



Determination of anthropogenic input of Ru, Rh, Pd, Re, Os, Ir and Pt in soils along Austrian motorways by isotope dilution ICP-MS

Johannes Fritsche, Thomas Meisel*

General and Analytical Chemistry, University of Leoben, Franz-Josef-Strasse 18, 8700 Leoben, Austria

Received 3 June 2003; received in revised form 21 November 2003; accepted 29 November 2003

Abstract

A joint study with the Federal Environment Agency of Austria was carried out to determine the distribution of Ru, Rh, Pd, Os, Ir and Pt (PGE) and Re in soils along major motorways. Emphasis was put on Ir as to date little is known about its anthropogenic input as this metal is now also used in automobile catalytic converters. Soil samples were analysed by ICP-MS through online-coupling of a chromatographic column to separate the PGEs from interfering matrix constituents. At all sampled sites not only Rh, Pd and Pt but also Ir and Re significantly exceed natural background values; concentrations reached 13 ng/g, 25 ng/g, 134 ng/g, 1.1 ng/g and 9.8 ng/g, respectively. The analytical procedure proved to be very selective and sensitive, and therefore applicable to routine soil analysis. © 2003 Elsevier B.V. All rights reserved.

Keywords: Platinum group elements; Rhenium; Catalytic converter; Soil; Isotope dilution

1. Introduction

In order to abate the ever increasing emissions from automobiles, legislation in many countries has set limit values for the main exhaust pollutants HC, CO and NO_x. These values are revised continually and reflect the state of the art in emission abatement technology. The only way to meet the limit values in cars equipped with gasoline engines is through the installation of catalytic converters. In Austria the application of this technology has been mandatory since 1987 and as of the year

2000 approximately 52% of all registered cars have been fitted with catalytic converters (UBA, 2001).

Even though the catalytic converter has played a vital role in reducing the emissions of noxious substances, it has also gained attention due to the emission of platinum, palladium and rhodium – elements of the platinum group (PGE) which catalyse the conversion of HC, CO and NO_x to H₂O, CO₂ and N₂. Platinum, Pd and Rh have triggered concern as the increasing release of these elements may pose a future health risk (Gebel, 1999; Gomez et al., 2002; Merget and Rosner, 2001; Palacios et al., 2000).

From its introduction in automobiles in the 1970s to its current technology, the catalytic con-

*Corresponding author. Tel.: +43-3842-402-1200; fax: +43-3842-402-1202.

E-mail address:
thomas.meisel@notes.unileoben.ac.at (T. Meisel).

verter has gone through several phases of development. Initially only HC and CO were treated in the Pt-based oxidation catalyst. Now widely used are the three-way catalysts based on Pt and Rh with a ratio of 5:1 and the high temperature three-way catalyst with variable combinations of Pt, Pd and Rh (e.g. 5:1 in a Pd/Rh catalyst or 1:14:1 in a Pt/Pd/Rh catalyst); (Amatayakul and Ramnäs, 2001; Heck and Farrauto, 2001; Zereini et al., 1997a). These catalytic converters contain 1–3 g of precious metals, depending on the size of the vehicle engine (Zereini et al., 1993). More recently Ir is also applied as active metal by some automobile manufacturers (Rao and Reddi, 2000). To meet stringent standards of future emission regulations, new technologies for low and ultra low emission vehicles (LEV and ULEV) are tested. Catalytic converters for such vehicles work at temperatures up to 1050 °C and contain a higher precious metal loading at an increased converter volume. Progress has also been made in the development of applications for diesel engines. Catalytic converters in diesel engines have to deal with high loads of soot, unburned fuel and sulfates and therefore require sophisticated technologies to convert exhaust emissions (Farrauto and Heck, 1999; Heck and Farrauto, 2001; Rabl, 2002). Currently, the diesel oxidation catalyst based on Pt and Pd is used to oxidise CO and HC in the engine exhaust gas (Moldovan et al., 2002).

Through chemical and thermal processes, PGEs bound to aluminium oxide particles are abraded from the converter surface and released into the environment at a rate of approximately 0.5 µg of Pt per kilometre (Helmers, 1997; Merget and Rosner, 2001). Recent studies indicate that a minor fraction of the PGEs is not emitted in elemental form but in compounds of various solubility, e.g. palladium nitrate (Amossé and Delbos, 2002).

Generally PGEs show little mobility in soils under natural conditions. However, evidence suggests that certain PGE-species bound to soil particles could be remobilised and thus enter the food chain through uptake by plants (Hees et al., 1998; Lustig and Schramel, 2000; Zereini et al., 1997b).

Few data are available to evaluate the health risk of automotive PGE-emissions. It is known that certain Pt species have a sensitising potential

and that metallic Pd can cause contact dermatitis. There is no evidence that Pt and Pd as well as Rh and Ir pose any health risk to the general population (Gebel, 1999; Merget and Rosner, 2001).

Various studies have been carried out to investigate the abundance of Pt, Pd and Rh in roadside soils, but information is sparse about any Ir accumulation. Results of the most investigations confirmed significant accumulations of Pt, Pd and Rh and showed characteristic distribution patterns. Concentrations decreased to natural background levels within a few metres from the edge of the traffic lane and within a few centimetres from the soil surface. Furthermore, concentrations of Pt, Pd and Rh clearly correlate with traffic density, vehicle speed and concentrations of other traffic borne heavy metals accumulated in roadside soils (e.g. Cu, Zn, Pb). To date in Austria no information is available about the distribution of PGEs in any environmental compartment.

Abundance of PGEs in the immediate vicinity of heavily travelled roads may exceed natural background levels by a factor of 100 or more but mostly lie below 100 ng/g. Moreover, constituents of the complex soil matrix may cause severe interferences during PGE-determination. Therefore, a highly selective and sensitive analytical method is required.

A survey in cooperation with the Federal Environment Agency of Austria was carried out to determine the distribution of traffic borne PGEs in roadside soils. The results will set a base of knowledge for further investigations of other environmental compartments. The use of iridium as a novel active metal in catalytic converters ought to be reflected in elevated concentrations in roadside soils. By application of a new analytical procedure, essential information will be obtained for routine PGE-analysis of soils. Last but not least, the whole procedure would be greatly simplified if sufficiently accurate PGE-concentrations could be determined by means of microwave digestion.

2. Experimental

2.1. Sites and sampling

In order to determine the distribution of PGEs and Re, roadside soil samples from five major



Fig. 1. Soil sampling sites of roadsides along major Austrian motorways.

traffic routes across Austria were analysed. Their location is shown in Fig. 1. The sites were selected upon several criteria such as traffic density, access to roadside, elevation and gradient of the traffic line. Only grass-covered sites without any barriers that could intercept airborne particles were considered. Table 1 lists all sampled sites with their corresponding characteristics. All motorway sections, except the one on the A9, were opened prior to 1987, so the respective soil samples mirror the complete PGE accumulation since the introduction of the catalytic converter. In addition to roadside soils, samples were taken from Lungau, an alpine region with negligible traffic, which represented an ideal, unpolluted reference site.

At each site a transect of six samples was set up. Each sample consisted of 20 subsamples, which were taken along parallel lines at three different distances from the edge of the road (0.2, 2 and 10 m) and in two depth ranges (0–5 and 5–10 cm from the soil surface). Depending on the

accessibility of the sites the subsamples represented a road section between 50 and 100 m.

Two samples in those depth ranges already mentioned were taken from the reference site in Lungau, again with 20 subsamples each, spread over an area of approximately 200 m². All the 32 samples with 4–6 kg of soil per sample were collected.

2.1.1. Reagents and standards

Hydrochloric and nitric acid used for sample digestion as well as diluted hydrochloric acid required as eluent were subboiled before use. Water for all acid dilutions was of ultrapure grade (Milli-Q, Millipore Cooperation).

For the determination of Re- and PGE-concentrations – except Rh – by isotope dilution a multi-element-spike enriched in ⁹⁹Ru, ¹⁰⁸Pd, ¹⁸⁵Re, ¹⁹⁰Os, ¹⁹¹Ir and ¹⁹⁸Pt was calibrated with single element standards (High-Purity Standards, Charleston, SC, USA). Separate ‘PGE’ (Ru, Rh, Pd, Re, Ir and Pt)- and Os-standards were diluted to 5 ng/ml from 10 μg/ml and 1000 μg/ml, respectively, single standards (High-Purity Standards).

To evaluate the applied analytical procedure the certified reference materials BCR-723, WGB-1 and TDB-1 were analysed. The road dust BCR-723 (available at IRMM, Geel/Belgium) was selected because its PGE-concentrations were of the same level, which were expected in the soil samples. Low concentrations of Rh and Pt were validated by analysis of the geological reference materials WGB-1 (gabbro) and TDB-1 (basalt), both distributed by CCRMP-CANMET, Ottawa.

Table 1
Sampling sites and their characteristics

Site	Opened to traffic	Vehicles per day	Speed limit (km/h)	Precipitation (mm/year)	Comment
A14, Rankweil	1972	22 072	130	1270	–
A13, Brennersee	1971	22 212	130	1066	Elevation 1300 m
A9, Liesingtal	1993	15 011	130	956	–
S36, Knittelfeld	1985	20 182	130	781	–
A23, Südost-Tangente	1970	56 679	130	514	–
Lungau	–	–	–	838	Reference site

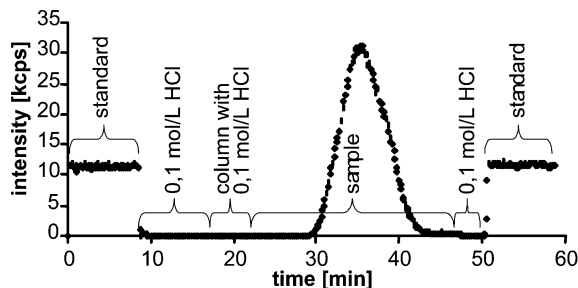


Fig. 2. Chromatogram of ^{198}Pt , recorded by the ICP-MS. It shows the sequence by which every sample was analysed.

2.2. Sample preparation and analysis

The collected soil samples were dried at ambient air temperature and then sieved to obtain the < 2 mm soil fraction. In order to take the site specific soil characteristics into account the soil-pH, electrical conductivity as well as total carbon (TC), total organic and total inorganic carbon (TOC and TIC, respectively) of each sample were determined. The samples were then dried at 105°C and ground in an agate mortar and pestle for further analysis.

PGE- and Re-concentrations were determined by ICP-MS through application of the isotope dilution technique. Precise results throughout the entire concentration range were aimed at by use of a novel analytical procedure described by Meisel et al. (2003). This procedure, which was originally developed for the analysis of geological materials, requires only few sample preparation steps: First, to the sample of approximately 1 g a corresponding amount of the multi-element spike solution was added. The samples in quartz glass vessels were then mixed with 2 ml conc. HCl and 5 ml conc. HNO_3 , sealed and digested in a high pressure asher (HPA-S, Anton Paar, Graz, Austria) at 300°C and 120 bar for 3 h. Upon cooling the isotope ratios of Os was measured by sparging volatile OsO_4 directly into the ICP-MS (HP4500 Agilent Technologies). For more details see Meisel et al. (2001). In the following steps, undigested material was removed by centrifugation and the samples were dried to remove most of the concen-

trated acid. The residue was then dissolved in approximately 2 ml of 0.1 mol/l HCl and the resulting sample solution separated from any solids using a syringe filter ($0.45\ \mu\text{m}$). Finally, the samples were fed into a cation exchange column, which was directly coupled to the ICP-MS. Thus, the PGEs and Re were separated on-line from other matrix constituents and the measurement could be monitored for any interfering species of these constituents. A chromatogram recorded in the described manner by the ICP-MS is shown in Fig. 2.

Concentrations of Re and PGEs – except Rh – were calculated from the following isotope ratios: $^{101}\text{Ru}/^{99}\text{Ru}$, $^{102}\text{Ru}/^{99}\text{Ru}$, $^{108}\text{Pd}/^{105}\text{Pd}$, $^{108}\text{Pd}/^{106}\text{Pd}$, $^{106}\text{Pd}/^{105}\text{Pd}$, $^{187}\text{Re}/^{185}\text{Re}$, $^{193}\text{Ir}/^{191}\text{Ir}$, $^{195}\text{Pt}/^{198}\text{Pt}$ and $^{194}\text{Pt}/^{198}\text{Pt}$. Background intensities and isobaric interferences of ^{102}Pd on ^{102}Ru , ^{106}Cd on ^{106}Pd , ^{108}Cd on ^{108}Pd and ^{198}Hg on ^{198}Pt were corrected prior to the calculation of the ratios. Rhodium was determined through its peak area, which was set into relation to the area of another PGE – a technique by which the other PGEs are functioning as internal standards. Fig. 3 illustrates the integration ranges in a chromatogram of Rh. Details on the calculation method can be found in Meisel et al. (2003).

Total procedural blanks and one reference materials (BCR-723, WGB-1 or TDB-1) were included in every set of five to seven samples. Their analysis was performed concurrently with the soil samples.

In addition to the PGEs and Re other traffic borne heavy metals were analysed. Their correla-

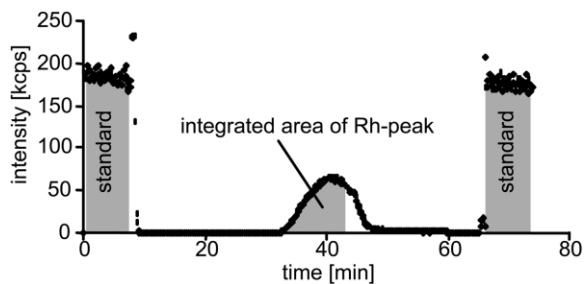


Fig. 3. Chromatogram of a Rh-measurement. The marked areas illustrate the integration ranges for the subsequent calculation of the Rh-concentrations.

tion would confirm, that catalytic converters are the prime source of PGE-emissions. For this purpose, 0.3 g of soil were microwave digested and analysed by element-specific methods. ICP-OES (Optima 3000 DV, Perkin Elmer Instruments) was applied for V, Cr, Co, Ni, Cu, Zn and Pb; GF-AAS (SIMAA 6000, Perkin Elmer Instruments) for Cd; FI-FU-AAS (AA800 with FIMS 400, Perkin Elmer Instruments) for Sb and HG-AAS (FIMS 400, Perkin Elmer Instruments) for Hg. Details can be found in Fritsche (2003).

Finally, three soil samples and the reference materials BCR-723 and WGB-1 were digested by microwave and analysed for PGEs in the aforementioned manner. The results were then compared with the determined PGE-concentrations obtained by application of the high pressure asher. Sufficiently, precise results would qualify microwave digestion for routine PGE-analysis by the Federal Environment Agency of Austria.

3. Results and discussion

3.1. Roadside soils

As only acids of subboiled quality were used for the digestion of the samples and the elution of the sample solutions, very low limits of determination could be achieved. Table 2 shows the statistical data of eight total procedural blanks, which were analysed during this study. The highest individual values were determined for Pt with 52 pg, which resulted in a limit of determination of 0.18 ng.

Table 2 also summarizes the results of the analysed reference materials BCR-723, WGB-1 and TDB-1. BCR-723 showed good reproducibility for Pd, Re, Os and Pt with R.S.D.s < 6%. Concentrations of the certified elements were within the uncertainty range, except Pd in TDB-1, which reached a mean value marginally above the upper limit.

Table 2
PGE- and Re-concentrations in total procedural blanks (TPB) and certified reference materials BCR-723, WGB-1 and TDB-1 in (ng/g)

Sample		n	Ru	Rh	Pd	Re	Os	Ir	Pt
TPB	Mean	8	−0.005	–	0.001	0.000	0.001	−0.008	0.017
	S.D.		0.006	–	0.005	0.003	0.001	0.006	0.016
	R.S.D. (%)		135	–	450	826	185	75	95
	Limit of detection		0.014	–	0.015	0.009	0.004	0.010	0.064
	Limit of determination		0.058	–	0.046	0.031	0.012	0.050	0.176
BCR-723	Mean	5	0.85	11.8	4.52	6.65	0.46	0.53	82.4
	S.D.		0.29	1.4	0.23	0.09	0.01	0.58	1.0
	R.S.D. (%)		35	11	5.2	1.3	2.3	109	1.2
	Certified value		–	12.8	6.0	–	–	–	81.3
	Uncertainty		–	±1.2	±1.8	–	–	–	±3.3
WGB-1	Mean	5	0.14	0.20	12.2	1.18	0.59	0.20	4.75
	S.D.		0.02	0.03	1.70	0.04	0.08	0.01	1.06
	R.S.D. (%)		15	16	14	3.4	13	7.2	22
	Certified (*informational value)		0.30*	0.32*	13.90	–	–	0.33*	6.10
	Uncertainty		–	–	±2.10	–	–	–	±1.60
TDB-1	Mean	4	0.18	0.48	24.2	0.80	0.11	0.07	4.98
	S.D.		0.003	0.06	2.47	0.03	0.01	0.01	0.25
	R.S.D. (%)		2.0	13	10	3.1	14	18	5.0
	Certified (*informational value)		0.3*	0.7*	22.4	–	–	0.15*	5.8
	Uncertainty		–	–	±1.4	–	–	–	±1.1

Table 3
Summary of PGE- and Re-concentrations of roadside soil samples in (ng/g)

Sample	Distance from edge of road (m)	Depth (cm)	<i>n</i>	Ru	Rh	Pd	Re	Os	Ir	Pt
Natural background ^a	–	–	–	0.1	0.06	0.4	0.4	0.05	0.05	0.4
Sa-Lun-1	–	0–5	1	0.02	0.03	0.36	0.13	0.04	0.04	0.28
Sa-Lun-2	–	5–10	1	0.03	0.05	0.29	0.24	0.09	0.03	0.16 ^b
St-Kni-00-1	0.45	0–5	1	0.79	3.11	6.77	0.96	–	0.44	32.4
St-Kni-00-2	0.45	5–10	1	5.77	1.17	1.97	0.53	2.36	0.89	25.6
St-Kni-02-1	2.55	0–5	1	0.15	1.96	1.54	0.23	0.14	0.09	12.7
St-Kni-02-2	2.55	5–10	1	0.79	0.19	2.28	0.22	1.03	0.29	1.57
St-Kni-10-1	10.50	0–5	1	0.12	0.17	0.90	0.05	0.08	0.12	1.13
Vo-Ran-00-1	0.20	0–5	2	0.89	13.2	21.2	9.80	0.25	1.1	134
Vo-Ran-00-2	0.20	5–10	2	0.29	12.6	24.5	5.41	0.07	0.15	102
Vo-Ran-02-1	2.20	0–5	1	0.07	1.05	1.57	2.18	–	0.11	9.14
Vo-Ran-02-2	2.20	5–10	1	0.01	0.40	0.91	1.35	0.03	0.04	3.62
Vo-Ran-10-1	10.20	0–5	1	0.02	0.48	0.79	0.28	0.03	–	2.89
Wi-Sot-00-1	0.65	0–5	2	0.55	3.39	6.00	0.88	0.04	0.09	38.9
Wi-Sot-00-2	0.65	5–10	2	0.10	0.15	1.13	0.65	0.04	0.24	2.01
Wi-Sot-02-1	2.65	0–5	2	0.23	1.52	6.41	0.71	0.04	0.18	27.2
Wi-Sot-02-2	2.65	5–10	2	0.23	0.36	0.86	1.22	0.08	0.11	6.78
Wi-Sot-10-1	6.50	0–5	1	0.07	0.74	1.75	0.78	0.06	0.10	7.04

^a Concentrations in the continental crust (Wedepohl, 1995).

^b Below limit of determination.

At all sampled sites along traffic routes, PGEs and Re are significantly accumulated and exceed natural background values more than 100-fold. Concentrations at the reference site in Lungau correspond with average values for the continental crust published by Wedepohl (1995). PGE-concentrations of all samples are listed in Table 3. The highest concentrations of the classical catalytic converter metals – Rh, Pd and Pt – were found in the immediate vicinity (0.2 m) of the A14 at Rankweil with values of 13 ng/g, 25 ng/g and 134 ng/g, respectively. Corresponding concentrations along the S36 and A23 were below these values despite the 2.5-fold traffic density on the A23 (more than 50 000 vehicles per day). These lower concentration-levels could be attributed to less precipitation in eastern Austria, which would result in less infiltration of road runoff and, therefore, less accumulation of PGEs in roadside soils. Moreover, frequent traffic jams due to excessive winter tourism may contribute to the high abundance of Rh, Pd and Pt along the A14. Minor accumulations of Rh, Pd and Pt were also found

at the sampling sites along the A9 and A13. However, these two sites were excluded from further consideration, as their selection turned out to be erroneous since recent alterations through road construction had occurred that was overlooked when selecting the sampling sites.

Characteristic distribution patterns shown in Fig. 4 were encountered in the soils along the A14, S36 and A23. Rhodium-, Pd- and Pt-concentrations decreased to natural background values within the first 12 m from the edge of the road. The vertical decrease was less dramatic – concentrations in the second depth range (5–10 cm) next to the road edge were still significantly elevated.

Besides Rh, Pd and Pt a similar distribution pattern was evident for Ir at the site along the A14 (Fig. 5). At a distance of 0.2 m from the road Ir reached 1.1 ng/g – more than 20 times the natural background value. Elevated concentrations were also determined for the samples of the S36 and the A23, although the results of the S36 seem to be influenced by the composition of the regional bedrock (serpentinite).

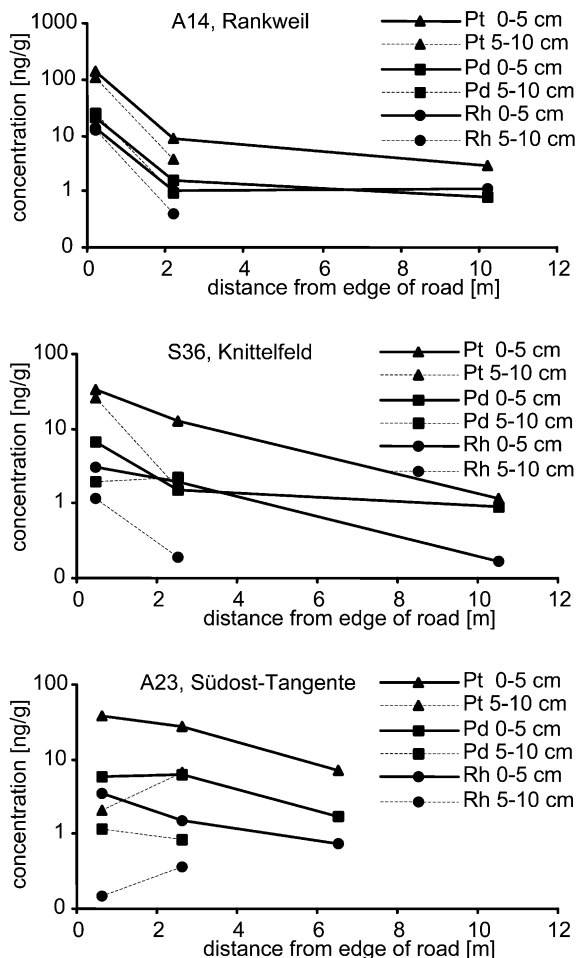


Fig. 4. Concentrations of Rh, Pd and Pt in roadside soils along the A14, S36 and A23.

Accumulations of Ru and Os at the A14 and S36 are minor and in the case of the S36 to some extent due to the bedrock as indicated above. However, the distribution patterns suggest that these metals were emitted from automobiles.

Notable concentrations were found for Re, especially along the A14 with up to 10 ng/g. Remarkable in this respect is the high Re-concentration in the road dust reference material BCR-723 with 6.7 ng/g. The origin of this significant accumulation is yet unknown although input from car traffic seems to be apparent.

In a further step ratios of Rh, Pd and Pt were calculated. For this task only the samples closest

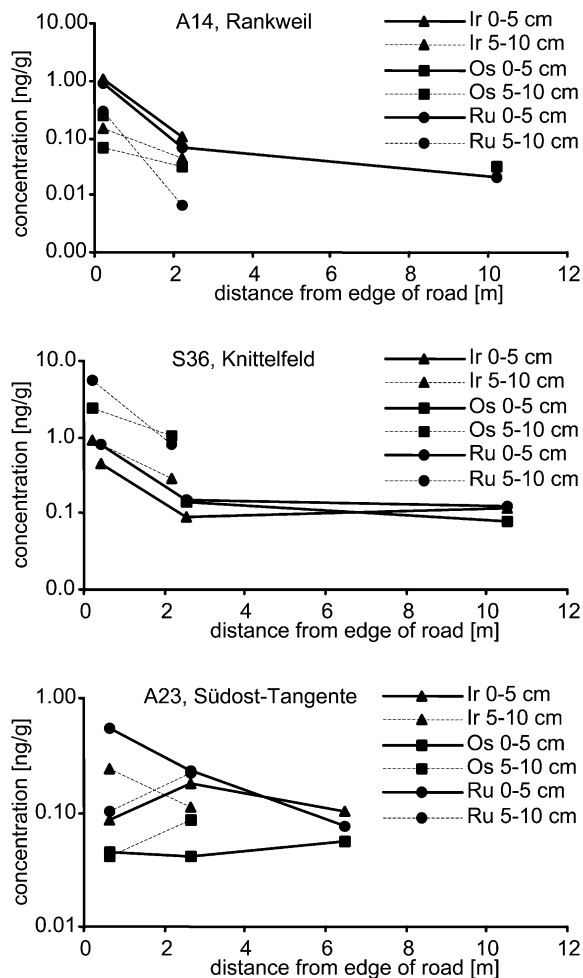


Fig. 5. Concentrations of Ru, Os and Ir in roadside soils along the A14, S36 and A23.

to the road edge were considered. The Pt/Pd-, Pt/Rh- and Pd/Rh-ratios, which are listed in Table 4, vary little around their averages of 6.3, 10.9 and 1.7, respectively. These results do not mirror PGE-ratios found in any particular type of catalytic

Table 4
Ratios of Rh, Pd and Pt in soil samples taken within 0.7 m from the edge of the road. Values are background-corrected

Site	Pt/Pd	Pt/Rh	Pd/Rh
A14, Rankweil	6.5	10.2	1.6
S36, Knittelfeld	5.2	10.7	2.1
A23, Südost-Tangente	7.3	11.8	1.6

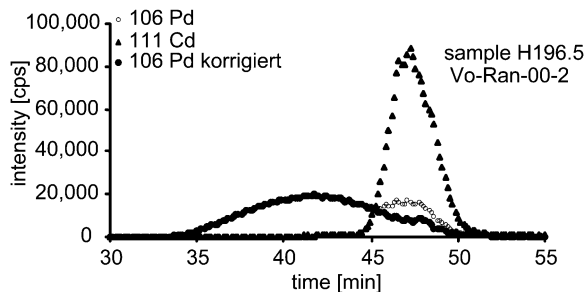


Fig. 6. Chromatogram of ^{106}Pd of a roadside soil sample. ^{111}Cd was recorded to correct ^{106}Pd for the interference of ^{106}Cd .

converter but seem to reflect the variety of PGE-combinations applied during the last decade.

The analytical results of the various soil parameters showed no abnormalities. Neither soil-pH, electrical conductivity nor TC, TOC or TIC correlated with PGE- or Re-concentrations. It can be concluded, that the characteristics of the soils investigated in this study have no influence on the mobility of PGEs.

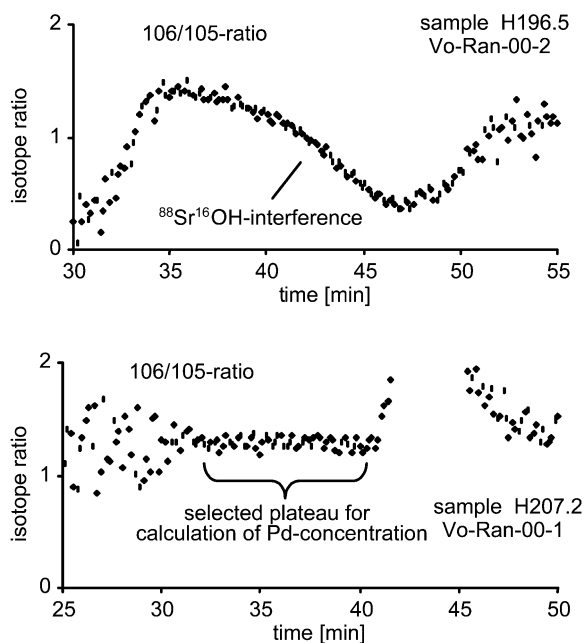


Fig. 7. $^{106}\text{Pd}/^{105}\text{Pd}$ -ratio of samples affected and unaffected by the $^{88}\text{Sr}^{16}\text{OH}$ -interference.

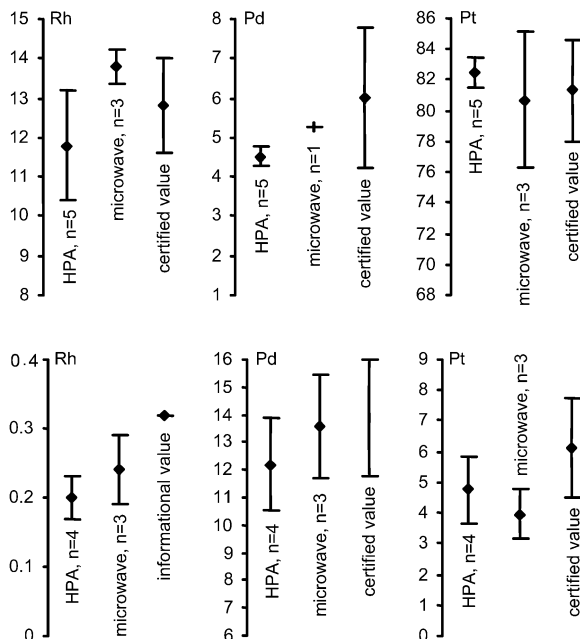


Fig. 8. Comparison of high pressure ashers (HPA) and microwave digestion procedures: concentrations (ng/g) and standard deviations of Rh, Pd and Pt in reference materials BCR-723 (above) and WGB-1 (below).

Inconsistent results were obtained by correlating concentrations of PGEs with other traffic borne heavy metals. The samples from the S36 showed good correlation of Rh, Pd and Pt with Cr, Co, Ni, Cu, Pb, Sb and Zn. Along the A14 Rh, Pd, Ir and Pt correlated only with Co, Zn and Sb. For the samples from the A23 no correlation could be determined. It has to be considered that the A23 runs through industrial areas along the periphery of Vienna – industrial emissions may, therefore, mix with traffic borne emissions.

Although correlations of Rh, Pd, Pt and also Ir with the aforementioned heavy metals are ambiguous, their high abundances and distinctive distribution patterns indicate their origin of the catalytic converter.

3.2. Analytical procedure

The on-line coupling of the cationic exchange column to the ICP-MS proved to be a very selective and sensitive method. However, as in any

other analytical method, interferences from matrix constituents occurred and had to be identified and corrected where possible. Isobaric and polyatomic interferences were detected frequently on Ru, Pd, Ir and Pt but were not systematic in any way. Cadmium and Hg were responsible for the most important isobaric interferences on Pd and Pt. As isotopes of these elements were eluted towards the end of the PGE-peaks (Fig. 6 gives an example), their effect on the PGE-ratios was minor. Moreover, isobaric interferences from Cd and Hg were corrected by measuring the abundance of ^{111}Cd and ^{199}Hg . More challenging appeared the occurrence of polyatomic interferences. Species of Zr, Y and Sr interfered primarily with Pd by affecting the plateaus of the calculated Pd-ratios. Fig. 7 compares the $^{106}\text{Pd}/^{105}\text{Pd}$ -ratio of a sample seriously affected by the $^{88}\text{Sr}^{16}\text{OH}$ -interference with another sample free of such an interference. The $^{88}\text{Sr}^{16}\text{OH}$ -interference in this example has altered the Pd-ratio to such an extent, that the calculation of the Pd-concentration was not possible. However, through the determination of three isotope ratios and correction of the aforementioned interferences by their formation rates, accurate results could be obtained.

The application of the microwave digestion procedure rendered PGE-concentrations in line with those obtained by HPA digestion. As shown in Fig. 8 Rh- and Pd-values of the reference materials BCR-723 and WGB-1 were slightly lower and Pt-values slightly higher. Although these results imply that microwave digestion is sufficient for routine analysis of PGEs, digestion parameters and sample weight need to be optimised and closer attention has to be paid to the first sample preparation steps.

4. Conclusions

Considerable accumulations of Rh, Pd and Pt in roadside soils has been verified. The minor but nonetheless significant accumulations of Ir are evidence of its increasing use in catalytic converters. Excessively rising traffic density, further development of catalytic converters due to more stringent laws and widespread implementation of catalytic converters in diesel engines will require

the monitoring of PGE-concentrations, in particular with regard to their potential health risk. Such a monitoring will be especially important for Ir and Re since to date virtually nothing is known about their behaviour in the environment and its risk for humans.

This study has demonstrated that the analytical procedure of Meisel et al. (2003) is applicable to routine PGE-analysis in soils. The results also suggest that sample digestion by microwave is sufficient for the purpose of PGE-determination in the proposed monitoring programme.

Acknowledgments

This study was carried out in cooperation with and financed by the Federal Environment Agency of Austria (UBA). The support of Mag. Alarich Riss and Dr Andrea Hanus-Illnar, both UBA, was greatly appreciated. We would like to thank Mr Messerschmidt of ISAS, Dortmund for the additional analysis of some of the soil samples. Janine McKelson and two anonymous reviewers are thanked for their helpful comments.

References

- Amatayakul W, Ramnäs O. Life cycle assessment of a catalytic converter for passenger cars. *J Clean Prod* 2001;9:395–403.
- Amossé J, Delbos V. Dispersion dans l'environnement routier et urbain de Pt, Pd, et Rh émis par les pots d'échappement catalytiques. Étude de la spéciation des éléments. *C R Chim* 2002;5:1–6.
- Farrauto RJ, Heck RM. Catalytic converters: state of the art and perspectives. *Catal Today* 1999;51:351–360.
- Fritsche J. Anthropogener Eintrag von Platingruppenelementen in straßennahe Böden. Umweltbundesamt Wien 2003 Monographien: in print.
- Gebel T. Toxikologisches Gefährungspotential der platingruppenelemente platin, palladium und rhodium. In: Zereini F, Alt F, editors. Emissionen von Platinmetallen. Berlin: Springer-Verlag, 1999. p. 269–280.
- Gomez B, Palacios MA, Gomez MM, Sanchez JL, Morrison G, Rauch S, McLeod C, Ma R, Caroli S, Alimonti A. Levels and risk assessment for humans and ecosystems of platinum-group elements in the airborne particles and road dust of some European cities. *Sci Total Environ* 2002;299:1–19.
- Heck RM, Farrauto RJ. Automobile exhaust catalysts. *Appl Catal* 2001;221:443–457.
- Hees T, Wenclawiak B, Lustig S, Schramel P, Schwarzer M, Schuster M, Verstraete D, Dams R, Helmers E. Distribution

- of platinum group elements (Pt, Pd, Rh) in environmental and clinical matrices. *Environ Sci Pollut Res* 1998;5:105–111.
- Helmers E. Platinum emission rate of automobiles with catalytic converters. *Environ Sci Pollut Res* 1997;4:100–103.
- Lustig S, Schramel P. Platinum bioaccumulation in plants and overview of the situation for palladium and rhodium. In: Zereini F, Alt F, editors. *Anthropogenic platinum-group element emissions*. Berlin: Springer-Verlag, 2000. p. 95–104.
- Meisel T, Moser J, Fellner N, Wegscheider W, Schoenberg R. Simplified method for the determination of Ru, Pd, Re, Os, Ir and Pt in chromitites and other geological materials by isotope dilution ICPMS and acid digestion. *Analyst* 2001;126:322–328.
- Meisel T, Fellner N, Moser J. A simple procedure for the determination of platinum group elements and rhenium (Ru, Rh, Pd, R, Os, Ir and Pt) using ID-ICP-MS with an inexpensive on-line matrix separation in geological and environmental materials. *J Anal Atom Spectrom* 2003;18:720–726.
- Merget R, Rosner G. Evaluation of the health risk of platinum group metals emitted from automotive catalytic converters. *Sci Total Environ* 2001;270:165–173.
- Moldovan M, Palacios MA, Gomez MM, Morrison G, Rauch S, McLeod C, Ma R, Caroli S, Alimonti A, Petrucci F, Bocca B, Schramel P, Zischka M, Pettersson C, Wass U, Luna M, Saenz JC, Santamaia J. Environmental risk of particulate and soluble platinum group elements released from gasoline and diesel engine catalytic converters. *Sci Total Environ* 2002;296:199–208.
- Palacios MA, Gomez M, Moldovan M, Gomez B. Assessment of environmental contamination risk by Pt, Rh and Pd from automobile catalyst. *Microchem J* 2000;67:105–113.
- Rabl P. *Information über Abgase des Kraftfahrzeugverkehrs*. Augsburg: Bayerisches Landesamt für Umweltschutz, 2002:1–9.
- Rao CRM, Reddi GS. Platinum group metals (PGM); occurrence, use and recent trends in their determination. *Trend Anal Chem* 2000;19:565–586.
- UBA *Umweltsituation in Österreich: Sechster Umweltkontrollbericht*. Wien: Umweltbundesamt, 2001.
- Wedepohl KH. The composition of the continental crust. *Geochim Cosmochim Acta* 1995;59:1217–1232.
- Zereini F, Alt F, Rankenberg K, Beyer JM, Artelt S. Verteilung von Platingruppenelementen (PGE) in den Umweltkompartimenten Boden, Schlamm, Straßenstaub, Straßenkehrgut und Wasser. *UWSF - Z Umweltchem Ökotox* 1997;3:193–200.
- Zereini F, Skerstupp B, Alt F, Helmerts E, Urban H. Geochemical behaviour of platinum-group elements (PGE) in particulate emissions by automobile exhaust catalysts: experimental results and environmental investigations. *Sci Total Environ* 1997;206:137–146.
- Zereini F, Zientek C, Urban H. Konzentration und Verteilung von Platingruppenelementen (PGE) in Böden. *UWSF-Z Umweltchem Ökotox* 1993;5:130–134.