palladium. A study on palladium determination by adsorptive accumulation of the metal complex with dimethylglyoxime by stripping voltammetry has been published [23]. The detection limit is of 0.05 $\mu\text{g/l}$ Pd for liquid samples and 50 ng/g for solid samples. Recently, a method based on palladium preconcentration in a flow-through electrochemical cell has been developed. The detection limit of 0.05 ng/ml Pd was obtained by graphite furnace atomic absorption spectrometry (GFAAS) [24]. A new study shows the separation for ruthenium, palladium, rhenium, osmium, iridium and platinum, as bromo complexes, by anion exchange resin [25].

Current literature does not provide IC method for preconcentration and determination (on-line) of palladium. Nevertheless, in liquid chromatography (HPLC) a reversed-phase approach for the determination of rhodium and palladium has been developed. The method is based on detection UV after complexation of metals with sodium diethyldithiocarbamate [26]. Detection limits for Pd(II) and Rh(III) are 2.7 and 2.8 $\mu\text{g/l}$, respectively.

The aim of this work was to develop an IC method for palladium preconcentration and determination. Due to the fact that the palladium forms stable

anionic chloride complexes, strongly retained by an anion exchanger, the method is based on the separation of palladium as PdCl_4^{2-} by anion exchange mechanism with the eluent containing hydrochloric acid. The detection is based on post-column derivatization reaction with KI and the reaction product (PdI_4^{2-}) is detected spectrophotometrically at the wavelength of maximum absorption of complex. To lower the detection limit, a preconcentration step has been coupled. The cation and anion mechanisms were investigated for the preconcentration of palladium.

The method developed has been applied to a synthetic complex matrix (mixture of noble metals and transition metals) and to a certified sample (BCR reference material, CRM 277, estuarine sediment), verifying the applicability of the technique, optimized through this work, to a real sample.

2. Experimental

2.1. Apparatus

The ion chromatograph consisted of a Model 4000i (Dionex, Sunnyvale, CA, USA) equipped with a gradient pump and a Rheodyne injector Model 7125. The volume of the sample loop was 100 μl . For separation, the analytical columns were IonPac AS4 (250 \times 4 mm I.D.) and IonPac AG4 (50 \times 4 mm I.D.) from Dionex. For preconcentration measurements the guard columns IonPac AG4 (50 \times 4 mm I.D.), IonPac AG11 (50 \times 4 mm I.D.) and IonPac CG10 (50 \times 4 mm I.D.) were used. IonPac AS4 and IonPac AG4 stationary phases have a polystyrene–divinylbenzene substrate agglomerated with a completely aminated anion-exchange latex. The IonPac AG11 has an etilvinylbenzene–divinylbenzene substrate agglomerated with a completely aminated anion-exchange latex. The functionalities of IonPac AS4 and AG4 are alkylammonium quaternary groups and for IonPac AG11 are alkanolammonium quaternary groups. The ion-exchange capacity is approximately 20 μeq for AS4, 4 μeq for AG4 and 9 μeq for AG11 columns. The CG10 resin is based on a polystyrene–divinylbenzene substrate with sulfonic functional groups and the capacity of this column is approximately 16 μeq . The eluent solution contained

HCl and HClO_4 at the optimised concentration. The eluent flow-rate was 1.3 ml/min. Detection was achieved by a spectrophotometric detector, at wavelength 407 nm after post column derivatization with KI, HCl and Na_2SO_3 at proper concentrations. A chromatographic data system (AI-450, Dionex) was used for data collection and for the integration of peak areas. Chromatograms were recorded at room temperature. Dead volume, 1.2 ml, was evaluated by the negative peak due to water.

BCR sample dissolutions were performed in tetrafluoromethoxyl (TMF) bombs, with a Milestone MLS-1200 Mega (Milestone, Sorisole, Italy) microwave laboratory unit.

2.2. Reagents and solutions

Palladium powder 99.999%, palladium 1010 $\mu\text{g}/\text{ml}$ in 5% wt. HCl were from Aldrich (Milwaukee, WI, USA), potassium iodide, anhydrous sodium sulphite and hydrochloric acid were from Fluka (Buchs, Switzerland), nitric acid, tin(II) chloride dihydrate were from Merck (Darmstadt, Germany), perchloric acid, hydrazine were from Carlo Erba (Milan, Italy).

Hydrochloric and nitric acid were purified by a sub-boiling treatment (K. Kurner, Rosenheim, Germany). All aqueous solutions were prepared by high purity water obtained with a Milli-Q system (Millipore, Bedford, MA, USA). Eluents were filtered through 0.22- μm filters before use (Millipore). After optimization, due to the stability achieved, the post-column reagent has been weekly prepared.

3. Results and discussion

3.1. Post-column reaction

In order to develop a selective method for palladium determination, a derivatization reaction has been studied. The reaction between palladium and iodide ion has been exploited. The reaction is very favoured ($\text{Log } K=24.5$) and leads to the formation of PdI_4^{2-} which shows maximum absorption at 407, 316 and 270 nm. The wavelength used for the palladium detection, after the optimization of the method, is at 407 nm, since it meets the minimum

noise of the chromatographic system. In order to optimise derivatization conditions and to obtain the maximum absorption of complex, the effect of KI concentration, as well as the effect of acidity (HCl) and of stabilizing agent (Na_2SO_3) has been studied.

3.2. Effect of sodium sulphite

Since the iodide ion is easily oxidated in contact with the air, the stability of the post-column reagent (PCR) over time has been evaluated. The absorption spectra of a fresh solution, recorded at different times, clearly show the occurrence of a reaction originating a band interfering at the Pd detection wavelength, 407 nm. The interference was avoided by stabilizing the post-column reagent solution. This was achieved through a detailed study on the effect of the addition of sodium sulphite to the reagent. It was proved that 1.6 mM Na_2SO_3 was a suitable concentration to keep PCR stable over time without significantly increase the background absorbance of the PCR.

3.3. Effect of hydrochloric acid concentration

The post-column reaction was carried out with reagent solution: 0.23 M KI (enough to ensure the total complexation of palladium), 1.6 mM Na_2SO_3 and from 5.0 mM to 2.4 M HCl. The study of the effect of hydrochloric acid on the absorbance of PdI_4^{2-} does not show any appreciable increase of the signal in the range of concentration of HCl evaluated in the reagent. The optimised concentration of HCl in the derivatizing solution is 10 mM.

3.4. Effect of KI concentration

At the optimised concentrations of HCl and Na_2SO_3 , the effect of KI concentration on the absorbance of PdI_4^{2-} was studied in the range 25–230 mM. This study had the aim of minimising the waste of reagent according to the maximum absorption of the complex. The best detection sensitivity was reached with a 50 mM KI solution.

3.5. Kinetics of the derivatization reaction

The reaction yield and the stability of PdI_4^{2-}

complex was studied as a function of the time, to guarantee the reproducibility of the absorbance measurements. The absorbance of complex was evaluated for 140 min at room temperature on a solution of palladium 3 mg/l, derivatized as optimised. The formation of the complex is instantaneous and does not show any significant increase in the range of time evaluated. To demonstrate that the formation of complex does not depend on the reaction temperature, the kinetics was also studied for the reaction conducted both at room temperature and at 40 °C. No significant variation for the complex formation is shown.

Therefore the optimum conditions for the derivatization procedure are 50 mM KI, 10 mM HCl and 1.6 mM Na₂SO₃, at room temperature.

3.6. Chromatographic separation

3.6.1. Eluent optimisation

The eluent composition was based on an H₂O–HCl mixture at different concentrations. To avoid the formation of Pd-hydroxy complexes and guarantee the presence of PdCl₄²⁻ species, standard solutions were in 1 M HCl.

The chromatographic behaviour of Pd as a function of HCl concentration was studied. By increasing the HCl concentration the retention time of Pd decreases, but, also with very high concentrations of acid such as 2.4 M, the chromatographic peak shows a poor symmetry.

In order to increase the eluent strength and to improve the symmetry of peak, the perchloric acid was introduced into the mobile phase. The HClO₄ concentrations investigated were between 0 and 0.1 M for both 2.4 and 1.1 M HCl. The addition of perchloric acid involves an increase in detection sensitivity, a decrease in standard deviation, reduced analysis time and an improvement in peak symmetry (asymmetry factor from 9.3 to 1.6). The optimised composition of mobile phase resulted 1.1 M HCl, 0.1 M HClO₄. In these conditions the method shows a good reproducibility both for the retention times (RSD<0.5%, *n*=10) and for the detection sensitivity (RSD<3.6%, *n*=10).

3.6.2. Reproducibility, detection limit and interferences

The method exhibited a good reproducibility

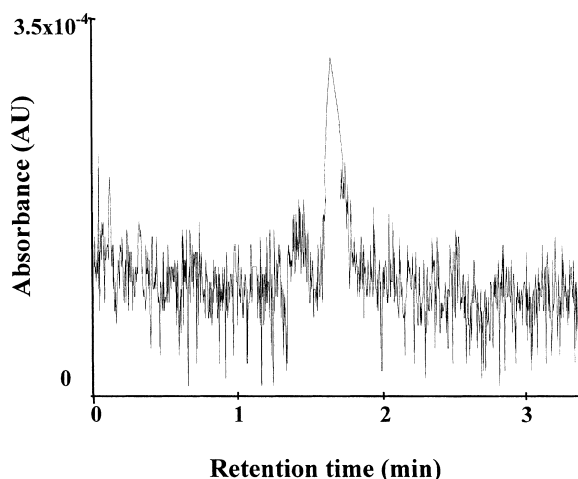


Fig. 1. Chromatogram of Pd (30 µg/l). Column: IonPac AS4. Eluent: 1.1 M HCl and 0.1 M HClO₄. Flow rate: 1.3 ml/min. Sample loop: 100 µl. PCR: 50 mM KI, 10 mM HCl, 1.6 mM Na₂SO₃. Detection: Vis 407 nm.

(RSD<3.8%, *n*=10) and a good linearity ($r^2=0.9989$, for seven levels of concentration in the range 0.030–1 mg/l). Fig. 1 shows a chromatogram of Pd at 30 µg/l, detection limit evaluated as three-times the noise signal.

Interferences from the other noble metals (Pt, Rh, Ir, Ru) and from heavy metals (Cu, Mn, Zn, Ni, Fe, Pb), commonly present in the real matrix, were also investigated. The spectrophotometric study (Fig. 2) demonstrated that Fe(III), Ru(III) and Pt(II) show an appreciable absorbance at 407 nm. Among these elements only Fe(III), which is eluted at 1.32 min and well resolved in respect to Pd at 1.64 min, could originate chromatographic interferences if present at Fe/Pd high concentration ratio (see below).

3.6.3. Preconcentration

To reduce the detection limit achieved, a procedure enabling palladium preconcentration has been studied. Both anion and cation exchange mechanisms were investigated. The preconcentration procedures have been performed on-line with a preconcentration ratio of 500. Solutions (50 ml) of palladium at 10 µg/l in nitric or hydrochloric acid were eluted at 1.5 ml/min through a guard column. Five replicates for each preconcentration step have been performed.

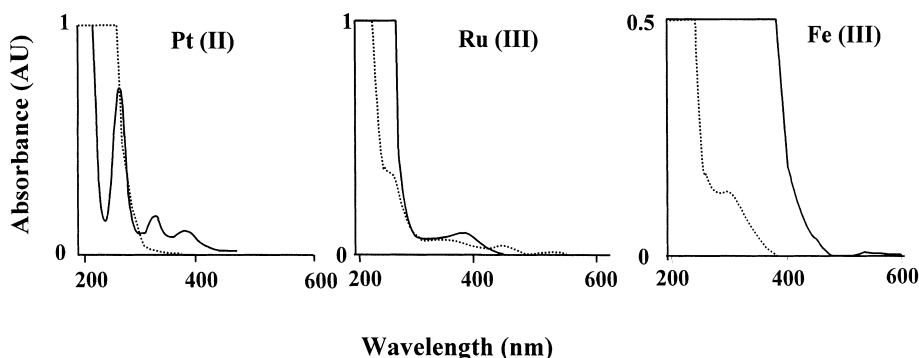


Fig. 2. Absorption spectra of PCR (dotted line) and possible interferents (solid lines). Metal concentrations: 3 mg/l each. Derivatization conditions as Fig. 1.

3.6.4. Preconcentration by cation-exchange mechanism

An IonPac CG10 guard column (cation exchanger) has been chosen as preconcentration substrate. Before each experiment, the column was conditioned with the eluent used as mobile phase. The palladium is retained as a cation Pd^{2+} from a nitric solution. The effect of HNO_3 concentration on the recovery yield of Pd has been studied (Table 1). The best preconcentration recovery was $54.4 \pm 3.8\%$ ($n=5$) for a concentration of 0.075 M of nitric acid.

3.6.5. Preconcentration by anion-exchange mechanism

IonPac AG4 and AG11 guard columns have been chosen and compared as preconcentration substrates. Before each experiment, the columns were conditioned with the eluent used as mobile phase. Since

the palladium is retained as PdCl_4^{2-} , the effect of HCl concentration of palladium solutions on the recovery yield was studied for both the columns (Table 2). The best preconcentration recovery, on IonPac AG4, was $91.8 \pm 7.6\%$ ($n=5$) at 0.030 M HCl concentration. The IonPac AG11 column enabled a recovery yield of $80.7 \pm 3.6\%$ ($n=5$) for 0.030 M hydrochloric acid concentration. The recovery of this column is lower than for the precolumn IonPac AG4, but, at this concentration of hydrochloric acid, the preconcentration shows a better reproducibility. The metal was eluted from the precolumn by 1.1 M HCl and 0.1 M HClO_4 .

In conclusion, the column IonPac AG11 shows better chromatograms: the Pd peak is more symmetric than the peak obtained with the column IonPac AG4 and the recovery shows a higher reproducibility, as RSD (%). Therefore the column IonPac AG11

Table 1
The effect of nitric acid concentration on the recovery yield of Pd

[HNO_3] M	Recovery (%)
0.000	36.4 ± 3.8
0.050	34.3 ± 0.8
0.075	54.4 ± 3.8
0.100	52.7 ± 3.8
0.200	7.5 ± 3.1
1.000	4.5 ± 28.5

Preconcentration column, IonPac CG10; preconcentration flow-rate, 1.5 ml/min; sample, 50 ml, 10 $\mu\text{g/l}$ Pd. Preconcentration factor, 500. Chromatographic conditions as Fig. 1. RSD% calculated on $n=5$ replicates.

Table 2
Comparison of preconcentration performance of IonPac AG4 and AG11 precolumns

[HCl] M	Recovery (%)	
	AG4	AG11
0.000	11.0 ± 6.0	0
0.015	66.5 ± 6.4	71.7 ± 3.4
0.030	91.8 ± 7.6	80.7 ± 3.6
0.050	70.8 ± 7.6	68.4 ± 3.8
0.100	74.1 ± 7.5	64.0 ± 3.7
0.200	60.7 ± 7.2	61.2 ± 3.8

Preconcentration flow-rate, 1.5 ml/min; sample, 50 ml, 10 $\mu\text{g/l}$ Pd. Preconcentration factor, 500. Chromatographic conditions as Fig. 1. RSD% calculated on $n=5$ replicates.

was chosen for the determination of low concentrations of palladium. The lower recoveries from AG11 column in respect to the AG4 can be ascribed to the different composition of the two phases and to the different interactions of PdCl_4^{2-} with the substrates. Since the AG11 column has alkanolammonium functionalities, additional interactions of palladium with the OH groups of the resin have to be expected.

The preconcentration procedure enabled a detection limit of 300 ng/l Pd with a relative standard deviation 8.3% ($n=5$).

3.7. Reference material

In order to evaluate the suitability of the method for the analysis of environmental samples, the procedure has been applied to a BCR reference material (CRM 277) that represents an estuarine sediment [27].

The sample was dissolved by microwave digestion with aqua regia in tetrafluoromethoxy (TFM) bombs. Before use, the bombs were cleaned by microwave treatment with 5 ml of concentrated ultra-pure nitric acid, cooled and washed with ultra-pure water.

To 0.2 g of the sample was added 6 ml of HCl and 2 ml of HNO_3 , both the acids were concentrated and ultra-pure. The heating program was: 5 min at 250 W, 5 min at 400 W and 5 min at 600 W. After a cooling step, the treatment involved the addition of 1 ml of concentrated and ultra-pure hydrofluoric acid and further heating: 5 min at 250 W, 5 min at 400 W and 5 min at 600 W. The sample was then transferred in PTFE vessels, dried, and for three times added with 2 ml of concentrated ultra-pure hydrochloric acid and dried again. This last step allows the removal of fluoride ions if present. At the end the remainder of the sample was dissolved with 10 ml of 0.2 M ultra-pure hydrochloric acid, filtered and analysed. This HCl concentration, despite the recovery shown in Table 2, was chosen to ensure a complete dissolution of the sample. In parallel, blank solutions have been processed in the same way.

Among all metals present in the sample, Fe(III) has the higher concentration (46.3 mg/g) and an interference, during the chromatographic separation, has to be expected. The preconcentration step, for PdCl_4^{2-} enrichment, obviously preconcentrates

Fe(III) since it is present as chloro-complex FeCl_4^- and the estimated concentration of Fe(III), after preconcentration, is 926 mg/l. As mentioned Fe(III) does not interfere for amounts as similar as those of Pd, but at this level it must be removed so, a pre-treatment has been optimised.

Since Fe(II) does not form chloro-complex species, the reduction of Fe(III) to Fe(II) was the first approach followed. In order to reduce only Fe(III) and to avoid loss of Pd(II), the reducing agents evaluated were: SnCl_2 ($E^\circ \text{Sn}^{\text{IV}}/\text{Sn}^{\text{II}}=0.139$ V in 1 M HCl), Na_2SO_3 ($E^\circ \text{SO}_4^{2-}/\text{SO}_3^{2-}=-0.93$ V) and hydrazine ($E^\circ=-0.23$ V).

In presence of Sn(II) the reduction of Pd(II) to Pd occurred. In fact, a black deposition and a decrease of the original absorbance of PdCl_4^{2-} at 220 nm has been spectrophotometrically verified.

In considerations of the high amount of sulphite ion required to reduce Fe(III) (724 mg/l) and to the possible interference provided by $\text{SO}_4^{2-}/\text{SO}_3^{2-}$ Na_2SO_3 has not been used. The hydrazine reduces selectively Fe(III) but, at the concentrations evaluated (0.27–8.32 mM hydrazine), a colloid is originated involving a loss of analyte.

As an alternative way to remove Fe(III) H_3PO_4 was added to the sample as a ligand able to compete with chloride ions to avoid the presence of FeCl_4^- species. Within the investigated concentrations (0.015–1.05 M H_3PO_4) the 0.6 M value gave the best result.

The analysis of a 10 ml solution similar to the real sample (926 mg/l Fe(III), 10 $\mu\text{g/l}$ Pd(II), 0.2 M HCl and 0.6 M H_3PO_4) showed that most Fe(III) is removed but some traces are retained, probably adsorbed, into the precolumn (Fig. 3a). A washing step (1.0 ml, 0.6 M H_3PO_4) of the AG11 precolumn, after the preconcentration and before the chromatographic analysis, ensured the complete removal of Fe(III) (Fig. 3b).

The blank value of the complete analytical procedure was evaluated. The entire sample preparation process, including the preconcentration step, was applied to five independent blank samples. Each of the resulting solutions showed that Pd was not present in detectable amount.

The standard addition method was used for the determination of palladium in the certified sample and spikes were added to the raw material before

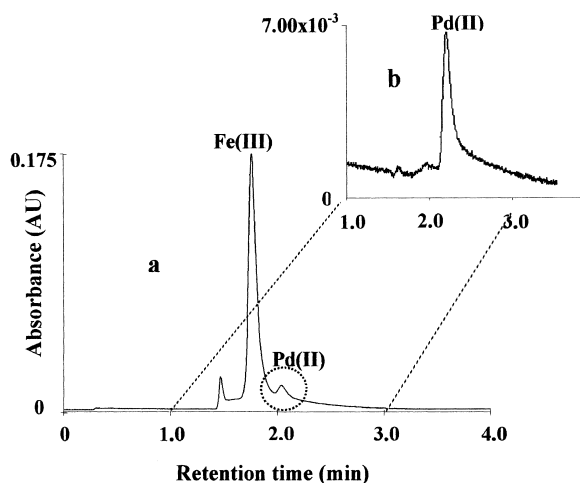


Fig. 3. Chromatograms of a sample containing 10 $\mu\text{g/l}$ Pd and 926 mg/l Fe, after the pre-treatment with 0.6 M H_3PO_4 : (a) without and (b) with the washing step. Preconcentrator, IonPac AG11; loading flow-rate, 1.5 ml/min; washing solution, 1 ml 0.6 M H_3PO_4 . Analytical column, IonPac AS4; eluent, 1.1 M HCl and 0.1 M HClO_4 ; flow-rate, 1.3 ml/min. PCR: 50 mM KI, 10 mM HCl, 1.6 mM Na_2SO_3 . Detection, Vis 407 nm.

dissolution. A series of 0.2 g CRM 277 samples (three unspiked, three added with Pd to reach the final concentration of 4 $\mu\text{g/l}$, and three added with Pd to reach the final concentration of 8 $\mu\text{g/l}$) were processed at the same time. The solutions (10 ml, 0.2 M HCl), obtained following the dissolution step described above, were filtered, added in 0.6 M H_3PO_4 , preconcentrated in the precolumn IonPac AG11 (flow-rate 1.5 ml/min) and after the washing step, eluted to the analytical column. Fig. 4 shows the chromatograms obtained.

The concentration found for Pd (standard addition method: regression coefficient (r^2) 0.991 and relative standard deviation 5.6%) was 0.47 $\mu\text{g/g}$ which compares well with the certified value of 0.5 $\mu\text{g/g}$.

The D.L. value (3σ criterion) evaluated from the real sample analyses resulted 1.3 $\mu\text{g/l}$. The increase of the value, in respect to the data obtained for the standard solutions, could be ascribed to a competition against the analyte, during the preconcentration step, of anions and anionic species coming from the matrix.

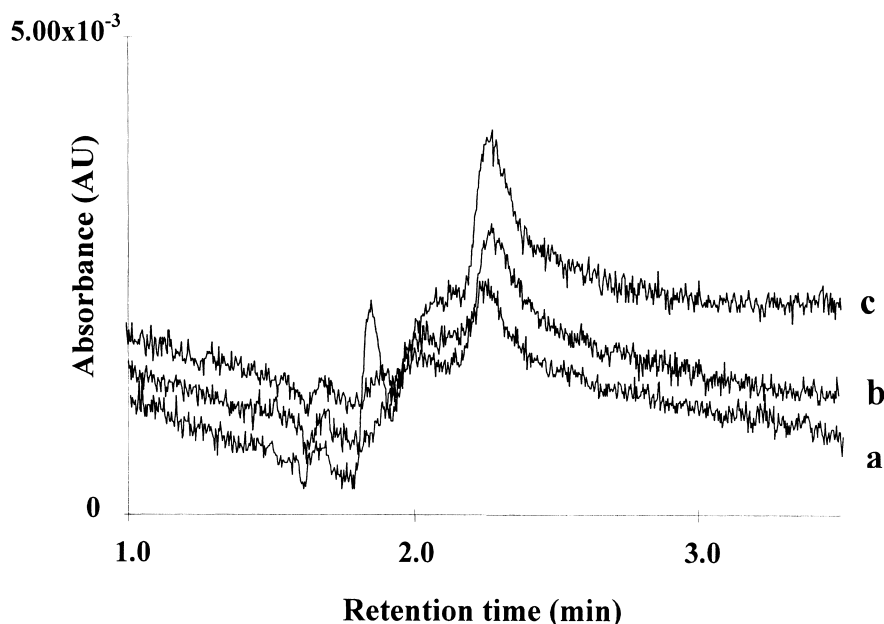


Fig. 4. Chromatograms of reference material: (a) unspiked; (b,c) spiked with 0.04 and 0.08 μg of Pd, respectively. Experimental conditions as Fig. 3.

4. Conclusion

An ion chromatographic method, based on anion exchange mechanism, has been developed for the determination of palladium. The method is based on separation of palladium as anion PdCl_4^{2-} by an IonPac AS4 column and a 1.1 M HCl+0.1 M HClO_4 eluent. The spectrophotometric detection is based on post-column derivatization of palladium to PdI_4^{2-} that absorbs at 407 nm. Derivatization conditions were optimized in order to achieve the best yield of reaction. The method developed enabled the determination of palladium at concentration levels of 30 $\mu\text{g/l}$. Coupling a developed preconcentration procedure, based on anion-exchange enrichment of PdCl_4^{2-} , the Pd detection limit was lowered to 300 ng/l. After a detailed study, on matrix interferences and their removal, the method gave satisfactory results for the analysis of a certified sample.

Acknowledgements

Financial support from the Ministero dell'Isruzione, dell'Università e della Ricerca (MIUR, Rome) and from the University of Torino is gratefully acknowledged.

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