

Determination of Platinum and Rhodium in Environmental Matrixes by Solid Sampling-Electrothermal Vaporization-Inductively Coupled Plasma Mass Spectrometry

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Electrothermal vaporization from a graphite furnace was used in combination with inductively coupled plasma mass spectrometry (ICPMS) for the determination of Pt and Rh in environmental matrixes. Solid samples of tunnel dust, grass, and atmospheric aerosol collected on a cellulose filter could be analyzed directly, such that sample dissolution—which is not self-evident for the determination of platinum group metals—could be avoided. By heating the graphite furnace according to a multistep temperature program, spectral interferences were avoided, since a “dry” plasma was obtained, while “parent” ions such as Cu, Zn, and Pb, giving origin to interfering molecular ions, were vaporized during the thermal pretreatment step. For tunnel dust, the most demanding sample matrix, a mixture of HCl and HF was used as a modifier to stimulate the vaporization of matrix components during the thermal pretreatment step and, hence, to alleviate matrix-induced analyte signal suppression during the actual vaporization step. Calibration was accomplished by means of single standard addition with an aqueous standard solution. The results obtained agreed within the experimental uncertainty with the corresponding reference values (certified values or results obtained using pneumatic nebulization ICPMS), while relative standard deviations of $\leq 15\%$ were typical for both Pt and Rh. In all samples, a Pt/Rh ratio of approximately 6–8 was established. For a typical sample mass of 2 mg, limits of detection were 0.35 ng/g for Pt and 0.05 ng/g for Rh.

Catalytic converters have proven their usefulness in reducing the amount of noxious car exhaust gases (CO, NO_x, and unburned hydrocarbons) released into the atmosphere.¹ The active components of such a catalytic converter are the platinum group metals (PGMs) Pt, Pd, and Rh. These PGMs catalyze the oxidation of CO and unburned hydrocarbons into CO₂ and into H₂O and CO₂, respectively (Pt, Pd), and the reduction of NO_x into N₂ (Rh).² However, as a result of wearing, ultratrace amounts of the aforementioned PGMs are continuously emitted into the atmo-

sphere while driving. To a large extent, this emission rate depends on the catalyst type. For the older pellet-type catalyst, Pt emission rates of 1–2 $\mu\text{g}/\text{km}$ were established,³ while for the more recent monolithic type, emission rates of 1–300 ng/km were reported.^{4–7} Despite the lower emission rate of the latter type, attention is required since due to the low natural abundance of these PGMs, the contribution from catalyst wearing to their total concentration in environmental compartments rapidly becomes the dominant factor and was established to lead to local enrichment.^{8–19}

Little is known about the biological effects of Pt, Pd, and Rh at the low concentration levels at which they currently occur in environmental samples. However, Pt-containing anticancer drugs—cisplatin being the best known—give rise to serious injurious side effects²⁰ (mainly nausea, nephrotoxicity, and hearing problems), while it is also known that (professional) exposure to higher Pt concentrations can potentially result in asthma or dermatitis (platinosis).²¹ Additionally, the fear that these PGMs may enter the food chain is not fictitious. Earlier experiments carried out at

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Table 1. Molecular and Doubly Charged Ions Hampering Accurate Determination of Rh, Pd, and Pt (Nonrestrictive Selection)

analyte nuclide (isotopic abundance, %)	potentially interfering ions (R) ^a
¹⁰³ Rh (100)	²⁰⁶ Pb ²⁺ (1300), ⁸⁷ Sr ¹⁶ O ⁺ (60 000), ⁸⁷ Rb ¹⁶ O ⁺ (73 000), ⁴⁰ Ar ⁶³ Cu ⁺ (7600), ³⁶ Ar ⁶⁷ Zn ⁺ (9500)
¹⁰⁴ Pd (11.1)	¹⁰⁴ Ru (74 400), ⁴⁰ Ar ⁶⁴ Zn ⁺ (8300), ⁸⁸ Sr ¹⁶ O ⁺ (29 800), ²⁰⁸ Pb ²⁺ (1200)
¹⁰⁵ Pd (22.3)	⁴⁰ Ar ⁶⁵ Cu ⁺ (7000), ⁸⁹ Y ¹⁶ O ⁺ (24 400)
¹⁰⁶ Pd (27.3)	¹⁰⁶ Cd (35 500), ⁴⁰ Ar ⁶⁶ Zn ⁺ (7000), ⁹⁰ Zr ¹⁶ O ⁺ (27 500)
¹⁰⁸ Pd (26.5)	¹⁰⁸ Cd (370 000), ⁴⁰ Ar ⁶⁸ Zn ⁺ (6500), ⁹² Zr ¹⁶ O ⁺ (27 400), ⁹² Mo ¹⁶ O ⁺ (49 700)
¹¹⁰ Pd (11.7)	¹¹⁰ Cd (50 800), ⁴⁰ Ar ⁷⁰ Ge ⁺ (5900), ⁴⁰ Ar ⁷⁰ Zn ⁺ (6300), ⁹⁴ Mo ¹⁶ O ⁺ (21 300), ⁹⁴ Zr ¹⁶ O ⁺ (27 900)
¹⁹⁴ Pt (32.9)	¹⁷⁸ Hf ¹⁶ O ⁺ (8100), ¹⁷⁷ Hf ¹⁶ OH ⁺ (11 600)
¹⁹⁵ Pt (33.8)	¹⁷⁹ Hf ¹⁶ O ⁺ (8100), ¹⁷⁸ Hf ¹⁶ OH ⁺ (10 600)
¹⁹⁶ Pt (25.3)	¹⁸⁰ Hf ¹⁶ O ⁺ (8100), ¹⁷⁹ Hf ¹⁶ OH ⁺ (12 000)

^a The mass resolution required for separating the analyte signal from the interfering signal with sector field ICPMS is given in parentheses.

our laboratory showed that Pt—at least when available in a water-soluble form—is efficiently taken up by and incorporated in plants.²² For further and more detailed information on PGM enrichment in various environmental compartments and the associated risks, the reader is referred to a recent book on this subject and the references therein.²³ It is however clear that—although the understanding of the toxicological effects of these PGMs is far from complete—further investigation is required and a continuous monitoring of the concentration of these PGMs in various sample types is mandatory.

However, few analytical techniques show sufficient sensitivity for the determination of Pt, Pd, and Rh in environmental samples. With techniques such as atomic absorption (AAS) or optical emission (OES) spectrometry, preconcentration cannot be avoided.^{24–26} Neutron activation analysis (NAA) is a powerful method for trace element determination, but for the PGMs, the use of matrix/trace separation techniques for enhancing the sensitivity or avoiding interferences is generally also required.^{27–29} Additionally, due to the complexity and cost of the required instrumentation, this method can hardly be considered a routine approach. Stripping voltammetry on the other hand is a powerful technique for the determination of ultratrace amounts of Pt, Pd, and Rh,^{30,31} but the demands in terms of sample pretreatment are very stringent because the technique is very susceptible to interferences. As an example, the determination of Pt requires complete mineralization of the sample, as the occurrence of residual C, surfactants, and HNO₃ leads to severe interferences.³² Therefore, it is generally accepted that, for this kind of analysis,

ICPMS is recommended.³³ However, this does not mean that, with ICPMS, the determination of the PGMs of interest is self-evident and straightforward. On the contrary, PGMs are not only difficult to dissolve, but due to their low concentration in various samples of interest, accurate determination by ICPMS is also jeopardized by the occurrence of many spectral interferences. For Rh, Pd, and Pt, molecular and doubly charged ions potentially hampering their determination are shown in Table 1. Also the mass resolution required for resolving the analyte signal from that of the interfering ion (with sector field ICPMS) has been given.³⁴ Of course, several research groups have tackled this problem of spectral interferences and developed strategies, permitting overlap to be avoided, reduced, or corrected for.

Parent et al.³⁵ reported the determination of Pt in cordierite—a Mg–Fe–Al silicate used as the catalyst body. The merits of three strategies to overcome the overlap of Pt⁺ and HfO⁺ signals were compared. In two of these approaches, the contribution of HfO⁺ to the total signal intensity was mathematically corrected for. The HfO⁺/Hf⁺ ratio was either determined (a) using a Hf standard solution (while the ZrO⁺/Zr⁺ ratios measured in a standard and in the sample solution were used to correct for the influence of the concomitant matrix on the amount of oxide formation) or (b) via addition of Hf to the actual sample solution. In a third approach, Pt and Hf were separated from one another, using adsorption chromatography after chelation of Pt with bis-(carboxymethyl)dithiocarbamate. While the accuracy of the results obtained via mathematical correction was adequate, a poor repeatability was established. After Pt/Hf separation, accurate and precise results could be obtained if isotope dilution was used, providing automatic correction for the nonquantitative and variable recovery of the target element. Müller and Heumann³⁶ determined Pt, Pd, Ru, and Ir in samples of environmental origin (soil, road dust). The materials of interest were dissolved using aqua regia in a high-pressure asher (HPA). Undissolved silicate particles were filtered off after it had been verified that these do not contain a measurable fraction of the target elements. Anion exchange chromatography was used to isolate the target elements from the matrix and, hence, to avoid spectral interferences, while the use of isotope dilution provided automatic correction for nonquantitative

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Table 2. Instrumental Operation Conditions and Data Acquisition Parameters for ETV-ICPMS Measurements

Perkin-Elmer Sciex Elan 5000 ICP Mass Spectrometer			
rf power (W)	1000		
Ar gas flow rates (L/min)			
plasma	12		
auxiliary	1.2		
carrier	1.1		
sampling cone	Ni, 1.0-mm aperture diameter		
skimmer	Ni, 0.75-mm aperture diameter		
lens voltages	<i>a</i>		
Perkin-Elmer HGA-600MS Electrothermal Vaporization Unit			
sample mass (mg)	0.4–0.7 for tunnel dust		
	2–3 for grass/aerosol-loaded filter		
chemical modifier ^{<i>b</i>}	10 μL of 23 M HF + 10 μL of 12 M HCl		
step	temp (°C)	ramp (s)	hold time (s)
drying	100	10	30
slow heating ^{<i>b</i>}	200	30	10
thermal pretreatment	1400	10	30
analyte vaporization	2700	0	10
Data Acquisition Parameters			
scanning mode	peak hop transient		
signals monitored	¹⁰³ Rh ⁺ , ¹⁹⁵ Pt ⁺ , ⁴⁰ Ar ₂ ⁺		
dwell time per acquisition point (ms)	30		
no. of acquisition points per spectral peak	1		
no. of sweeps per reading	1		
total measurement time (s)	10		
data processing mode	integration		

^a Optimized using PN; no further tuning required when switching to ETV. ^b Only for analysis of tunnel dust.

tative recoveries. No attempt was done to also determine the monoisotopic Rh, for which isotope dilution is not applicable. Köllensperger et al.³⁷ attempted to determine Pt, Pd, and Rh in a road dust sample and succeeded in obtaining accurate results without subjecting the sample digests to a trace/matrix separation technique. Interference-free determination of Pt was enabled by using membrane desolvation of the sample aerosol, which provided a sufficient reduction of the HfO⁺/Hf⁺ ratio. For the determination of Rh, aerosol desolvation had to be combined with the highest mass resolution setting ($R = 8000$) of the sector field ICPMS instrument used. Finally, for Pd, even these measures were not sufficient and the contribution of SrO⁺ to the total signal intensity at the mass-to-charge ratio of interest had to be mathematically corrected for. In another paper by the same research group,³⁸ however, anion exchange chromatography—preferably coupled on-line with the ICPMS instrument—was used for interference-free measurement of Pd. Also, Rauch et al.³⁹ attempted to determine Pt, Pd, and Rh in road dust and river sediment samples using a sector field instrument operated at high-mass resolution. Pt and Rh could be measured interference-free as the signals interfering with the determination at low-mass

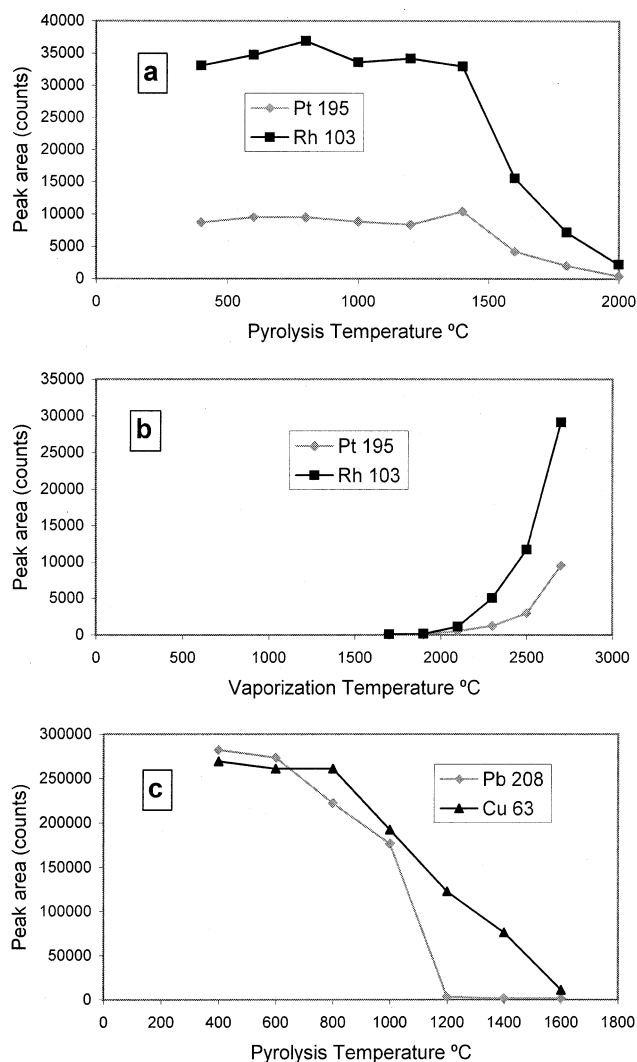


Figure 1. (a) Pyrolysis curves for Pt and Rh. Signal intensities observed for ¹⁰³Rh⁺ and ¹⁹⁵Pt⁺ as a function of the pretreatment temperature, while the vaporization temperature was kept constant at 2700 °C. Amounts vaporized were 10 pg for Pt and 1 pg for Rh in 10 μ L of an aqueous standard solution. (b) Vaporization curves for Pt and Rh. Signal intensities observed for ¹⁰³Rh⁺ and ¹⁹⁵Pt⁺ as a function of the vaporization temperature. Amounts vaporized were 10 pg for Pt and 1 pg for Rh in 10 μ L of an aqueous standard solution. (c) Pyrolysis curves for Cu and Pb. Signal intensities observed for ⁶³Cu⁺ and ²⁰⁸Pb⁺ as a function of the pretreatment temperature, while the vaporization temperature was kept constant at 2700 °C. Amounts vaporized were 100 pg for Cu and 100 pg for Pb in 10 μ L of an aqueous standard solution.

resolution and the analyte signals were resolved from one another at $R = 10000$. The loss in ion transmission efficiency—and, hence, signal intensity—accompanying an increase in mass resolution was counteracted by using a USN for sample introduction. For Pd, even the maximum mass resolution attainable did not suffice to resolve all spectral interferences. Finally, Simpson et al. demonstrated that spectral overlap of the PGM analyte signals with those of oxide ions can be overcome by using O₂ as a reaction gas in a dynamic reaction cell⁴⁰ to convert the interfering MO⁺ species into the corresponding higher oxides MO_n⁺.

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Table 3. Signal Intensity (Peak Area) and Apparent Pt or Rh Concentration Observed for 1 or 100 ng of "Parent" Element (Giving Origin to an Interfering Molecular or Doubly Charged Ion) Introduced into the Furnace^a

parent element interfering ion(s)		blank (Milli-Q water)	"parent" element	
			1 ng	100 ng
Hf ¹⁷⁹ HfO ⁺ and ¹⁷⁸ HfOH ⁺	peak area apparent Pt content (pg)	115 (17)	153 (39) not significant	131 (45) not significant
Cu ⁴⁰ Ar ⁶³ Cu ⁺	peak area apparent Rh content (pg)	591 (82)	644 (90) not significant	1032 (101) 0.014
Zn ³⁶ Ar ⁶⁷ Zn ⁺	peak area apparent Rh content (pg)	591 (82)	617 (92) not significant	453 (40) not significant
Sr ⁸⁷ SrO ⁺ and ⁸⁶ SrOH ⁺	peak area apparent Rh content (pg)	591 (82)	534 (84) not significant	679 (34) not significant
Rb ⁸⁷ RbO ⁺	peak area apparent Rh content (pg)	591 (82)	478 (87) not significant	601 (34) not significant
Pb ²⁰⁶ Pb ²⁺	peak area apparent Rh content (pg)	591 (82)	589 (85) not significant	629 (71) not significant

^a Uncertainties are expressed as standard deviations for $n = 5$ and are given in parentheses.

During the last two decades, the possibilities of electrothermal vaporization (ETV) for sample introduction into ICPMS have been evaluated.⁴¹ However, to the best of our knowledge, the potential that this method shows to directly handle solid samples has not been explored for PGM determination. In this work, an alternative approach for the determination of Pt and Rh was developed by using ETV from a graphite furnace as a means of sample introduction into the ICP. Solid samples were analyzed directly, such that dissolution and the associated risks—incomplete dissolution of the PGMs and contamination—could be avoided while the limits of detection (LODs) and the sample throughput were improved. Additionally, optimization of the multistep temperature program enabled interference-free measurement. No attempt was made to determine Pd in the samples of interest as the setup used is characterized by a high background level of Pd, due to the continuous use of this element as a chemical modifier in other applications.

EXPERIMENTAL SECTION

Instrumentation. A Perkin-Elmer HGA-600MS electrothermal vaporizer coupled to a Perkin-Elmer Sciex Elan 5000 quadrupole-based ICP-mass spectrometer was used. The electrothermal vaporization unit was equipped with a model AS-60 autosampler. Pyrolytic graphite-coated tubes and cups (cup-in-tube technique for solid sampling⁴²) were used throughout. Both the left- and the right-hand contact cylinder were modified (a cutout was made) to permit convenient insertion and removal of the cup. The HGA-600MS was interfaced to the ICP via an 80-cm-length (6-mm-i.d.) Teflon tubing. The operation of the HGA-600MS was completely computer-controlled. During the thermal pretreatment steps of the temperature program, opposing flows of argon gas (0.3 L/min) originating from both ends of the graphite tube removed all the vapors through the dosing hole of the cup. Before the vaporization

step was started, a graphite probe was pneumatically activated to seal this dosing hole. Subsequently, a valve located at one end of the HGA workhead directed the carrier argon flow originating from the far end of the graphite tube directly to the argon plasma at a flow rate of 1.0 L/min. To prevent the cup from being "launched" from the tube when switching from the internal flow (0.3 L/min) to the carrier flow (1.0 L/min), the HGA-600MS was equipped with an adjustable pneumatic delay (Martonair BM/1430).⁴³ A microbalance (Sartorius M3P) with a readability of 1 μ g was used for weighing the samples. The multielement capabilities of the ETV-ICPMS setup were systematically studied and reported on in a previous paper.⁴⁴

For the grass and atmospheric aerosol samples, Pt reference values were obtained using pneumatic nebulization sector field ICPMS after dissolution. For this purpose, an Element sector field ICPMS instrument was used. For sample introduction, the Element is equipped with a Spetec peristaltic pump, a Meinhard Tr-30-A3 concentric nebulizer, and a double-pass Scott-type spray chamber with surrounding liquid jacket, maintained at 5 °C using a recirculating refrigeration–heating system and drained by the peristaltic pump. All measurements were carried out at low-mass resolution ($R = 300$). The signal intensity for ¹⁹⁵Pt⁺ was monitored, while the contribution of HfO(H)⁺ to the total signal intensity (<10%) was mathematically corrected for, whereby the HfO⁺/Hf⁺ ratio was determined on the basis of additions of Hf to the sample solution.³⁵ Ir was added to blank, sample, and standard solutions to act as an internal standard, correcting for nonspectral interferences, signal drift and instrument instability.

Samples and Standards. (1) Reagents and Standards. Water was doubly distilled and further purified using a Milli-Q water purification system (Millipore). The 14 M HNO₃ and 12 M HCl were purified by sub-boiling distillation in quartz equipment. The 23 M HF was obtained from Merck (analytical purity grade). Pt and Rh solutions were prepared from commercially available 1 g/L standards (Merck) by appropriate dilution with 0.12 M HCl.

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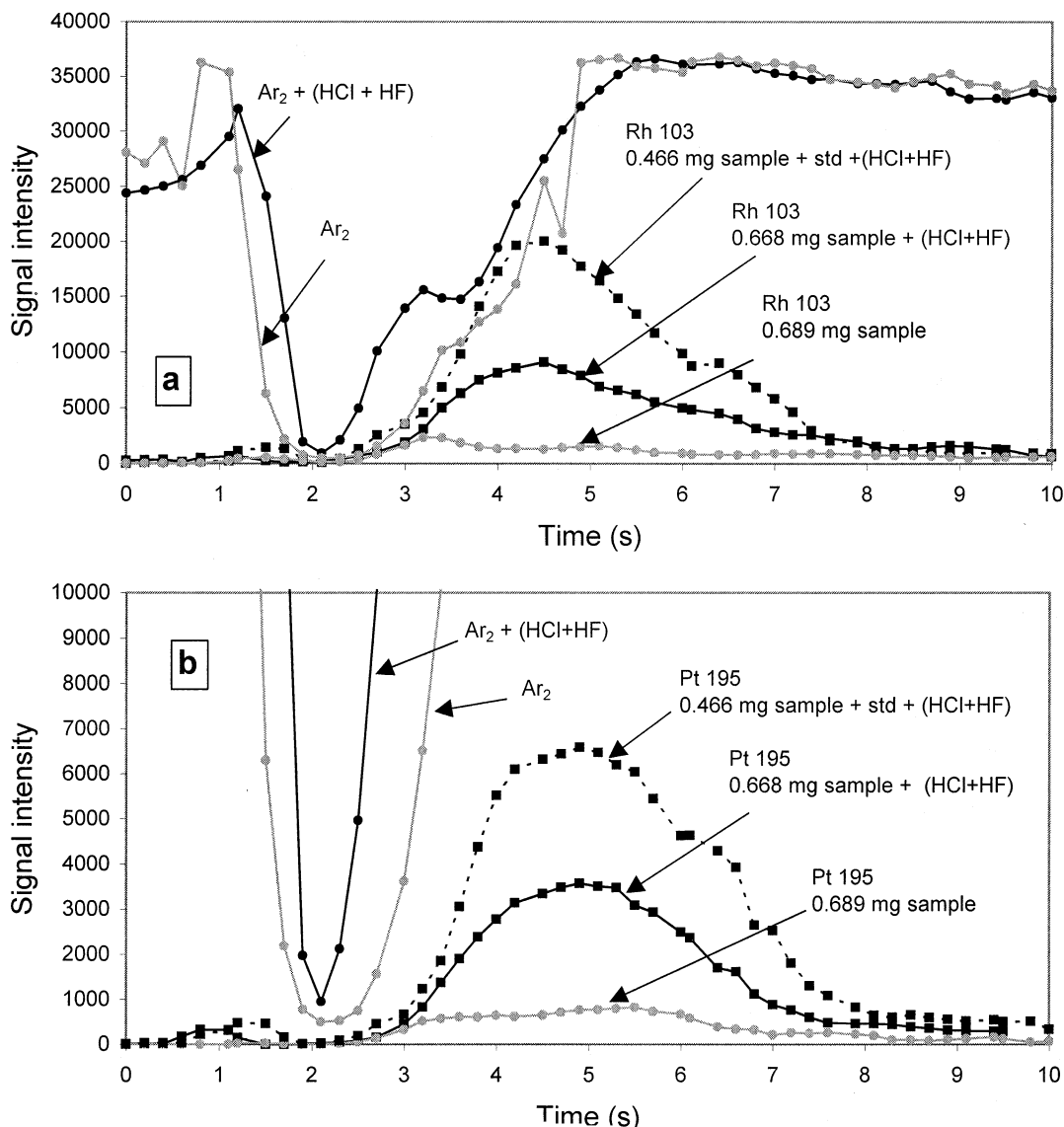


Figure 2. (a) Signal profiles (signal intensity as a function of time) for $^{103}\text{Rh}^+$ and $^{40}\text{Ar}_2^+$ observed on ETV-ICPMS analysis of solid samples of tunnel dust in the absence and presence of a chemical modifier ($10\ \mu\text{L}$ of $12\ \text{M}$ HCl and $10\ \mu\text{L}$ of $23\ \text{M}$ HF): (1) $0.689\ \text{mg}$ of tunnel dust ($8.9\ \text{pg}$ of Rh; peak area 8805 counts); (2) $0.668\ \text{mg}$ of tunnel dust with addition of the chemical modifier ($8.6\ \text{pg}$ of Rh; peak area 30530 counts); (3) $0.466\ \text{mg}$ of tunnel dust with addition of both the chemical modifier and $10\ \text{pg}$ of Rh from an aqueous standard solution ($16.0\ \text{pg}$ of Rh; peak area 57751 counts). (b) Signal profiles (signal intensity as a function of time) for $^{195}\text{Pt}^+$ and $^{40}\text{Ar}_2^+$ observed on ETV-ICPMS analysis of solid samples of tunnel dust in the absence and presence of a chemical modifier ($10\ \mu\text{L}$ of $12\ \text{M}$ HCl and $10\ \mu\text{L}$ of $23\ \text{M}$ HF): (1) $0.689\ \text{mg}$ of tunnel dust ($56\ \text{pg}$ of Pt; peak area 2600 counts); (2) $0.668\ \text{mg}$ of tunnel dust with addition of the chemical modifier ($55\ \text{pg}$ of Pt; peak area 9320 counts); (3) $0.466\ \text{mg}$ of tunnel dust with addition of both the chemical modifier and $100\ \text{pg}$ of Pt from an aqueous standard solution ($138\ \text{pg}$ of Pt; peak area 22310 counts).

(2) Samples. Tunnel Dust. The tunnel dust analyzed was a (candidate) certified reference material (CRM) obtained in the context of our participation in an international certification campaign,⁴⁵ attempting the determination and certification of its contents of the PGMs Pt, Pd, and Rh. Hence, the ETV-ICPMS results could be compared with the corresponding certified values.⁴⁶

Grass. Along the Belgian highways E17 ($>68\ 000$ vehicles/16 h) and E40 ($>62\ 000$ vehicles/16 h), two sampling sites in the

vicinity of Ghent were selected. Grass samples were taken over the full length of the strip ($\sim 2\ \text{m}$) and between 0 and 10 cm from the edge of the road. To evaluate the Pt content found for these sampling sites, samples were also taken at a rural area. As no effort was made to clean the leaf surfaces, the PGM contents determined should be interpreted as the sum of the material deposited on and incorporated into the tissue. After homogenization, the grass samples were weighed and subsequently dried at $60\ ^\circ\text{C}$ to constant weight. The water content was calculated from the weight difference observed. Subsequently, the dry grass was ground using the brittle fracture technique, dried at $60\ ^\circ\text{C}$, and stored in polyethylene vessels kept in a desiccator until analysis.

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Table 4. Solid Sampling ETV-ICPMS Results for the Determination of Pt and Rh in a Tunnel Dust CRM

Pt (ng/g) solid sampling ETV-ICPMS		Rh (ng/g) solid sampling ETV-ICPMS	
A (n = 5)	99.5	A (n = 5)	13.5
B (n = 5)	87.5	B (n = 5)	11.6
C (n = 5)	102.1	C (n = 5)	12.7
D (n = 5)	91.6	D (n = 5)	12.2
E (n = 5)	88.3	E (n = 5)	14.8
F (n = 5)	59.5	F (n = 5)	10.0
G (n = 5)	93.6	G (n = 5)	10.5
H (n = 5)	94.4	H (n = 5)	14.0
I (n = 5)	89.1	I (n = 5)	11.7
J (n = 5)	114.3	J (n = 5)	9.0
average	92.0	average	12.0
st dev	14.0	st dev	1.8
95% CI	10.0	95% CI	1.3
certified value	81.3 ± 4.6	certified value	12.9 ± 1.5

Fractions of this grass sample were also taken into solution for analysis with pneumatic nebulization sector field ICPMS. For this purpose, ~0.3 g of dry grass was taken and transferred into a quartz destruction vessel (content, 30 mL); 2.0 mL of 14 M HNO₃ and 0.5 mL of 10 M HCl were added and the sample was subjected to a heating program (40 min at 120 °C, 90 min at 240 °C) in a high-pressure asher (Kürner). After destruction, the content of the each quartz vessel was quantitatively transferred to a 25-mL volumetric flask, which was adjusted to volume using 0.1 M HCl. Five samples were prepared per sampling site. Blanks were obtained using the same procedure but with no sample intake.

Atmospheric Aerosol. Atmospheric aerosol was collected from the aforementioned sampling site along highway E17 on a Whatman No. 41 cellulose filter according to the VDI-2463 procedure.⁴⁷ A high-volume sampler (Becker VT25) was used at an air flow rate of ~20 m³/h for sampling purposes, while the total volume of air the particles with an aerodynamic equivalent diameter of <100 µm were sampled from was measured using a dry gas meter (Contigea G25). The sampling period was 48 h. Fractions (0.2 g) of the filter were also taken into solution using the same dissolution procedure as used for the grass, and the digests obtained were appropriately diluted and subjected to analysis using pneumatic nebulization sector field ICPMS for obtaining reference values for Pt.

Procedure for Solid Sampling ETV-ICPMS. For tunnel dust and grass, appropriate amounts of sample were introduced into the sample cup and their weight was accurately determined. For aerosol-loaded filter material, the sample was first weighed and subsequently loaded into a sample cup using a pair of tweezers coated with PTFE to prevent contamination. In both cases, the sample cup was then inserted into the furnace for subsequent analysis using an insertion tool available from Perkin-Elmer. Finally, the chemical modifier (tunnel dust only) was added using the autosampler. The operating conditions are summarized in Table 2.

Every determination consisted of (1) the monitoring of the blank value—three replicates of an empty cup (grass), of the

chemical modifier (tunnel dust), or of a blank filter (aerosol-loaded filter); (2) five replicate measurements of the sample (0.4–0.7 mg for tunnel dust; 2–3 mg for grass and aerosol-loaded filter); and (3) five replicate measurements of the sample to which 10 µL of Rh and Pt standard solution was added. The concentration of the standard solution was always selected such that the amounts of Pt and Rh added were at least similar to that in the samples. For the measurement of the solid samples and the solid samples plus the standards, the median of the five replicates was taken as the representative value instead of the mean. In this way, it is possible to avoid the detrimental influence of possible outliers.⁴⁸ One determination can be carried out in approximately 25–30 min (35–40 min for the tunnel dust).

RESULTS AND DISCUSSION

Graphite Furnace Temperature Program. As in the literature, the determination of PGMs by means of graphite furnace AAS has been reported,^{24–26} ETV-ICPMS should be capable of sensitive PGM analysis, especially since AAS requires atomization of the target elements, while in the case of ETV-ICPMS, volatilization, enabling transport of the target elements into the ICP, suffices. Grégoire described the use of solution ETV-ICPMS for the determination of higher concentrations of PGMs in geological samples,⁴⁹ but the major difficulty for the determination of ultratrace amounts of these elements in environmental matrixes is the risk of spectral overlap (cf. Table 1). Marshall and Franks⁵⁰ demonstrated that since the use of ETV for sample introduction gives rise to a “dry” plasma, the signal intensity for O-containing molecular ions is substantially reduced. In earlier work,^{44,51} it was demonstrated that, by using an appropriate furnace temperature program, the vaporization of elements with a different volatility can be separated from one another in time. Therefore, the graphite furnace temperature program was optimized to achieve complete removal of spectral interferences and a maximum signal-to-background ratio.

Optimization of the temperature program was carried out using a standard solution containing Pt and Rh. Aliquots introduced into the furnace contained 10 pg of Pt and 1 pg of Rh. The results obtained are summarized in Figure 1a and b. Figure 1a shows that a thermal pretreatment temperature up to 1400 °C can be used without resulting in premature analyte losses. Optimization of the vaporization temperature on the other hand (Figure 1b) shows that, due to the refractory character of the target elements, the maximum attainable temperature (2700 °C) should be used. The large difference in sensitivity established is mainly the result of the differences in isotopic abundance between the analyte nuclides monitored (100% for ¹⁰³Rh versus 33.8% for ¹⁹⁵Pt) in ionization potential (7.46 V for Rh versus 9.0 V for Pt) and possibly also in vaporization efficiency.

If thermal pretreatment is carried out at 1400 °C, Cu and Pb—the presence of which gives rise to the occurrence of interfering molecular ions, such as ⁴⁰Ar⁶³Cu⁺ and ²⁰⁶Pb²⁺ (Table 1)—are efficiently removed (Figure 1c). It was already demonstrated in a previous paper that Zn, which may give rise to ³⁶Ar⁶⁷Zn⁺, is also

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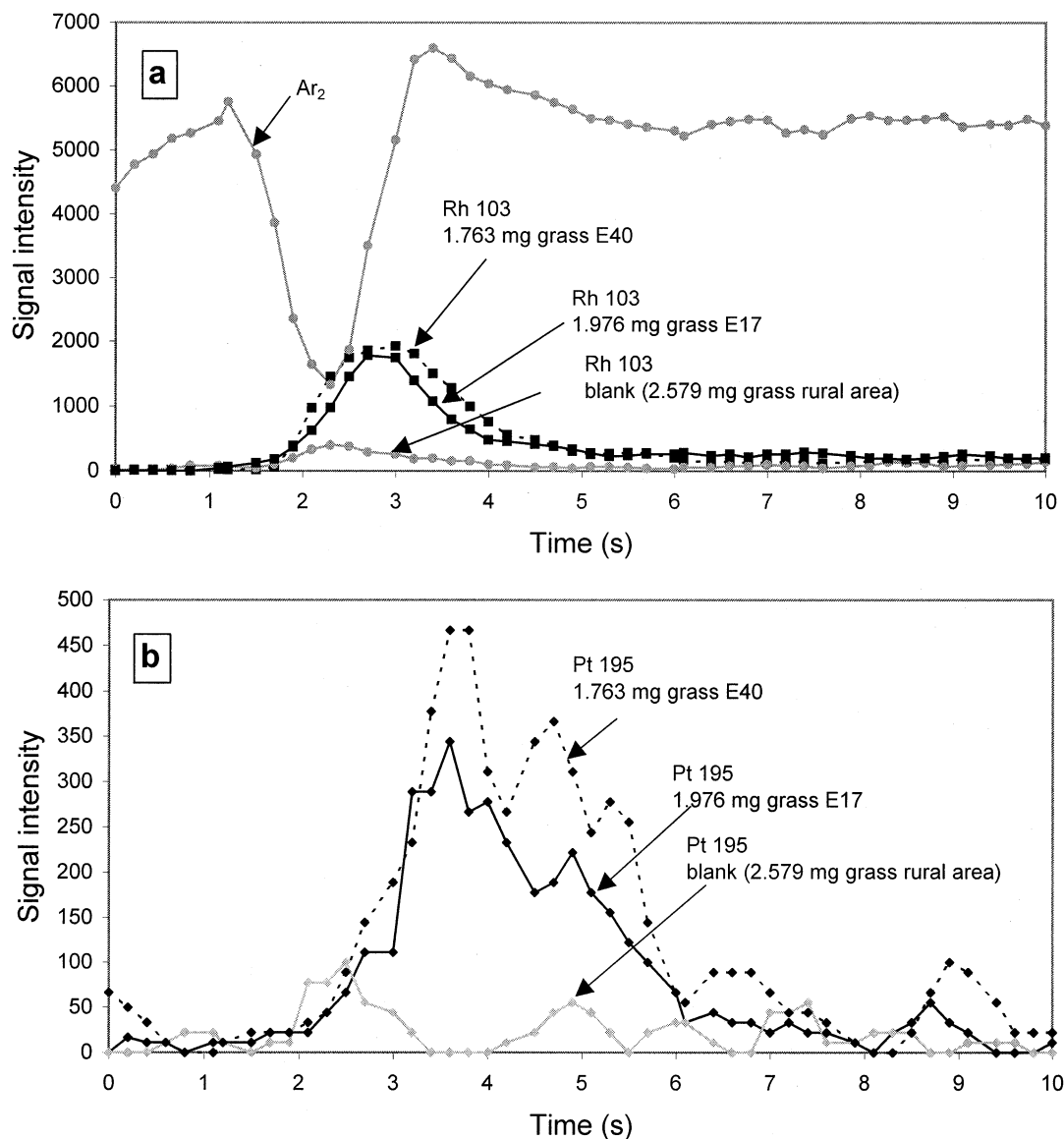


Figure 3. (a) Signal profiles (signal intensity as a function of time) for $^{103}\text{Rh}^+$ and $^{40}\text{Ar}_2^+$ observed on ETV-ICPMS analysis of solid samples of grass: 1.976 mg of grass from E17 (Rh ~ 0.4 pg; peak area 4072 counts); 1.763 mg of grass from E40 (Rh ~ 0.4 pg; peak area 4497 counts); 2.579 mg of grass from rural area (Rh peak area 1178 counts). (b) Signal profile (signal intensity as a function of time) for $^{195}\text{Pt}^+$ observed on ETV-ICPMS analysis of solid samples of grass: 1.976 mg of grass from E17 (Pt ~ 3 pg; peak area 909 counts); 1.763 mg of grass from E40 (Pt ~ 3 pg; peak area 1216 counts); 2.579 mg of grass from rural area (Pt peak area 219 counts).

completely removed at this temperature.⁴⁴ The experimental conditions and data acquisition parameters used for analysis are summarized in Table 2. To obtain the lowest LODs possible, the major isotopes (^{103}Rh and ^{195}Pt) were used for both elements of interest. The argon dimer ($^{40}\text{Ar}_2^+$) signal was monitored as an indication of signal suppression as a result of matrix components covolatilizing with the analyte elements.⁵²

From Table 1, it can be seen that molecular ions containing Cu, Zn, Rb, Sr, and Hf and doubly charged ions of Pb interfere with the determination of Pt and Rh at the mass-to-charge ratios of interest. In the tunnel dust, these "parent" elements are present at a concentration level of $\sim 100 \mu\text{g/g}$, which is 3–4 orders of magnitude higher than that of the target elements (10–100 ng/g). By using standard solutions, the efficacy of the temperature

program in removing these parent elements was systematically investigated. The results are summarized in Table 3. From the "apparent" analyte concentrations observed on analysis of solution aliquots containing 100 ng of the parent element (which corresponds to a $100 \mu\text{g/g}$ level for a typical sample mass of 1 mg), it is clear that the thermal pretreatment succeeds in reducing the contribution to the total signal to an acceptable level. In fact, in all but one (Cu) instances, the signal obtained was not significantly different from the corresponding blank value (empty cup).

Chemical Modification for the Analysis of Tunnel Dust.

After optimization of the furnace temperature program (using standard solutions), solid samples of the tunnel dust were subjected to analysis. Monitoring of the argon dimer ($^{40}\text{Ar}_2^+$) signal revealed that the analyte signals were subject to serious signal suppression (Figure 2). The tunnel dust matrix contains refractory oxides at the percent level— SiO_2 , CaO , and Al_2O_3 —that covolatilize

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Table 5. Solid Sampling ETV-ICPMS Results for the Determination of Pt and Rh In/On Grass Sampled along the E17 and E40 Highways^a

Pt (ng/g) E17 solid sampling ETV-ICPMS		Rh (ng/g) E17 solid sampling ETV-ICPMS	
A (n = 5)	1.44	A (n = 5)	0.24
B (n = 5)	1.48	B (n = 5)	0.18
C (n = 5)	1.36	C (n = 5)	0.26
average	1.43	average	0.23
st dev	0.06	st dev	0.04
95% CI	0.16	95% CI	0.10

pneumatic nebulization ICPMS	
average	1.65
st dev	0.13
95% CI	0.16

Pt (ng/g) E40 solid sampling ETV-ICPMS		Rh (ng/g) E40 solid sampling ETV-ICPMS	
A (n = 5)	1.51	A (n = 5)	0.17
B (n = 5)	1.29	B (n = 5)	0.20
C (n = 5)	1.56	C (n = 5)	0.24
average	1.46	average	0.20
st dev	0.14	st dev	0.03
95% CI	0.36	95% CI	0.09

pneumatic nebulization ICPMS	
average	1.75
st dev	0.15
95% CI	0.19

^a The Pt reference values were obtained by means of pneumatic nebulization sector field ICPMS after sample dissolution.

Table 6. Solid Sampling ETV-ICPMS Results for the Determination of Pt and Rh in Atmospheric Aerosol Collected on a Whatman No. 41 Cellulose Filter^a

Pt (ng/g) solid sampling ETV-ICPMS			Rh (ng/g) solid sampling ETV-ICPMS		
	filter	aerosol		filter	aerosol
A (n = 5)	6.08	95.5	A (n = 5)	1.00	15.7
B (n = 5)	6.45	101.3	B (n = 5)	0.95	14.9
C (n = 5)	6.63	104.1	C (n = 5)	0.94	14.7
average	6.4	100.3	average	0.96	15.1
st dev	0.3	4.4	st. dev.	0.03	0.5
95% CI	0.7	10.9	95% CI	0.08	1.3

Pt (ng/g) pneumatic nebulization ICPMS	
	aerosol
average	115.4
st dev	3.4
95% CI	4.2

^a The Pt reference value was obtained by means of pneumatic nebulization sector field ICPMS after sample dissolution.

with the analyte elements and give origin to nonspectral interferences. Therefore, it was determined whether the addition of an aliquot of a concentrated acid (HF, HCl, or HNO₃) improved the situation. A mixture of HF and HCl was found to offer the best performance and resulted in a 4-fold enhancement of the analyte signal intensities. The signal enhancement observed can be the result of (a) a more efficient removal of matrix compounds during

the sample pretreatment step, such that the signal suppression is mitigated, or (b) the formation of more volatile analyte compounds during the vaporization step, leading to an increased analyte transport efficiency and, hence, signal intensity. The latter hypothesis had to be abandoned since, for a standard solution, the signal intensities for ¹⁹⁵Pt⁺ and ¹⁰³Rh⁺ were not affected on addition of HCl and HF. Although halide compounds of the PGMs may be volatile (e.g., boiling point of RhCl₃, 717 °C), they can probably not be formed under the reducing conditions in the graphite furnace, but a reduction to metallic Pt and Rh probably occurs instead.⁵³ From Figure 2, on the other hand, the ⁴⁰Ar₂⁺ signal reveals a slight reduction in signal suppression on addition of the HCl/HF mixture. Finally, for the tunnel dust, an additional heating step at a moderate temperature (200 °C) was required since immediate thermal pretreatment at 1400 °C brings about a violent reaction between the acids added and the matrix. On occasion, this violent reaction even resulted in removal of the cup out of the tube. This additional step was not required for the grass samples or for the aerosol-loaded cellulose filters (for which no acids were added). It should also be mentioned that it was assured that the use of this modifier did not introduce additional interferences—the possible formation of ⁶⁸Zn³⁵Cl⁺ and ⁶⁶Zn³⁷Cl⁺ is not a problem as any Zn present would be volatilized during the thermal pretreatment, as is discussed in the previous section.

Nevertheless, when a mixture of HCl and HF is used as a chemical modifier, the ⁴⁰Ar₂⁺ signal reveals that signal suppression remains important. Therefore, the signal intensity for identical amounts of a target element in (a) a standard solution and (b) a solid sample of tunnel dust, respectively, was observed to be substantially different, and therefore, external calibration using an aqueous standard solution was not feasible. Therefore, the merits of single standard addition with an aqueous standard solution were tested, as this approach was proved successful in the majority of the solid sampling ETV-ICPMS work, carried out at our laboratory.⁵⁴ By plotting the analysis results (Pt and Rh concentration) as a function of the amount of tunnel dust sample introduced into the furnace, a negative trend was observed above a sample mass of 0.7 mg. Above the latter value, the sample can no longer be adequately pretreated or the matrix-induced signal suppression becomes too pronounced. Since working with sample masses below 0.4 mg becomes impracticable, sample masses between 0.4 and 0.7 mg were used for analysis of the tunnel dust.

Sample Analysis. Subsequently, the approach developed was used for the analysis of the tunnel dust candidate CRM. Ten analyses, each consisting of three measurements of the blank (see the Experimental Section for a description), five measurements of the sample (0.4–0.7 mg), and five measurements of the sample to which an appropriate amount of standard solution was added, were carried out. For each of the 10 replicate determinations, the median is given in Table 4. The average of these 10 values shows a good agreement with the corresponding reference value for both analyte elements,⁴⁶ while the precision—~15% relative standard deviation (RSD)—is adequate for the purpose, taking into account the low analyte concentrations involved. Probably this rather high value has to be attributed to some heterogeneity in the distribution

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of the trace elements over the sample matrix at the submilligram amounts of sample taken. Additionally, it is worth pointing out that the experimental Pt/Rh elemental ratio obtained—7.7, standard deviation of 1.6—is in agreement with that reported by Petrucci et al. for roadside dust.⁵⁵

The analytical approach developed was also used for the determination of Pt and Rh in grass sampled along highly trafficked highways in the vicinity of Ghent. From the signal profiles presented in Figure 3, it can be seen that, for both Pt and Rh, there is a significant difference in analyte signal intensity, and hence, analyte content, between grass originating from a rural area and that sampled along the E17 and E40 highways. Matrix removal is easier for material of plant origin than for the tunnel dust,⁵⁶ and therefore, no modifier (HCl and HF) was added. The PGM concentration in/on grass is a factor 50 lower than that in the road dust. However, owing to the more efficient matrix removal during the thermal pretreatment step, and hence, the reduced signal suppression, sample amounts of 2–3 mg could be used for grass. The results obtained are summarized in Table 5. For Pt, the result obtained compares well with the reference value obtained using pneumatic nebulization sector field ICPMS, after sample dissolution. Due to the extremely low concentration, no reliable reference value could be obtained by means of pneumatic nebulization sector field ICPMS for Rh (the LOD was not sufficiently low). Nevertheless, it can be pointed out that the Pt/Rh elemental ratio obtained for grass by means of ETV-ICPMS—6.2, standard deviation of 1.1 for E17 samples and 7.3, standard deviation of 1.3 for the E40 samples—is nearly identical to that observed in road dust. As this was the sample with the lowest analyte content, experiments were carried out to calculate the LODs for both analytes. These were found to be of 0.35 ng/g for Pt and 0.05 ng/g for Rh for a sample mass of 2 mg (3s definition). Although comparison of LODs is not always self-evident as these values depend to a large extent on the sample preparation, it is obvious from ref 33 that these values are better than or at least competitive with those of other approaches.

Finally, the contents of Pt and Rh were also determined in atmospheric aerosol, collected on a cellulose filter. Fractions of the filter (2–3 mg) were introduced into the furnace and analyzed.

The results obtained were summarized in Table 6, where they are expressed in both (a) nanogram of analyte element per gram of sample and (b) nanogram of element per gram of collected airborne particles. The total mass of atmospheric particles collected on the filter was determined by weighing the (dried) filter before and after sampling. Also, in this instance, the Pt/Rh elemental ratio—6.6, standard deviation of 0.4—shows a fair agreement with that in roadside dust. Finally, for Pt, the solid sampling ETV-ICPMS result is in good agreement with the reference value, obtained using pneumatic nebulization sector field ICPMS after sample dissolution.

CONCLUSIONS

This work has demonstrated that ETV-ICPMS is capable of providing sufficiently accurate and precise analysis results for the ultratrace contents of Pt and Rh in samples of environmental interest (road dust, plant material, atmospheric aerosol collected on a filter). By optimizing the furnace temperature program, the occurrence of spectral interferences can be avoided, as a result of removal of the parent ions during the thermal pretreatment step. As solid samples are analyzed directly, no dissolution is required and the sample throughput is considerably increased (one determination requires ~30 min). For a typical sample mass of 2 mg, LODs of 0.35 ng/g for Pt and 0.05 ng/g for Rh were obtained. In this work, no attempt was made to determine Pd as well, due to “historical” contamination of the ETV unit used. However, on the basis of the furnace behavior of the parent ions giving origin to molecular ions interfering with the determination of this target element and our previous experiences with this element,⁵⁷ also determination of this PGM should be possible.

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