

Ion chromatography with inductively coupled plasma mass spectrometry, a powerful analytical tool for complex matrices Estimation of Pt and Pd in environmental samples

M.C. Bruzzoniti^a, S. Cavalli^b, A. Mangia^c, C. Mucchino^c, C. Sarzanini^{a,*}, E. Tarasco^a

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

^bDionex s.r.l., Via Tulipani 1, 20090 Pieve Emanuele, Milan, Italy

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

Abstract

A new method for palladium and platinum direct determination in environmental samples is proposed by coupling ion chromatography with quadrupole inductively coupled plasma MS. In order to optimise Pd and Pt separation and to minimise interference from matrix in real samples, several anionic and cationic stationary phases have been compared at different mobile phase compositions. In particular, the effect of acidity and of the addition of oxalic acid to the eluent on separation and detection performance has been studied, and the anion-exchange column AG11 turned out to be more suitable. After chromatographic and mass spectrometer parameter optimisation, several potential interferences and the main quality parameters of the method, according to the Eurachem-CITAC recommendations, were evaluated: the detection limit for Pt was 5 ng l^{-1} while the value for Pd was 230 ng l^{-1} . The method was successfully employed in the determination of platinum group elements in urban road dust and atmospheric particulates and the complete absence of matrix spectral interferences was demonstrated.

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1. Introduction

Environmental contamination by the platinum group elements (PGEs), mainly related to automotive catalytic converters, is exponentially increasing and its reliable and accurate quantification is a mandatory task [1–4]. The wide use of palladium and platinum not only in automotive catalytic converters but as a

drug (Pt) and in food production (Pd) [5] has led to a more uncontrolled release of those metals in the environment, with respect to the one due to the traditional chemical industry. Moreover the platinum group elements derived from automotive catalytic converters are released as nanocrystallites (particles with less than $3 \mu\text{m}$ in diameter) due to thermal cracking of the catalyser structure and to mechanical abrasion [6–8]. Those particles are not blocked by the upper respiratory system and can deeply interact with the lungs. Although the bioavailability and toxicology of PGEs is still an open question, the determination of basal concentrations of those metals

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

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

has a key role since an increase of their level is expected near high traffic areas [9,10].

The heterogeneous composition of samples and the low concentration levels of palladium and platinum involved make the direct measurement of analytes really difficult. Several analytical techniques have been employed with this matrix in recent years and most of the advantages and drawbacks have been reviewed, as far as platinum determination is concerned, by Balcerzak [11]. Since sensitivity is the main requirement, a lot of attention was given to electrochemical techniques, namely adsorptive stripping voltammetry, and several methods have been proposed both for Pd and Pt [12–14] but, due to difficult sample treatment, they are not easy-to-use and robust.

Inductively coupled plasma MS is another leading technique for elemental trace analysis due to its great sensitivity, speed and accuracy, but some important analytes, such as PGEs, are interfered with either by polyatomic species or oxides: even the very expensive high-resolution sector field ICP-MS could not overcome the problem [15]; several approaches, with different analytes, have been attempted to achieve reliable data such as: matrix elimination by electrothermal vaporisation (ETV) [16] or by desolvation devices [17], plasma power reduction to achieve “cold plasma condition” [18] and polyatomic cluster disruption with the use of a collision cell [19]. The first two suffer from poor repeatability, whereas the cold plasma is not applicable due to the high ionisation energy required by Pd and Pt, while the latter is not suitable since the kinetic energy needed to break Pt- and Pd-based clusters is very high, with unpredictable consequences in the quadrupole mass filter. The mathematical correction of interferences has been pursued [20] but, due to the low concentration of analytes and the huge amount of interferences, the authors concluded that Pd could not be evaluated with the necessary accuracy.

A fast and reliable way to overcome spectral interferences is the prior separation of interferences: most of the proposed methods achieve both the separation and the preconcentration of the analytes by using microcolumns [21], anion-exchange of Pt chloro or bromo complexes [22,23], cation-exchange columns [24], but none of them involved the on-line determination of Pt and Pd. A brief review of

methods used for dissolution and separation of PGEs in difficult samples is given in Ref. [25].

The aim of this work was to develop and validate an on-line ion chromatography–inductively coupled plasma mass spectrometry (IC–ICP-MS) hyphenated method for direct palladium and platinum determination at ng l^{-1} concentration levels by using a suitable mobile phase in order to achieve the required selectivity and to prevent plasma perturbation and the clogging or rapid deterioration of the interface cones.

2. Experimental

2.1. Chromatographic system

The apparatus consisted of a GP 40 gradient pump (Dionex, Sunnyvale, CA, USA), and an EV 750-100 Rheodyne injector with electric actuator. The volume of the sample loop was 25 μl in the method development stage and 250 μl during the validation step. All the columns used, namely IonPac AG4A-SC, AG10, AG11, AG15, AG16 (50 \times 4 mm I.D.) (Dionex) are detailed in Table 1. The eluent flow-rate was set in the range 1.0–1.2 ml min^{-1} .

2.2. ICP-MS system

A PlasmaQuad 3 (ThermoElemental, Winsford, UK) equipped with Fassel torch, standard cooled (8 °C) impact bead spray chamber, concentric Meinhard nebuliser and an ASX-500 autosampler (CETAC, Omaha, NE, USA) and a Perimax 12 peristaltic pump (Spetec, Erding, Germany) was used. Instrumental and operating conditions were optimised daily with the factory-suggested tune solution.

2.3. Coupling IC and ICP-MS, automation and data acquisition

The two systems were directly coupled by fitting a polyether ether ketone (PEEK) tubing into the nebuliser and the complete automation of the system, including the autosampler, was achieved via the mass spectrometer software, Plasmalab v. 1.06.05

Table 1
Stationary phase specifications

Column	AG4A-SC	AG10	AG11	AG15	AG16
Particle diameter (μm)	13	8.5	13	9	9
Particle porosity	Micro	Macro	Micro	Macro	Super
Substrate X-linking (%)	55	55	55	55	55
Column capacity ($\mu\text{equiv./column}$)	4	34	9	45	34
Hydrophobicity	Medium-low	Low	Medium-low	Medium	Low
Functional group	Alkyl quaternary ammonium	Alkanol quaternary ammonium	Alkanol quaternary ammonium	Alkanol quaternary ammonium	Alkanol quaternary ammonium
Latex diameter (nm)	85	65	85	Grafted	80
Latex X-linking (%)	0.5	5	6	Grafted	1
pH stability	0–14	0–14	0–14	0–14	0–14
Solvents compatibility (%)	0–100	0–100	0–100	0–100	0–100

and the external accessory card, by creating a suitable script with the visual programming interface.

Data acquisition was performed with Plasmalab software, while peak integration was carried out with the Chemstation software (Agilent Technologies, Palo Alto, CA, USA).

For sample digestion a microwave MW 1200 MEGA system (FKW-Milestone, Sorisole BG, Italy) was used.

2.4. Reagents and solutions

Zn stock solution (1000 mg l^{-1}) was from RudiP-ont (Milan, Italy), Pt, Pd, Cu and Pb stock solutions (1000 mg l^{-1}) were from Carlo Erba (Milan, Italy), Rh stock solution (1000 mg l^{-1}) was from Merck (Darmstadt, Germany), Sr, Y and Rb stock solutions (1000 mg l^{-1}) were from BDH (Poole, UK), W and Hf stock solutions (1000 mg l^{-1}) were from Ultra Scientific (North Kingstown, RI, USA) and Ge stock solution (1000 mg l^{-1}) was from High-Purity (Charleston, SC, USA). HCl (37%, v/v) was from BDH, HNO_3 (65%, v/v) was from J.T. Baker (Deventer, The Netherlands), HClO_4 (70%, v/v) was from Carlo Erba and anhydrous $(\text{COOH})_2$ (>99% purity) was from Fluka (Buchs, Switzerland).

Zr, Tb and Gd stock solutions (1000 mg l^{-1}) were obtained by dissolution of $\text{Zr}(\text{NO}_3)_4$ in HCl 8% and Tb_2O_3 , Gd_2O_3 in HNO_3 6%, respectively. Mo stock solution (1000 mg l^{-1}) was prepared by dissolution of metallic Mo (99.995% purity). Ultrapure water with conductivity $<0.1 \mu\text{S}$ (DI water) was obtained from a MILLI-Q system (Millipore, Bedford, MA,

USA). Standard and working solutions were prepared from the stocks with diluted HCl (1.1 M). $(\text{COOH})_2$ 0.5 M stock solution was prepared in DI water by dissolution of the anhydrous $(\text{COOH})_2$.

Different mobile phases containing HCl, HNO_3 and HClO_4 , respectively, were prepared in DI water by dilution of their concentrated acids, whereas the mobile phase containing $(\text{COOH})_2$ was prepared by diluting the 0.5 M stock solution.

On all the working solutions, a preliminary acquisition with the mass spectrometer in scan mode was performed in order to assess their purity.

2.5. Method validation

The validation process of the method based on cold plasma ICP-MS technique was performed according to EURACHEM guidelines [26].

Detection (y_D) and quantitation (y_Q) limits were expressed as signals based on the mean blank (\bar{x}_b) and the standard deviation of blank responses (s_b):

$$y_D = \bar{x}_b + 2t s_b \quad y_Q = \bar{x}_b + 10s_b$$

where t is the constant of the t -Student distribution (one-tailed) depending on the confidence level (a 95% confidence level was chosen) and degrees of freedom (d_f). \bar{x}_b and s_b were calculated by performing 10 blank measurements.

The concentration values of the detection limit (LOD) and quantitation limit (LOQ) were obtained by projection of the corresponding signals y_D and y_Q through a calibration plot $y = f(x)$ onto the concentration axis. Linearity was verified up to two

orders of magnitude always performing six measurements at each concentration level.

Homoscedasticity was verified by applying the Bartlett test; lack-of-fit and Mandel's fitting test were also performed to check the goodness of fit and linearity. The significance of the intercept (significance level 5%) was established by carrying out an *F*-test.

3. Results and discussion

Due to the fact that both palladium and platinum form stable anionic chlorocomplexes, strongly retained by an anion-exchanger and on the basis of a new chromatographic separation method recently developed for Pd determination by some of the authors (Bruzzoniti et al., unpublished research), the first attempt was to achieve the separation of Pt and Pd on anion-exchange columns by HCl eluents and detection by ICP-MS. The performance of different kinds of anion-exchange columns (capacity, porosity, functional groups, etc.), shown in Table 1, was evaluated.

Preliminary experiments were performed to simulate the chromatographic separation at flow-rate up to 1.2 ml min^{-1} and hence to evaluate the stability of the background detection response of the ICP-MS when concentrations of HCl as high as 1 *M* were used. In fact, these concentrations are required to elute Pd and Pt chlorocomplexes from the chromatographic columns as detailed below.

The performance of the mentioned columns was evaluated using two eluent compositions: (i) 1 *M* HCl and (ii) 1 *M* HCl, 20 mM HClO_4 . Further experiments were aimed to improve the peak symmetry and to reduce analysis time, and on the basis of experimental evidence (Bruzzoniti et al., unpublished research) ClO_4^- ion proved to have higher affinity for anion-exchangers and to improve peak shape and detection sensitivity.

In order to evaluate if coprecipitation of trace amounts of Pd and Pt occurs when Pb (due to its high concentration in urban particulate) is present in hydrochloric solution, 100 ng l^{-1} of Pt and Pd were analyzed in the presence of Pb with the AG4A-SC column and 1 *M* HCl eluent. Other interferents have been evaluated after the following preliminary study

on column selection, and both spectral and chromatographic interferences have been considered. The mass acquisition was performed in continuous mode on m/z 105 for Pd, m/z 195 for Pt, m/z 103 for Rh and m/z 206 for Pb.

With AG4A-SC and eluent (i) the separation of Pb, Rh and Pd is not achieved, while Pt is eluted with two peaks at about 110,000 ms and close to the void volume. As expected, an increase of eluent strength in eluent (ii) still reduces any difference in selectivity.

With an AG11 column, both with eluent (i) and (ii), it was possible to separate Rh, Pt and Pd, while Pb and Rh coelute in the void volume. Pd and Pt are present in two forms; in particular Pt with eluent (ii) shows two species eluting, one close to void volume and the other at about 180,000 ms.

The high capacity of AG15 ($45 \text{ } \mu\text{equiv. column}^{-1}$) within eluent (i) retains Pd (eluting only after a long washing procedure with HCl), and Pt splits into at least three anionic forms and completely elutes only with a washing step with HCl. Anionic forms appear also for Pb and separation from the anionic species of Rh is precluded.

Although each metal elutes in a single peak, with eluent (ii), the Pd peak is asymmetric and the Pt peak is large and late eluting ($t_R = 230,000 \text{ ms}$). The AG16 column ensures separation between Pd and Pt with eluent (i), but not that of Pb and Rh, while resolution between Pd and Pt is lost with eluent (ii).

On the basis of the whole results, the AG10 and AG11 columns were the ones with the best separation performance (retention times, peak symmetry) for the noble metals with shorter retention time (AG11). The chromatograms at m/z 105 for Pd and m/z 195 for Pt with the AG10 column are reported in Fig. 1.

At this stage, even if the peak shapes were not optimal, further experiments were planned in order to ascertain if the proposed method was effective in avoiding the interference problem.

The effect of interferences was studied on the AG10 column since, with its high capacity and rather good separation performance, it is possible to elute them quite far from the void volume. Interferences were injected at a concentration of 10 mg l^{-1} each in a solution containing amounts of Pd and Pt as low as $10 \text{ } \mu\text{g l}^{-1}$. The following main interferences, usually

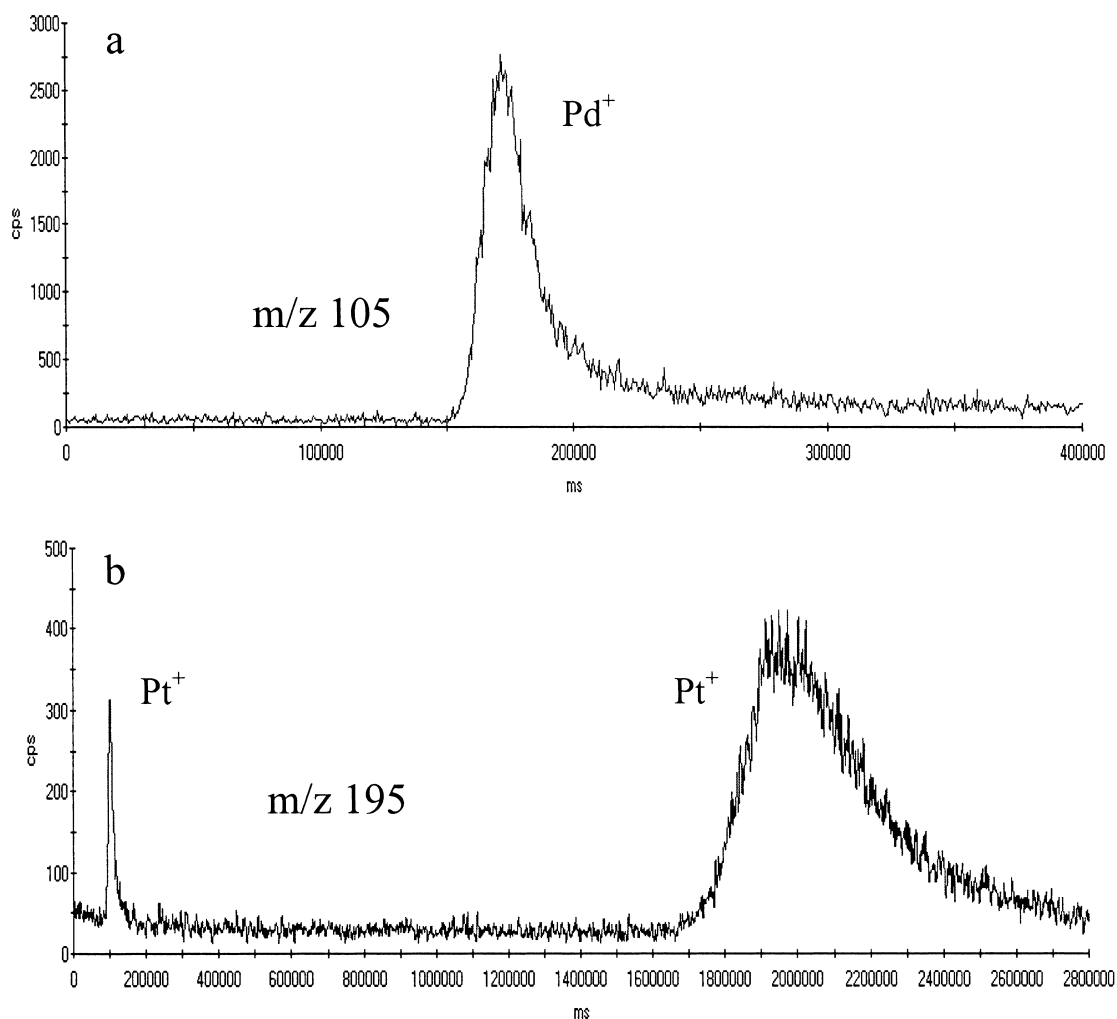


Fig. 1. Chromatograms: (a) m/z 105, (b) m/z 195; sample, $33 \mu\text{g l}^{-1}$ of Pd and Pt; column, IonPac AG10; eluent, 1.1 M HCl and 50 mM HClO_4 ; flow-rate, 1.2 ml min^{-1} ; sample loop, 25 μl .

found in brakes, silencers and catalytic converters, were considered: ^{104}Pd : yttrium ($^{89}\text{Y}^{16}\text{O}^+$), copper ($^{40}\text{Ar}^{65}\text{Cu}^+$), zirconium ($^{91}\text{Zr}^{14}\text{N}^+$) and zinc ($^{68}\text{Zn}^{37}\text{Cl}^+$); ^{195}Pt : hafnium ($^{179}\text{Hf}^{16}\text{O}^+$), gadolinium ($^{40}\text{Ar}^{155}\text{Gd}^+$) and terbium ($^{36}\text{Ar}^{159}\text{Tb}^+$). Moreover, the behaviour of some other common elements in those matrices like Ga, Sr, and Mo was taken into account.

The study on interferences was performed with a single standard solution of the elements by acquiring simultaneously at the m/z of the considered interference, and at m/z 105 or 195. The results pointed out

that Sr, Y, Ga, Cu and Mo eluted on void volume and in no way can chromatographically interfere. Moreover, Y, Ga, Mo gave no peak at m/z 105, therefore the spectroscopic interference is absent, too. Noteworthy is the behaviour of zirconium that elutes as two chromatographic peaks: the main one at void volume but the other coeluting with Pd. This latter gave a very weak spectral interference on m/z 105 and has been taken into account in the subsequent checks on interferences.

On the contrary, Zn is retained by the column, thus representing a potential chromatographic inter-

ference, but since there is no signal at m/z 105 its interference can be neglected.

Concerning Pt determination, hafnium only was retained by the AG10 column, but its selectivity is different from that of Pt, nevertheless this element too was taken into account in the final interference study.

The good results achieved in the interference study triggered a further step in the optimisation of the chromatographic separation: since an increase of perchloric acid concentration in the eluent was not advisable due to the possible damage of the intro-

duction cones of the ICP-MS equipment, new mobile phases based on oxalate anion were tested.

The introduction of a new mobile phase (iii) 1 M HCl, 10 mM oxalic acid, gave an inversion in the selectivity with the AG10 column as clearly shown in Fig. 2 with a reduction in the retention time of Pt, but an increase, with a very asymmetric and broad peak, in the case of Pd. The behaviour of columns with less capacity such as AG11, AG4A-SC and AG16 was similar with a moderate reduction in the retention time for both the analytes and still with a very broad peak in the chromatogram at m/z 105.

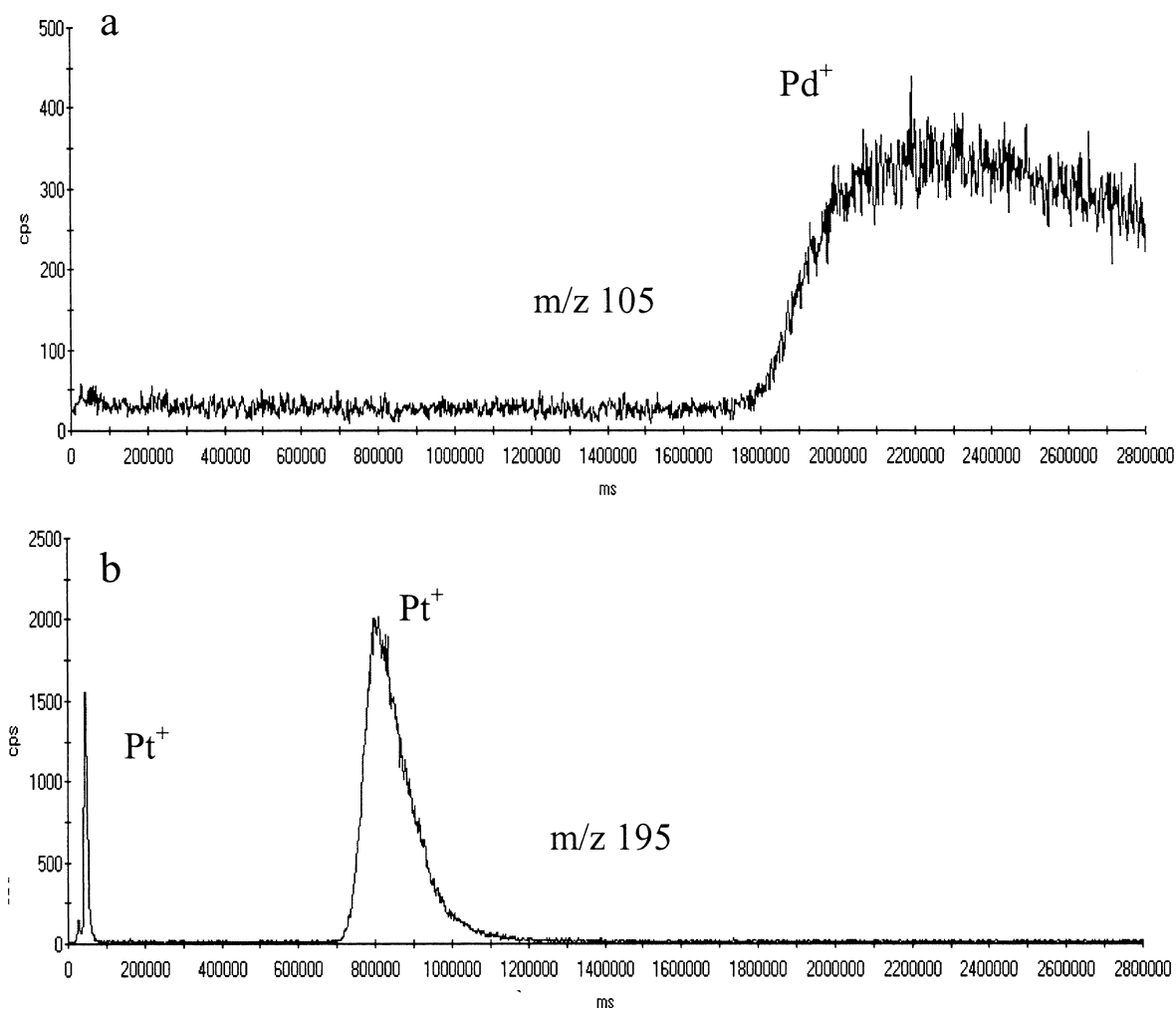


Fig. 2. Chromatograms: (a) m/z 105, (b) m/z 195; sample, 500 $\mu\text{g l}^{-1}$ of Pd and Pt; column, IonPac AG10; eluent, 1.1 M HCl and 10 mM oxalic acid; flow-rate, 1.2 ml min^{-1} ; sample loop, 25 μl .

Several compositions of the mobile phase were tested increasing the oxalic acid composition up to 50 mM or decreasing the HCl concentration down to 10 mM with different columns without an improvement in the peak shape. With the 10 mM HCl–20 mM oxalic acid mobile phase a strong retention of AG10 for both the analytes was observed and even the AG4A-SC selectivity showed a long retention time. Pd and Pt were subsequently eluted by using the (ii) mobile phase or more efficiently with 1 M HNO₃.

The fast elution obtained with the 1 M HNO₃

suggested the evaluation of nitric acid-based eluents. The chromatograms obtained with a new eluent composition, (iv) 10 mM HNO₃, 20 mM oxalic acid, and the use of a lower capacity AG4A-SC column are shown in Fig. 3. Pd and Pt eluted with a very weak peak at the void volume, and with a second symmetric and sharp peak in the case of Pt. During the column washout with 1 M HNO₃ a very strong signal was detected both at *m/z* 105 and *m/z* 195 indicating that the major part of the analytes was not eluted from the column.

Further optimisation of the mobile phase com-

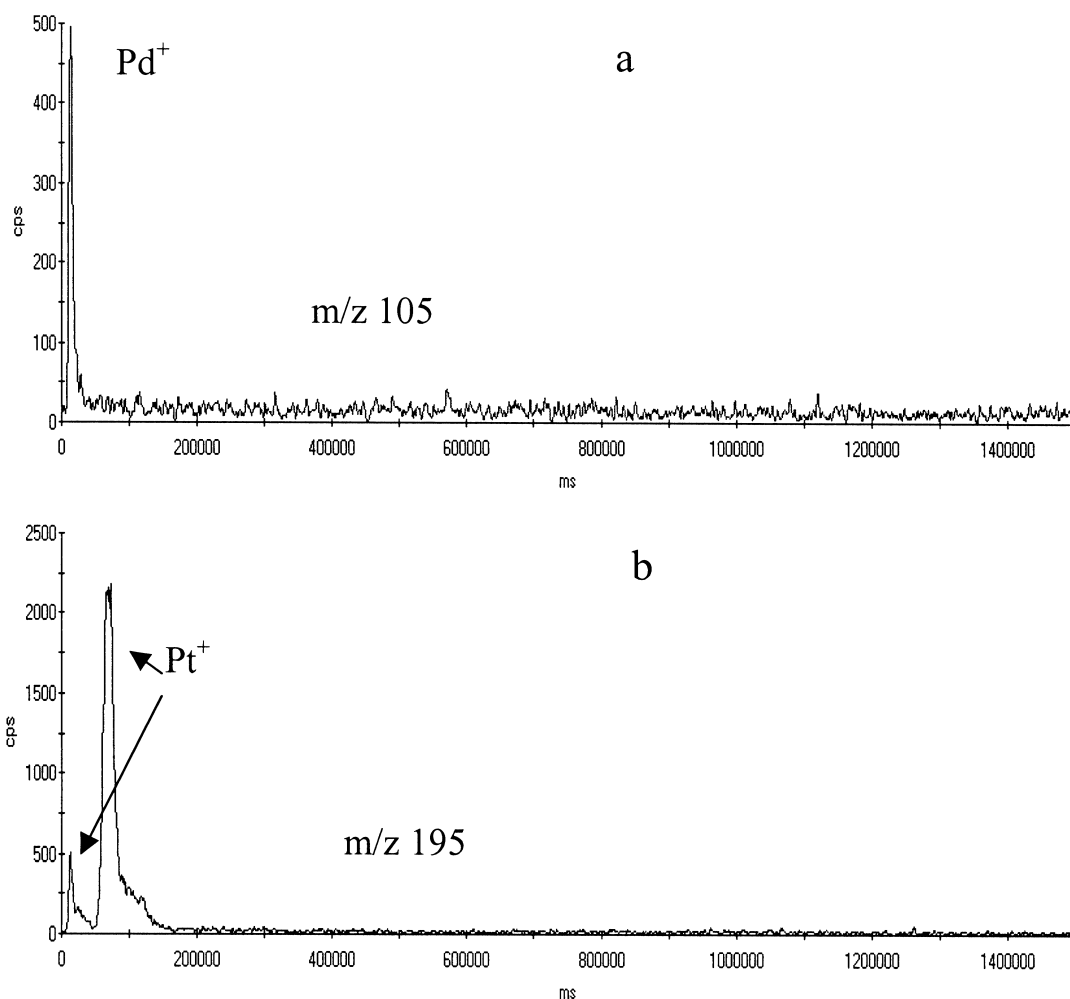


Fig. 3. Chromatograms: (a) *m/z* 105, (b) *m/z* 195; sample, 500 $\mu\text{g l}^{-1}$, of Pd and Pt; column, IonPac AG4A-SC; eluent, 10 mM HNO₃ and 20 mM oxalic acid; flow-rate, 1.2 ml min⁻¹; sample loop, 25 μl .

position, in isocratic mode, gave unsatisfactory results with the main anionic species of Pt and Pd still not eluted.

3.1. Gradient elution

A binary gradient elution was performed starting with a mobile phase composition similar to (iv) (A), then a gradient elution up to 1.5 M HNO₃ (B) followed by an isocratic step of B eluent. A gradient optimisation in terms of initial step time, slope of the ramp and final step duration was carried out and a

comparison between the low capacity columns AG4A-SC and AG11 was made. All the experiments were done with a loop of 250 μl to enhance sensitivity and at a mobile phase flow of 1 ml min⁻¹. The AG11 resulted in a better performance both in terms of retention time and peak symmetry.

After the optimisation procedure the following conditions resulted in the best performances: column, IonPac AG11; eluents, (A) 0.14 M HNO₃ and 18 mM oxalic acid, (B) 1.5 M HNO₃; gradient, 0–3 min eluent A, 3–4 min from A to B, 4–9 min B; flow-rate, 1.0 ml min⁻¹; sample loop, 250 μl;

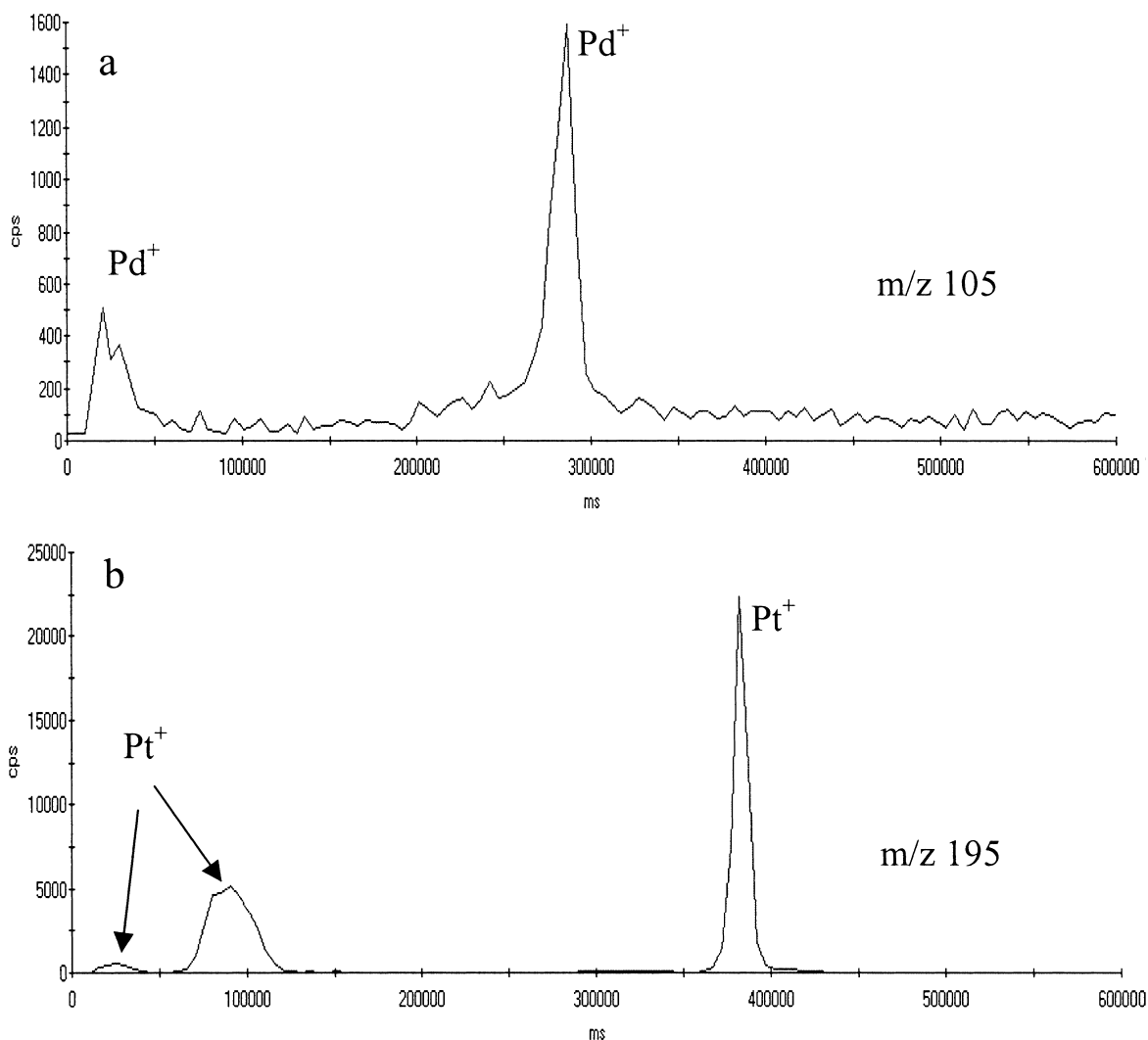


Fig. 4. Chromatograms: (a) m/z 105, (b) m/z 195; sample, 10 μg l⁻¹ of Pd and Pt. Chromatographic conditions, see text.

column reequilibration time, eluent A, 5 min. The separation of Pd and Pt was excellent as demonstrated by chromatograms reported in Fig. 4: both the analytes exhibited two peaks, but only the second has been taken into account for quantitative purposes.

In these conditions a further investigation on interferences has been performed by using standard solutions of Hf and Zr, and the chromatograms are

reported in Fig. 5. A spectral interference is present at m/z 195, but it is completely resolved by the chromatographic separation (Fig. 5d) while the interference at m/z 105 is negligible (Fig. 5b).

3.2. Method validation

The method was validated in terms of detection

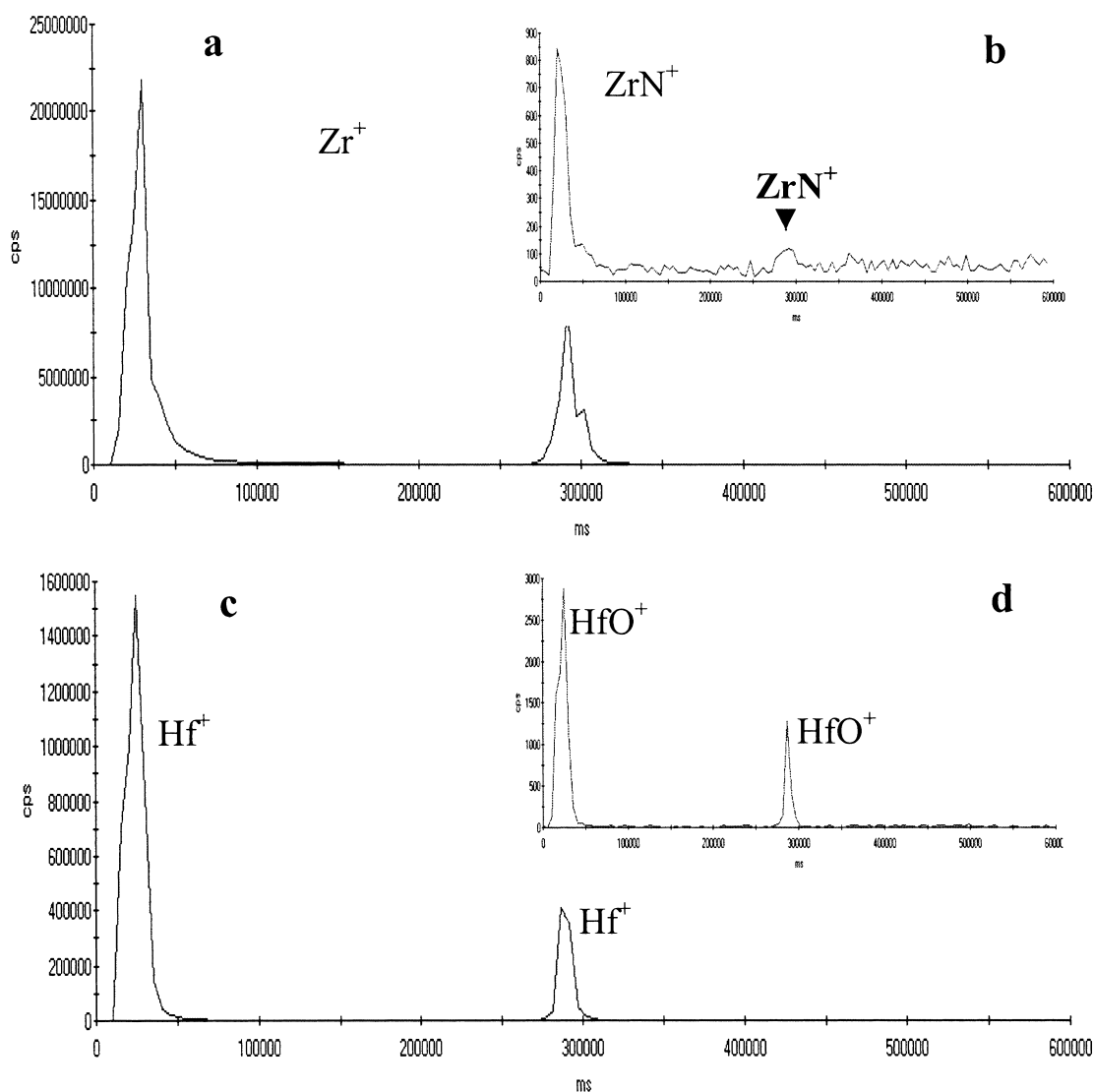


Fig. 5. Chromatograms: (a) m/z 91, (b) m/z 105; sample, 10 mg l^{-1} of Zr. (c) m/z 179, (d) m/z 195; sample, 10 mg l^{-1} of Hf. Chromatographic conditions as in Fig. 4.

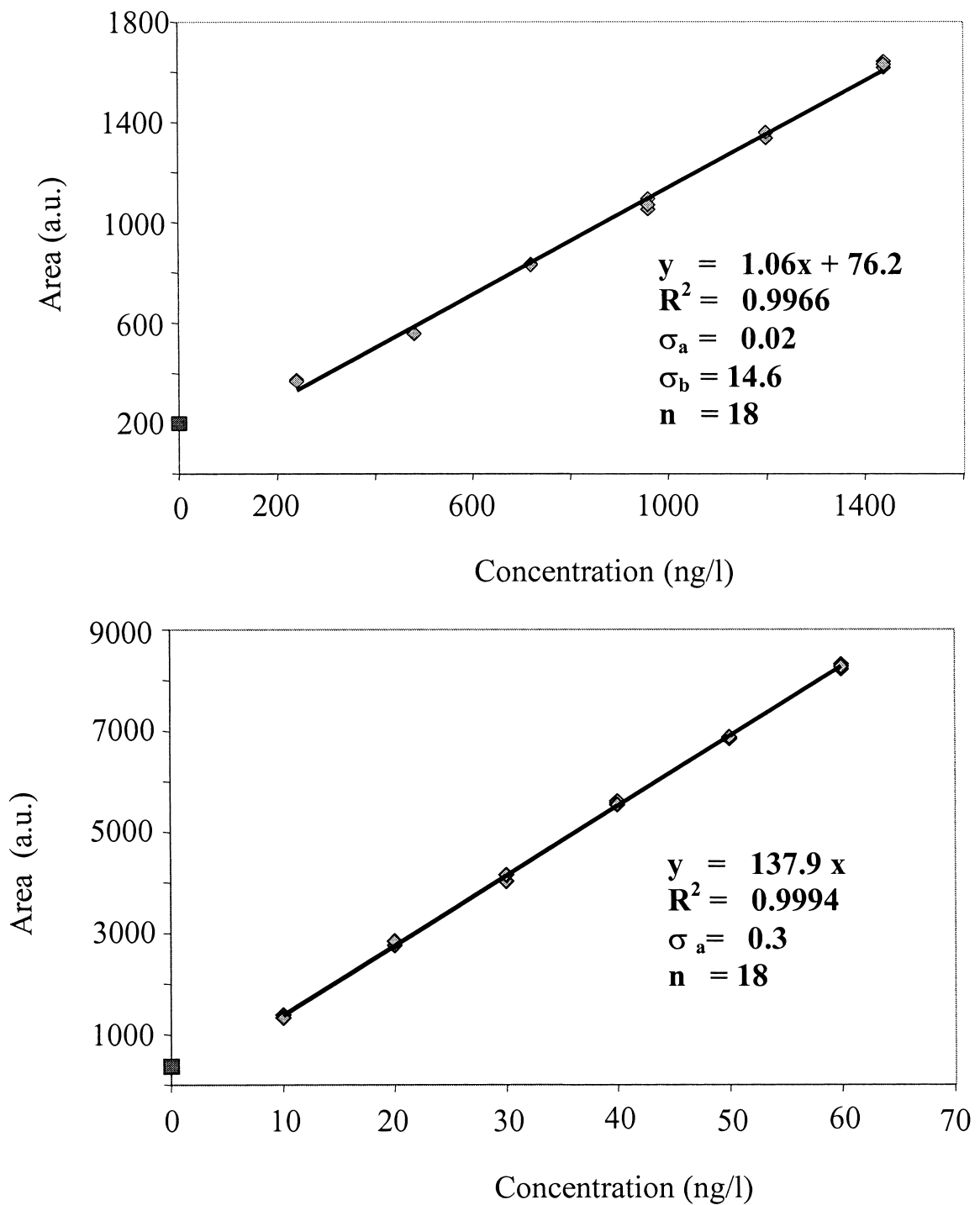


Fig. 6. Calibration curves with statistical parameters used in the calculation of detection and quantification limits for Pd (a) and Pt (b).

limits, quantification limits, linearity and precision by using the experimental setting providing optimised conditions. The integration was performed on the peak at 280 s for the ^{105}Pd chromatogram and on the peak at 380 s for ^{195}Pt . LOD and LOQ values were calculated by constructing an appropriate calibration curve, reported in Fig. 6a for Pd and Fig. 6b for Pt, satisfying the $0.5x_1 \leq \text{LOD} < x_1$ condition (where x_1 is the first concentration level): LOD and LOQ values, respectively, of 5.1 and 9.1 ng l^{-1} were obtained for Pt while 229 and 424 ng l^{-1} resulted in the case of Pd (Table 2): the blank value used was the mean of 20 replicates. A good linearity was also verified in the following ranges: 240–24,000 ng l^{-1} for ^{105}Pd and 10–10,000 ng l^{-1} for ^{195}Pt .

Mandel's fitting test (data not shown) was employed for the verification of linearity, whereas method precision was evaluated testing two concentration levels at 10 ng l^{-1} and 1000 ng l^{-1} for Pt and 500 ng l^{-1} and 5000 ng l^{-1} for Pd with RSD less than 5% in all cases, on a series of 10 measurements. No specific measurement was carried out for intra-day repeatability, since the linearity experiment duration with all the replicates was of more than 30 h and the good values obtained demonstrated an excellent stability and repeatability.

The intermediate precision was evaluated by performing an analysis of variance (ANOVA) on the data acquired over 6 days. ANOVA (data not shown) demonstrated that mean values were not significantly different ($P > 0.05$) at 95% confidence level. Since a reference material with suitable concentration of Pd and Pt was not available, only trueness was checked with spiked samples on three different concentration levels: results are shown in Table 2. The recovery ranged from 99.0 to 99.8% for Pt while the values for Pd were in the interval 101–104%. The values for Pd are not surprising since the value for the

starting sample is below the quantification limit and therefore its content is unknown.

3.3. Sample measurement

The developed method was then used for the determination of Pd and Pt in PM10 particulate. The cellulose nitrate filters were obtained, already weighed, from the local branch of the environmental protection agency (ARPA Emilia-Romagna). The samples used for the recovery test and trueness were taken from a PM10 sampler with a special four-position filter holder. Filters were subsequently treated with aqua regia (6+2 ml) in the microwave oven according to the procedure suggested by the equipment producer. Since a clear solution with a few carbonaceous particles was obtained, no hydrofluoric acid step was performed. The samples were then diluted to a final volume of 25 ml and the carbonaceous particles were left as sediment. The samples were measured in triplicate after a calibration with six standard solutions in the range of 5–30 ng l^{-1} for Pt and 250–750 ng l^{-1} for Pd. In all the samples it was not possible to quantify the palladium content, while the platinum values found are reported in Table 3. As expected, a very strong spectral interference on platinum was found in the samples, but the m/z 195 chromatogram reported in Fig. 7 clearly demonstrated that the problem was solved by the chromatographic separation.

4. Conclusions

It has been demonstrated that potential interferences for ICP-MS detection of Pt and Pd, coming from the matrix in real samples, can be avoided through the optimization of the separation step. Anion chromatographic phases within a gradient elution enable the separation of both interfering cationic species, by co-elution in the void volume, and more strongly anionic species, by their retention, from Pt and Pd. In this way ion chromatographic separation followed by ICP-MS detection allows the determination of Pt and Pd at trace levels with detection limit of 5 ng l^{-1} and 230 ng l^{-1} for Pt and Pd, respectively.

Table 2

Detection and quantitation limits for platinum and palladium. Symbols are according to EURACHEM/CITAC guidelines (L_d , y_D and y_Q expressed as arbitrary unit areas)

Analyte	L_d	y_D	LOD (ng/l)	y_Q	LOQ (ng/l)
Pd	260	320	229.8	527	424.6
Pt	538	670	5.1	1260	9.1

Table 3
Results from PM10 samples and recovery test for the evaluation of trueness

Date collected	PM10 ($\mu\text{g m}^{-3}$)	Pt solution (ng l^{-1})	Pt solid (ng kg^{-1})	Pd solution (ng l^{-1})
16 October 2001	132	9.82 ± 0.21	81.51	N.Q.
17 October 2001	132	13.68 ± 0.16	113.51	N.Q.
30 October 2001	176	14.82 ± 0.13	92.37	N.Q.
31 October 2001	48	13.30 ± 0.14	303.55	N.Q.
Recovery test				
29 October 2001	142	12.58 ± 0.15		N.Q.
Sample + spike1 ^a	141	17.57 ± 0.13		515.4 ± 2.5
Sample + spike2 ^a	140	22.49 ± 0.14		1020.3 ± 1.9
Sample + spike3 ^a	143	27.40 ± 0.17		1516.4 ± 1.3

^a Spikes: (1) Pt 5 ng l^{-1} , Pd 500 ng l^{-1} ; (2) Pt 10 ng l^{-1} , Pd 1000 ng l^{-1} ; (3) Pt 15 ng l^{-1} , Pd 1500 ng l^{-1} . N.Q., not quantified.

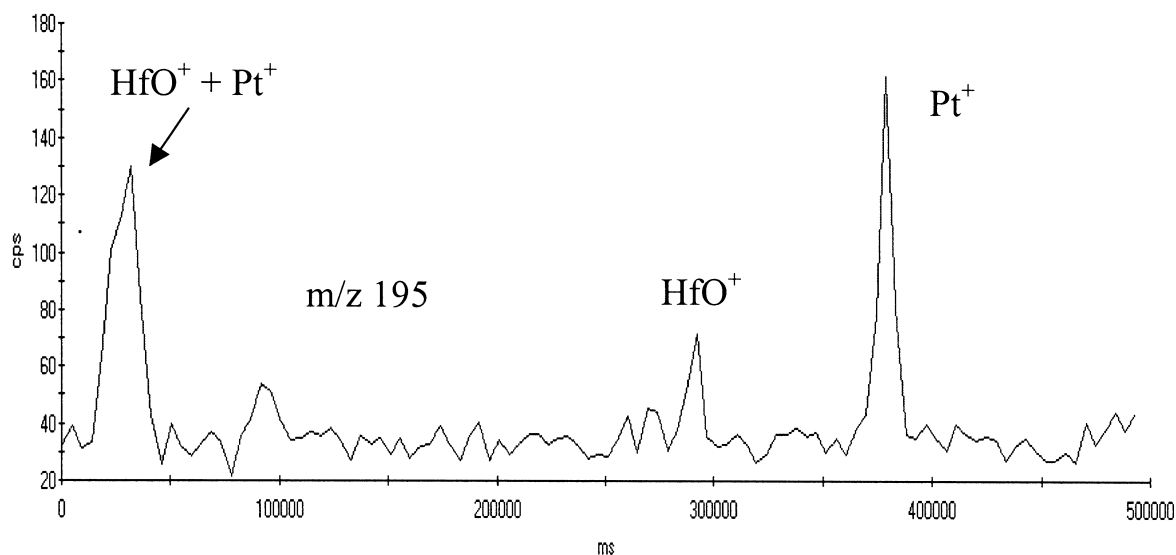


Fig. 7. Chromatogram at m/z 195 of a PM10 sample with the optimised chromatographic conditions (see text).

References

- [1] M.E. Farago, P. Kavanagh, R. Blanks, J. Kelly, G. Kazantzis, I. Thornton, P.R. Simpson, J.M. Cook, H.T. Delves, G.E.M. Hall, *Analyst* 123 (1998) 451.
- [2] C. Wei, G.M. Morrison, *Sci. Total Environ.* 146–147 (1994) 169.
- [3] P. Lucena, J.M. Vadillo, J.J. Laserna, *Anal. Chem.* 71 (1999) 4385.
- [4] E. Helmes, *Environ. Sci. Pollut. Res.* 4 (1997) 100.
- [5] V.I. Savchenko, I.A. Makaryan, *Platinum Metals Rev.* 43 (1999) 74.
- [6] B. Stenbom, *Microstructural Changes in Deactivated Noble Metal Catalysts*, Chalmers University of Technology, Göteborg (S), 1994, Ph.D Thesis.
- [7] P.C. Flynn, S.E. Wanke, *J. Catal.* 37 (1975) 432.
- [8] P. Wynblatt, N.A. Gjostein, *Prog. Solid State Chem.* 9 (1975) 22.
- [9] M.A. Palacios, M. Gomez, *Sci. Total Environ.* 182 (2000) 1.
- [10] H. König, R. Hertel, G. Rosner, *Atmos. Environ.* 26A (1992) 741.

- [11] M. Balcerzac, *Analyst* 122 (1997) 67R.
- [12] M. Georgieva, B. Pihlar, *Fresenius J. Anal. Chem.* 357 (1997) 874.
- [13] B. Godlewska-Zylkiewicz, M. Zaleska, *Anal. Chim. Acta* 462 (2002) 305.
- [14] C.M.G. van den Berg, G.J. Jacinto, *Anal. Chim. Acta* 211 (1988) 129.
- [15] M. Krachler, A. Alimonti, F. Petrucci, K.J. Irgolic, F. Forastiere, S. Caroli, *Anal. Chim. Acta* 363 (1998) 1.
- [16] L. Samuel, K. Nagagawa, T. Kimijima, *Fresenius J. Anal. Chem.* 356 (1996) 31.
- [17] N. Jacobowski, I. Feldmann, D. Stuewer, *Spectrochim. Acta B* 47 (1992) 107.
- [18] D. Wollenweber, S. Straßburg, G. Wünsch, *Fresenius J. Anal. Chem.* 364 (1999) 433.
- [19] S.F. Boulyga, H.J. Dietze, J.S. Becker, *Microchim. Acta* 137 (2001) 93.
- [20] M.B. Gomez, M.M. Gomez, M.A. Palacios, *Anal. Chim. Acta* 404 (2000) 285.
- [21] B. Godlewska-Zylkiewicz, B. Lesniewska, U. Gasiewska, A. Hulanicki, *Anal. Lett.* 33 (2000) 2805.
- [22] D.B. Colodner, E.A. Boyle, J.M. Edmond, *Anal. Chem.* 65 (1993) 1419.
- [23] A. Makishima, M. Nakanishi, E. Nakamura, *Anal. Chem.* 73 (2001) 5240.
- [24] I. Jarvis, M.M. Totland, K.E. Jarvis, *Chem. Geol.* 143 (1997) 27.
- [25] D.G. Pearson, S.J. Wodland, *Chem. Geol.* 165 (2000) 87.
- [26] 1st English ed, *The Fitness for Purpose of Analytical Methods: A Laboratory Guide to Method Validation and Related Topics*, EURACHEM Guide, LGC, Teddington, 1998.