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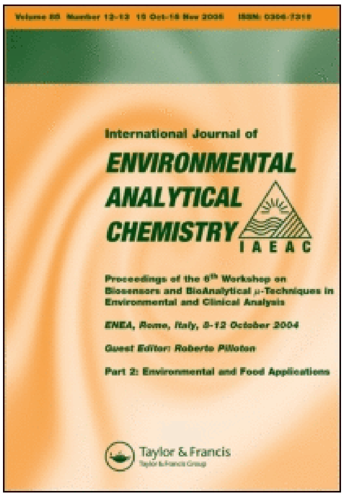

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Electrodeposition Sample Introduction for Ultra Trace Determinations of Platinum Group Elements (Pt, Pd, Rh, Ru) in Road Dust by Electrothermal Atomic Absorption Spectrometry

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ELECTRODEPOSITION SAMPLE INTRODUCTION FOR ULTRA TRACE DETERMINATIONS OF PLATINUM GROUP ELEMENTS (Pt, Pd, Rh, Ru) IN ROAD DUST BY ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY

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A novel method for the determination of the platinum group elements (PGEs: Pt, Pd, Rh, Ru) in environmental samples by electrothermal atomic absorption spectrometry (ET-AAS) was developed. Sample preparation involved complete microwave-assisted acid digestion of the matrix with HNO_3–HF–$HClO_3$/$HClO_4$ mixtures in a high-pressure Teflon bomb. Traces of PGEs were deposited on the inner wall of a graphite tube in a flow-through cell of 1 ml volume. A flow system for this preconcentration was constructed. For the electrodeposition, a three-electrode arrangement was used. The geometry of the cell, flow rate during electrodeposition, deposition potential and electrolyte composition were optimized. After the deposition step, the graphite tube was placed into the graphite furnace and an atomization program applied. Detection limits (LOD, $3\sigma_{\text{total procedure blank}}$, peak area) of 3.6, 0.5, 0.3 and 5.9 ng were obtained for Pt, Pd, Rh and Ru, respectively, reflecting preconcentration factors of 416, 503, 423 and 46, respectively. The detection limits were restricted by variations in the blank. Precision of replicate determination was typically 21% RSD at a concentration 25-fold above the LOD for a 100-mg sample mass. Reasonable agreement was found between results for CW7 road tunnel dust literature and for CRM NIES No. 8 Vehicle Exhaust Particulates. Calibration was achieved *via* the method of standard additions.

Keywords: Road dust; Automobile exhaust; Platinum group elements; High pressure microwave digestion; Electrochemical preconcentration; Electrothermal atomic absorption spectrometry

INTRODUCTION

Although the platinum group elements (PGEs) are amongst those of the lowest abundance in the earth crust, they are subject to high scientific and public interest. Awareness of the importance of PGEs in the environment arose over the past 20 years with the introduction of Pt, together with Pd and Rh, for use in catalytic converters for the reduction of pollutants in the automobile industry (exhausts) [1–3]. Although the great advantages of autocatalysts are obvious, there are however, some disadvantages with their usage. The most important concern is the release of PGEs

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to the environment as a result of surface abrasion of the catalytic converters during car operation. Because of the increasing concern over these elements as potential risks for human health, owing to possible direct contact by inhalation of dust, many efforts have been made in the past two decades to quantify them in different environmental matrices. A good possibility to reconstruct the recent changes in the chemical composition of the atmosphere is given by the study of dust collected in road-side sites.

To date, studies of the extent of PGEs in the environment have been mainly concerned with their accurate determinations. It is a very difficult task to measure the total amount of these metals in environmental samples not only because of the extremely low concentrations in which they are emitted, but also potential interferences. Therefore, rapid, sensitive and accurate determination of these metals in environmental matrices has led to the development and continuous improvement of various analytical methods concerning both sample digestion and the choice of the most appropriate instrumental technique to obtain exhaustive chemical information in the shortest time possible.

The main goal of the first stage of analysis is the achievement of quantitative and rapid digestion of the sample which determines, to a great extent, the quality of the results and the duration of the complete analytical scheme. The most important digestion techniques are classic cupellation (PbS and NiS), alkali fusion with Na_2O_2/NaOH, an acid attack at high temperature and pressure in closed vessels. The determination of PGEs in dust (road, street, urban, tunnel, airborne particulate) materials still relies primarily on acid digestion as the first step towards extracting PGEs from silica-containing matrices. This stage of sample preparation is an important area of trace analysis. Its aim is to present the sample to the analytical instrument in a form suitable for the analysis, and this is usually in the form of a particle-free aqueous solution. Generally, this will involve decomposition of organic compounds and dissolution of inorganic solids.

Several studies have already been published on the preparation of dust samples for wet chemical analysis. Dusts can be totally digested with an acid mixture in high-pressure PTFE bombs [4,5], high-pressure asher [6], closed vessel microwave oven [4,7–11] or by using open acid digestion [4,5,12,13]. Various parameters, such as the method of heating, working pressure and acids have a role to play in the digestion efficiency. The matrix composition is complex and it is difficult to achieve total dissolution of the samples. Therefore, digestion methods should be comprehensively investigated and fully described in order to be able to properly evaluate the contribution of the sample digestion step to the uncertainty in the final result. Digestion under pressure ("classical" or microwave-assisted) offers advantages over open-air digestion. As it allows working at higher temperatures, digestion under pressure is much faster (especially microwave-assisted acid digestion). In addition, a closed system limits the risks of loss or contamination of the sample, a supposedly better recovery of volatile elements and compounds and fewer possibilities for technical errors caused by spilling of hot digestion solutions. The quantities of acid(s) needed are generally lower than with ambient pressure methods. The use of low volumes of acid(s) allows small volumes of final solution to be handled and the detection limits to be improved. The principal acids used for dust digestion are HNO_3, HCl, $HClO_4$, HF, H_2SO_4 and H_2O_2.

Due to the low concentrations of PGEs in dust, quantitation of these elements can be error-prone even when the determinations are carried out using highly sensitive methods in combination with high-performance sample preparation techniques.

Several comprehensive reviews of the analytical chemistry of PGEs are now available [1,14–21]. Instrumental analysis following digestion procedures has recently included inductively coupled plasma optical emission spectrometry (ICP-OES), electrothermal atomic absorption spectrometry (ET-AAS), inductively coupled plasma mass spectrometry (ICP-MS), isotope dilution mass spectrometry (ID-MS), stripping voltammetry (SV) and neutron activation analysis (NAA) [1,14–17]. The last four methods can be applied to environmental samples without preconcentration, however preconcentration is frequently used with those analytical techniques. Additionally, NAA is an expensive method available to only a few laboratories and is too time consuming for routine analysis. Generally, however, such instrumental methods are not sensitive enough for direct measurements in the lower pg range. Therefore, these methods can only be applied to analyses of environmental samples in combination with sophisticated sample decomposition and additional analyte separation or preconcentration. For this purpose, an effective combined procedure based on solid-phase extraction [18,19], solvent extraction [17], ion exchange [17] and electrochemical deposition [17] have been developed. Developing analytical methods for the determination of PGEs presents a challenging task for analytical chemists because of the following factors: low concentration, inhomogeneous distribution, complex chemistry and speciation and lack of appropriate reference materials. It is imperative to develop several combinations of multistep analytical procedures in which the single steps (decomposition, separation, preconcentration, and determination) are all fully independent.

The method developed here is an extension of the work previously reported by Matusiewicz *et al.* [22] and this paper discusses the further application and evaluation of this concept.

This work focused on the methodology and evaluation of a graphite furnace electrodeposition system combined with an atomic absorption spectrometer for the determination of ultratrace levels of PGEs in road dust. A flow system was used for preconcentration. Special attention was paid to the improvement of the digestion method; we report the successful application of a mixed-acid digestion procedure as a means of sample preparation. Road dust taken from the ceiling of a tunnel is suggested to be the ideal example for an environmental silica-containing matrix. Unfortunately, certified reference materials with complex matrices and environmentally relevant PGE concentrations are not available to date and could therefore not be used for method validation. However, digestion and analysis techniques were evaluated by analyzing reference material CRM NIES No. 8 "Vehicle Exhaust Particulates" (National Institute for Environmental Studies, Japan) and a candidate road dust reference material CW7 [23,24], for which results were compared to independent literature data.

EXPERIMENTAL

Instrumentation

Measurements were performed with an AAS 3 atomic absorption spectrometer (Carl Zeiss, Jena, Germany) equipped with an EA 3 graphite furnace. The instrument includes a graphics display. Hollow cathode lamps were used as line sources and a deuterium hollow cathode lamp served as a continuum source (Narva, Germany) for

TABLE I Optimum instrumental operating conditions for the ET-AAS technique

Parameter	*Pt*	*Pd*	*Rh*	*Ru*
Wavelength (nm)	265.9	247.6	343.5	349.9
Slit width (nm)	0.2	0.2	0.2	0.2
Lamp current (mA)	10	5	5	10
Measurement time (s)	4	4	4	4
Read delay (s)	0	0	0	0
Background correction	ON	ON	ON	ON
Signal measurement	Peak area			
Signal type	Background-corrected AA			

TABLE II Temperature program for the graphite furnace EA3

Element	*Drying*				*Pyrolysis*				*Atomization*				*Cleaning*			
	Ramp °C/s	*Temp* °C	*Hold* s	*Gas flow* ml/min	*Ramp* °C/s	*Temp* °C	*Hold* s	*Gas flow* ml/min	*Ramp* °C/s	*Temp* °C	*Hold* s	*Gas flow* ml/min	*Ramp* °C/s	*Temp* °C	*Hold* s	*Gas flow* ml/min
Pt	20	105	30	160	200	1300	5	160	FP	2700	4	0, read	FP	2800	4	280
Pd	20	105	30	160	200	800	5	160	FP	2700	4	0, read	FP	2800	4	280
Rh	20	105	30	160	200	1200	5	160	FP	2700	4	0, read	FP	2800	4	280
Ru	20	105	30	160	200	1200	5	160	FP	2700	4	0, read	FP	2800	4	280

background correction (HCL technique, modulation frequency of 40 Hz). Standard pyrolytic graphite-coated graphite tubes without platform were used for all experiments (Carl Zeiss, Jena, Germany). Data were evaluated using peak area mode. The temperature program for the graphite furnace and instrumental experimental parameters are presented in Tables I and II, respectively.

The electrodeposition of the noble metals was performed in a laboratory-made set-up having a three-electrode potentiostat (ELPAN EP-20, Poland) connected to the working, counter and reference electrode arrangements in a quartz cell. A Carl Zeiss commercial pyrolytically coated graphite tube (30 mm × 6 mm o.d.) served as the working electrode. The counter electrode was a glassy carbon electrode (BAS MF 2012, 85 mm × 3 mm o.d.). The reference electrode was a saturated calomel electrode, separated from the analyte solution by a double bridge fitted with a Vycor disk with saturated KCl and 0.1 M KCl solutions used in the first and second bridge, respectively. Nitrogen was used to agitate the sample solutions. Solution was circulated through the flow-through cell and returned to the quartz cell using a peristaltic pump (model 304, ELMED, Poland). A schematic diagram of the flow electrolysis system is shown in Fig. 1. A flow-through cell, the main part of the proposed system, was designed for a flow of the solution along the inner walls of the graphite tube such that deposition of Pt, Pd, Rh and Ru occurred only in the central part of the tube.

Digestion in a closed vessel has a decided advantage over one in an open system. A laboratory-built prototype of a high pressure/temperature focused microwave heated digestion system for trace and ultra-trace analysis of difficult-to-digest samples, equipped with closed TFM-PTFE (Hostaflon TFM is a chemically modified PTFE) vessel (30 ml internal volume) based on a design outlined in detail by Matusiewicz [25] was employed for wet-pressure sample digestion. The power could be set from 1 to 200 W in 1 W steps. The maximum working pressure was 130 bar. The minimum

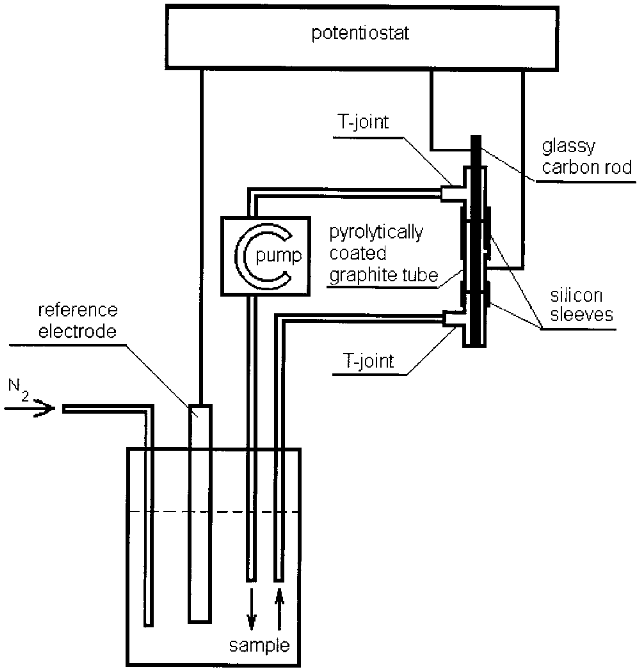

FIGURE 1 Schematic diagram of the flow-through electrodeposition system (not to scale).

volume in the vessel for ease of working was 2 ml. The pressure monitor system with feedback to enable microprocessor control of the pressure within the vessel was available. The maximum working pressure using the control pressure system was 110 bar. This digestion system enabled digestion parameters (in addition to forward and reflected microwave power) to be reported based solely on time and pressure, making the procedure more universally applicable and less dependent on the actual microwave system used.

Gases, Containers and Reagents

Compressed argon gas of N-50 purity (99.999%) obtained from BOC GAZY (Poznań, Poland), was employed as the carrier gas for the atomizer without further purification.

To ensure a good quality of the total analytical procedure and low blank values, all reagents have to be of Suprapure quality and all equipment must be carefully cleaned. The containers used must also be carefully cleaned. The quartz container was cleaned by immersion in dilute nitric acid (10% v/v) for 24 h, and then washed with pure water. The TFM-PTFE vessel was first hot-leached with concentrated HNO_3 for 10 min, followed by blank digestion and cleaning with water. This cleaning procedure is very important, especially for extremely low concentrations of PGEs, to avoid contamination.

Standard solutions were prepared from 1000 mg/l Pt, Pd, Rh and Ru atomic absorption standards (BDH, Poole, Dorset, UK). Working standard solutions were freshly prepared daily by diluting appropriate aliquots of the stock solution in high-purity water. Deionized water (model DEMIWA 5 ROSA, Watek, Czech

Republic) and doubly distilled water (the second and third distillation was carried out using quartz apparatus, Bi18, Heraeus, Hanau, Germany) was used to prepare all solutions.

All concentrated mineral acids (69% HNO_3, 40% HF, 20% $HClO_3$/7% $HClO_4$) used were of the highest quality (Suprapure, Merck, Darmstadt, Germany).

Samples

Materials were selected that matched the matrix and the PGE concentrations of samples from our current projects as closely as possible. The PGE concentrations are not certified and are only provisional in value.

Vehicle Exhaust Particulates (NIES CRM No. 8, National Institute for Environmental Studies, Ibaraki, Japan) was used as a sample. However, the PGE concentrations in this material are not certified.

The second material was the road dust sample CW7 "Road Dust" provided by the GSF-National Research Center for Environment and Health, Institute for Ecological Chemistry (Neuherberg, Germany) for an intercomparison study within a certification campaign "PACEPAC", 1998 [23,24] for the European Community. This interlaboratory study was organized as a test for certifying a reference material of similar composition (which is now in the certification phase (CW7)). The material was sampled in 1994 from the filter system (the ventilation shaft) of a highway tunnel in Styria, Graz (Austria). The grain size of the milled dust was $< 90\,\mu m$. The preparation and characterization of the test reference material is described in detail in [24].

In addition, the dust collected in October 1994 from the ceiling (electro filter) of Tanzenberg tunnel in Austria (Road Tunnel Dust) was used as a sample, representing dust obtained from a traffic tunnel. This dust was first passed through a Nylon sieve (1 mm) and then further homogenized (grain size $< 1000\,\mu m$) and characterized as described previously [2].

Sample Digestion Procedure

The *modus operandi* used to proceed with the digestion depends solely on the type of matrix and not on the subsequent determination step. Preparation of all standards and digestion of samples were conducted under typical laboratory conditions. Therefore, the high-pressure microwave-assisted digestion system, previously described [25], was used to completely digest the silica-containing matrices.

Complete digestion of samples is crucial for quantitative determination of PGEs using this method. Use of medium-pressure microwave digestion bombs (Milestone TFM-Teflon vessels) placed in the microwave cavity of a domestic microwave oven (model Elektronika 3C, USSR) with concentrated HNO_3, HF and $HClO_3$/$HClO_4$ acids was insufficient to completely dissolve the samples.

About 100 mg of sample was accurately weighed into a TFM-PTFE vessel ("bomb") to which was added 1 ml of 69% HNO_3, 1 m of 40% HF and 1 ml of 20% $HClO_3$/7% $HClO_4$. Samples were then digested in a high-pressure microwave-assisted digestion system. The digestion process is detailed in Table III (the pressure rose to 65–70 bar). After digestion, the completely clear, homogeneous solution (without any visible particles) in the digestion vessel was quantitatively transferred to a 10 ml calibrated

TABLE III Operating conditions for microwave-assisted digestion system

	Step 1	*Step 2*	*Step 3*
Power (W)	100	150	0
Hold time (min)	5	15	0
Cooling time (min)	0	0	30
Pressure[a] (bar)	20	70	0

[a] Control parameter.

flask and filled to the mark with water. In all cases, a corresponding blank was also prepared according to the above microwave-assisted digestion procedure.

General Analytical Procedure

The analytical procedure consists of two steps: electrodeposition of the analytes on the graphite tube electrodes by keeping them at suitable potential during the solution flow, and electrothermal atomization of collected analytes and measurement of atomic absorption signals.

The electrodeposition of Pt, Pd, Rh and Ru was performed using a flow-through electrodeposition unit (Fig. 1). The graphite tubes were cleaned before use by heating to 2800°C in the atomizer, while purging argon through them. After cooling, each graphite tube, a glass rod inside, was placed into the flow-through cell. To begin electrodeposition, the sample solution (25 ml) was pumped through the counter space of the cell using a peristaltic pump at a constant flow rate of 100 ml/min. A deposition potential of -0.9 V, -0.7 V, -0.9 V and -0.5 V was set at the working electrode for Pt, Pd, Rh and Ru, respectively. After a defined period of preconcentration time (30–60 min, nitrogen flow rate of 70 ml/min), the graphite tube was washed in a stream of pure water (about 50 ml), removed from the cell and dried at room temperature. For measurement (according to the temperature program, Table II), the graphite tube was transferred to the graphite furnace atomizer unit (EA 3) of the atomic absorption spectrometer. The standard additions method for calibration required during an analytical run were made in different graphite tubes by adding dilute single-element standard solutions to the samples before the digestion procedure (not to the digested samples).

Determination of the Overall Relative Efficiency

To determine the overall relative efficiency of the electrodeposition system, signals for a known mass of the measured elements, resulting from the electrochemical preconcentration, were compared with those obtained by direct injection of standard solutions. For the latter, the same time–temperature program as in Table II was used except that the preconcentration/sequestration steps were omitted and the drying hold time was prolonged to 50 s. Signals obtained following electrodeposition were compared to those measured when 20 µl volumes of solution were injected directly into the graphite tube, dried and atomized.

RESULTS AND DISCUSSION

The result of this study relates to three distinct aspects of the overall investigation: revisitation of the digestion mode, electrodeposition with preconcentration, and its application to practical analysis. Although these are related, there are development details for each, which are independent. Hence, it is convenient to discuss the development of the digestion procedure, electrolytic preconcentration and analysis technique separately.

Improvement of Sample Digestion Methodology

The use of acid mixtures under the high temperatures and pressures developed in closed vessels in a microwave cavity for the digestion of road dust samples is a crucial point for PGE determinations. Therefore, it was the technique tested in this study for complete analytical sample dissolution. Three different digestion procedures have been used to characterize the PGE concentration in the dust samples used for these experiments. These procedures were evaluated by visually inspecting the degree of dissolution and analyzing NIES certified reference material (CRM No. 8) for some elements.

First attempts involving the use of *aqua regia* and digestion using a medium-pressure digestion system led to pronounced quantities of undissolved material. Silicate-containing samples were not completely dissolved by *aqua regia*. In dust samples, silica and silicates are the major components. For example, the Vehicle Exhaust Particulates (NIES CRM No. 8) contain about 2.4–2.5% silica [1,26]. In addition, dark particles were still visible in the solution after digestion. This can be explained as due to the presence of undigested carbon in the samples; the carbon (sample consists mainly of soot) content amounts to approximately 80% in NIES CRM No. 8 [26,27]. Even the use of the maximum microwave-operating power (600 W) and extended digestion times (up to 1 h) did not lead to satisfactory results. In addition, the use of H_2O_2 did not help.

Generally, a study on the efficiency of acids for the digestion of urban dust, advises the use of a mixture of perchloric, hydrofluoric and nitric acids [4]. On the basis of this study, a nitric acid, perchloric acid, hydrofluoric acid matrix was first tested. Perchloric acid is a strong oxidizing agent and hydrofluoric acid is used to dissolve silicates. Surprisingly, if the sample was digested with that mixture of acids, small portions of the samples remained adhered to the vessel walls throughout the subsequent digestion. This drawback was overcome by modifying the microwave methodology, as discussed later.

An important observation was noted when a $HClO_3/HClO_4$ mixture was used in the procedure. A combination of 69% HNO_3, 40% HF, 20% $HClO_3$/7% $HClO_4$ (1 : 1 : 1) matrix was found to give the best results for these samples, although visible residues remained in some cases. $HClO_3/HClO_4$ acid mixtures therefore seem necessary for the complete digestion of dust.

The higher the working pressure, the more efficient and the more rapid the digestion. In our experience, the so-called high pressure digestion is the best way to achieve complete decomposition and dissolution of solid (powdered) samples. Thus, experiments were undertaken to investigate the potential advantages of the higher pressures and improved control offered by a high pressure/temperature focused microwave

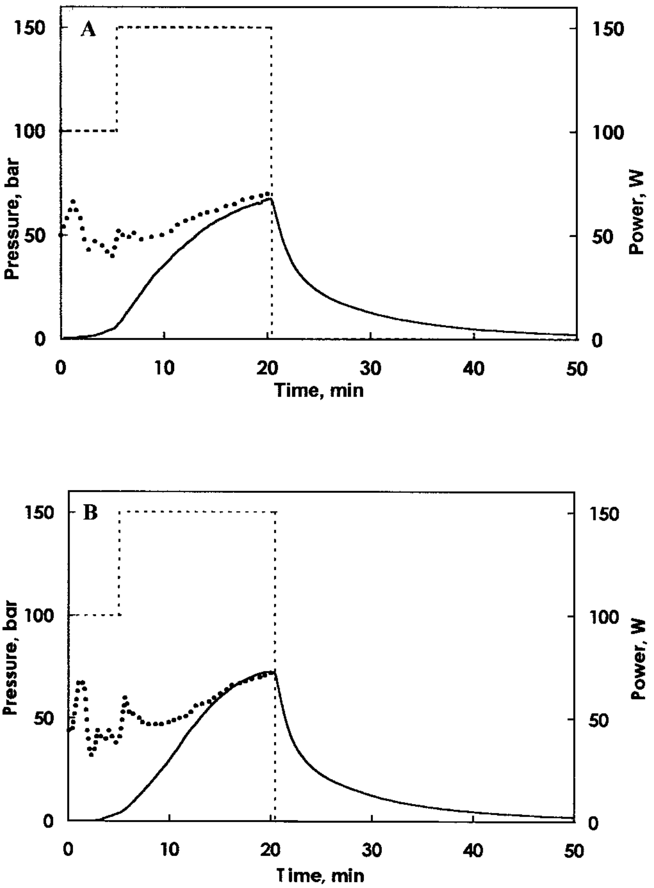

FIGURE 2 Pressure profiles obtained in the closed vessel as a function of microwave program (see text). (A) NIES CRM No. 8 "Vehicle Exhaust Particulates", (B) CW7 "Road Dust".

heated digestion system [25] using the same digestion reagents. Figure 2 shows the pressure and microwave power absorbed for the acid mixture tested; the long dotted line represents the program settings (incident microwave power); the dotted line, the microwave power absorbed by sample and acid mixture (reflected power); and the solid line, the pressure in the closed vessel. While attempting to achieve complete digestion of the samples, no problems were observed at these power settings. Condensation of acid droplets on the external part of the vessel was not observed, so the vessel was not damaged. A power of 150 W was retained as the optimal power.

NIES CRM No. 8 Vehicle Exhaust Particulates samples were digested for five digestion cycles in order to find the optimum. Each microwave program started with a 100-W step for 5–20 min followed by a 150-W step for 10 and 15 min. The mean recoveries for Ca, Cu, Mg and Pb was represented as a function of the 150-W step time. Recoveries increased with digestion time; all recoveries are around 100% within 4% RSD. This suggests that the digestion time is a significant parameter in reaching high recoveries from particulate matter, such as vehicle exhaust particulates. However, the working pressure increases with digestion time (up to about 70 bar).

Consequently, it was decided to retain a time of 15 min for the 150-W power step in the microwave program.

Obviously, only the combination of the three important factors: acid mixture ratios, high pressure and temperature and contact time leads to successful digestion of environmental samples and no residue is established, thus no additional, for example, fusion is necessary.

Analytical Blanks

Contamination of the instrument itself, or during the chemical pre-treatment used, gave rise to signals in the AAS instrument coming from the same element to be measured. Instrument contamination can be due to memory effects in the sample introduction system or in the interface. External contamination can also occur during the sample preparation step, due to impurities in the reagents used or leaching from the containers. In order to determine very low concentrations, it is necessary for the blank values to be as low as possible, stable and representative of the entire procedure used. The determination of PGEs is accompanied by the problem that there are many opportunities for introducing trace amounts of these analytes into the system.

Blanks were determined using the same treatment procedure as for samples. Although these experiments were not conducted in a clean room atmosphere, but in an ordinary laboratory, the major source of the blank was determined to be the acids. Only mineral acids are used in sample digestion, therefore blanks can be reduced easily. Even though the acids used were of the best quality available, trace amounts of the analytes in the reagents were preconcentrated in the graphite tube during the electrodeposition, resulting in blank signals. Absolute blanks of 0.5, 0.8, 0.2 and 2.5 ng for Pt, Pd, Rh and Ru, respectively, were achieved. However, it is primarily for the ultrasensitive techniques, notably those involving electrolytic preconcentration in combination with ET-AAS, that this contamination is observed to such an extent that it represents a marginal problem. It is clear that the detection limits achieved with this technique will be primarily limited by the substantial level of contamination of the acids.

Electrolytic Preconcentration

A technique for *in situ* measurement of PGEs in dust is to electrodeposit them onto graphite tube, which can then function as a furnace for atomic absorption analysis with electrothermal atomization [28,29]. An important feature of the described electrodeposition protocol is that it achieves efficient deposition of the analyte onto the graphite furnace. Subsequent withdrawal of the spent electrolyte ensures efficient separation of the analyte from the sample matrix. Thus, the volatilization and atomization processes are not influenced by the sample medium. This has obvious advantages when applied to difficult media such as dust and particulate matter. Flow-through electrodeposition has proved to be a simple and effective means of analyte preconcentration in electrically conducting solutions [28]. Here the microcell design based on the graphite tube of the atomizer was used directly for the flow-through electrodeposition as well as for detection by ET-AAS.

The variation in atomic absorption signal with the deposition potential is shown in Fig. 3. The maximum yield of the electroplating metals for Pt, Pd, Rh and Ru

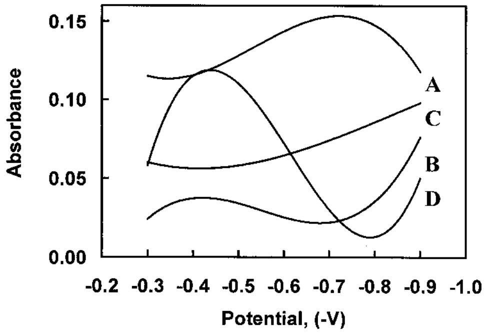

FIGURE 3 Dependence of the absorbance signal on the deposition potential for 25 ml of solution, flow rate 100 ml/min: (A) 0.04 ng/ml Pd, (B) 0.4 ng/ml Pt, (C) 0.04 ng/ml Rh, (D) 0.4 ng/ml Ru.

was obtained at − 0.9, − 0.7, − 0.9 and 0.5 V, respectively, versus a saturated calomel electrode (SCE). At more negative potentials, hydrogen evolution on the cathode reduced precision.

For a given deposition period, the sensitivity of the method depends on the rate of mass transport to the electrode during the electrolysis. This rate is affected by cell geometry, electrode design and stirring rate of the solution. The stirring can be done in different ways. A magnetic stirrer can be used, or a vertical stirring bar can be rotated by means of a synchronous motor placed above the cell. The stirring can also be affected by simply passing nitrogen through the solution at a constant flow rate. The latter was chosen in the present investigation, because it has the advantage that dissolved oxygen is simultaneously removed. Also, the hydrogen and oxygen gas, which can be formed at the working and counter electrodes during the electrolysis, are removed. Stirring by nitrogen gas is effective and reproducible, provided that a flow meter is used to control the flow rate. For the present work, a flow rate of 70 ml/min was always used. Flow rates above 100 ml/min caused splashing of the solution.

The flow rate of the sample solution during the preconcentration step influences the deposition efficiency. Maximum efficiency was obtained under compromise conditions at flow rates between 25 and 125 ml/min. A flow rate of 100 ml/min was chosen as optimal for all elements.

The sensitivity of the method can be increased by increasing the electrolytic deposition period. The variation of the absorption signal with deposition time is shown in Fig. 4 for PGEs. As can be seen, there is an approximately linear dependence of the signal on the deposition time. However, at higher concentrations of PGEs, the deviation from linearity becomes pronounced. Thus, a minimum 30-min electrolysis time was generally used in this work.

The temperature, in the range from room temperature up to 60°C, has no significant influence on the deposition rate. Further experiments were done with a constant temperature of 20°C. Higher temperatures were avoided for practical reasons.

Atomization Characteristics

The proposed technique utilizes electrothermal atomization, which is a great advantage when low concentration levels must be determined. A sample volume of 20–50 ml

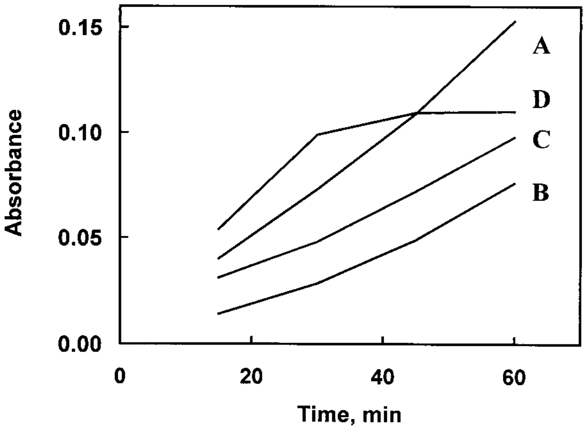

FIGURE 4 Effect of the deposition time on the absorbance signal for: (A) 0.04 ng/ml Pd, (B) 0.4 ng/ml Pt, (C) 0.04 ng/ml Rh, (D) 0.4 ng/ml Ru.

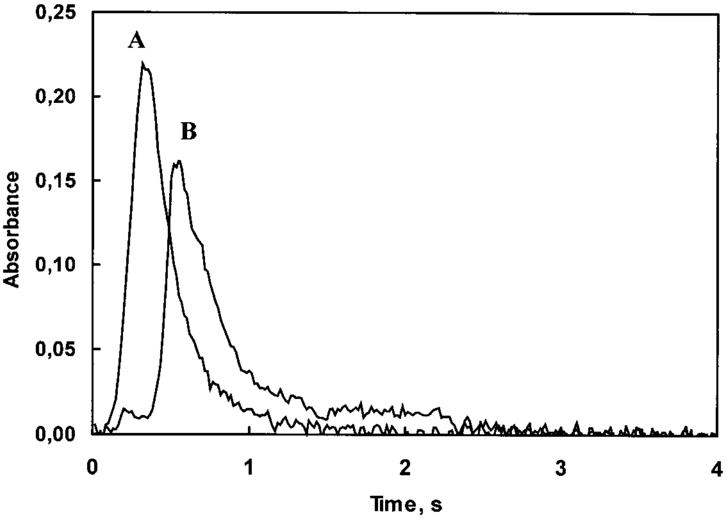

FIGURE 5 (A) Rhodium transient signal from a non-electrodeposited tube after direct injection of 20 μl 10 ng/ml Rh standard solution, (B) transient signal from electrodeposition sample introduction after preconcentrating 25 ml solution containing 0.024 ng/ml Rh (electrodeposition efficiency ~ 40%).

is required. If such a volume of sample is available, and time can be allowed for the deposition of all the PGEs in solution onto the graphite tube cell, the detection limit for this approach should be better than that of other electrothermal techniques, as they usually employ aliquots of only a few μl. Using electrodeposition of PGEs, the lifetime of the pyrolytically coated graphite tube was at least 50 firings.

The pyrolytic graphite coating influences the AAS signal for PGEs. With electrodeposition sample introduction, the PGE signals are broader and lower than for liquid sample introduction. (Fig. 5), but its integrated value changes little. Hence, the integrated signal was evaluated throughout this work.

Validation of the Method

The accuracy of the present method is not easily established, since there is no commercially available environmental reference material (road dust) containing PGEs at levels as low as those needed. Nevertheless, the application of reference materials is important for quality assurance and quality control. Therefore, the only means of testing and ensuring the accuracy and precision of the developed analytical procedure was by comparison of the results of the analyses obtained from different methods of determination together with published values. Standard reference material [vehicle exhaust particulates (NIES No. 8) and road dust (CW 7, PACEPAC, 1998), not yet certified for PGEs] were analyzed. Table IV presents the values for PGEs obtained in this study, together with literature data for the same samples. Calibration was achieved using the method of standard additions. All experimental concentrations agreed fairly well with the certified or literature (indicative) values. Although no interference study was undertaken, it is obvious that there are no systematic errors due to the presence of any of the matrices. However, even the method of standard additions cannot eliminate some possible matrix effects, only the method of standard additions was used to obtain "accurate" results.

In general, data for non-certified values in CRM NIES No. 8 sample are either in agreement with the proposed information values or comparable with literature data. However, the results for the PGEs analyzed in this work cannot be statistically evaluated (e.g., for rhodium there is excellent agreement of the data obtained in this work with that of two other laboratories having specified concentrations of about 24.5 ng/g). The agreement demonstrates the fitness for purpose of this method for

TABLE IV Results of the determination of PGEs (concentrations in ng/g ± SD of three parallel analyses) in environmental sample materials and comparison of results with literature data

Matrix/ element	*This work*	*Literature data*									
		[1]	[6]	[13]	[24]	[26]	[30]	[31]	[32]	[33]	[34]
CRM NIES No. 8 Vehicle Exhaust Particulates											
Pt	210 ± 60	210		170 ± 8 174 ± 6		190 ± 30	185 ± 14.3	160, av. 220	184 ± 25 191 ± 32	66, 1259, 193, 90, 296, 155 av. 160 ± 90 (exl. 1259)	
Pd	196 ± 29	297 ± 56				297 ± 56	180 ± 27.7			189, 332, 365, 147, 158, 188, av. 230 ± 94	
Rh	23.9 ± 4.0						23.9 ± 3.3		25 ± 1		
Ru	< LOD[a]						13.3 ± 2.1				
CW7, PACEPAC Road Dust											
Pt	26.7 ± 4.8				55 ± 8						50.6 ± 1.3
Pd	0.9 ± 0.4		3.4 ± 0.9		4.0 ± 1.3						
Rh	6.6 ± 1.1				10.3 ± 1.4						10.0 ± 1.5
Ru	213 ± 23										

[a] Below the limit of detection.

the study of very difficult-to-digest samples. On the other hand, comparison of the PGE results for the road dust sample (CW7) obtained by ET-AAS in connection with an electrolytic preconcentration and separation of interfering elements, with literature data for the same sample [6,24] demonstrates the necessity of reliable analytical methods for PGE determinations in environmental samples (Table IV). The given literature data for Pd and partly for Pt and Rh differ from the ET-AAS results, but show similar precision.

The poorer precision of our results appears relatively high in comparison with those obtained by other workers (Table IV) and may be linked to the relatively small sample mass taken for digestion (100 mg reported in experimental section). Such small sample sizes may produce a relatively large scatter of the measured value and an apparent low recovery due to the inhomogeneity of the sample. For instance, with a 100-mg sample of NIES No. 8, a good average value for Pt was obtained (210 ng/g), but the standard deviation (60) was poor. On the other hand, small standard deviation of the measured values were obtained for the Road Dust CW7. The precision of replicate determinations was typically around 21% RSD.

Analytical Figures of Merit

The analytical performance characteristics were evaluated for each element. The characteristic mass and the limit of detection (LOD) based on a $3\sigma_{\text{blank}}$ criterion, are summarized in Table V. All LODs were obtained using a 30-min preconcentration. Although lower detection limits could be achieved by applying a longer preconcentration time, this was not tested because it was not practical to extend the analysis time. The LOD was limited by the blank arising from the acids despite the Suprapur quality reagents used. Consequently, the detection limit, especially for Ru, could be improved further if this source of contamination could be eliminated.

The precision of replicate determinations was calculated from the RSD (%) of the mean of five replicate measurements of analyte standards using a mass 25-fold above the LOD. Precision was in the range of 22% (Pt), 10% (Pd), 7% (Rh) and 29%

TABLE V Analytical figures of merit

Parameter	*Pt*	*Pd*	*Rh*	*Ru*
Absolute detection limit (ng)	3.6	0.5	0.3	5.9
Detection limit[a] (3σ) (ng/ml)	0.143	0.020	0.014	0.236
Limit of determination (10σ) (ng/ml)	0.477	0.066	0.047	0.786
Detection limit[b] (3σ) (ng/ml)	6.384	1.394	0.601	5.417
Enhancement factor[c]	416	503	423	46
Sensitivity[d] (ng/ml)	0.011	0.001	0.003	0.015
Detection limit[e] (ng/g)	35.8	5.0	3.5	59.0
Total analytical blank (ng)	0.5	0.8	0.2	2.5
Recoveries[f] (%)	103 ± 11	107 ± 30	74 ± 9	106 ± 14
Precision (%RSD)	22	10	7	29

[a] For preconcentration from 25 ml sample solution, 30 min deposition time.
[b] Direct sampling of a 20 μl sample solution.
[c] Compared with direct injection of 20 μl of a standard solution.
[d] Slope of the calibration curve.
[e] For sample weights of 0.1 g.
[f] Mean ± SD, %, for dust sample CW7, $n = 3$.

(Ru) (evaluated as peak area) with an average of around 21%. This reflects the cumulative imprecision of all of the sample handling, digestion, electrodeposition and preconcentration, atomization and detection steps.

Digestion and analysis procedures were evaluated for CW7. Elemental recoveries are presented in Table V. Recovery reflect means from three 100-mg samples are given. All recoveries, except for Rh, are around 100% within 16% deviation. It should be kept in mind that scatter and deviation of recovery values are not only dependent on the digestion, preconcentration and analysis of the CW7 samples, but include other effects such as the weighing of the CW7 material and the small amounts of material involved (100-mg samples were used instead of the 250-mg samples recommended by IUPAC).

The overall efficiency of the electrolytic preconcentration on the graphite tube and digestion was evaluated by a comparison of the signal response from the direct injection of 20 μl volume of sample with analyte standard solutions containing the same masses of analytes on the same tube surface and subjected to an identical thermal program. Thus, preconcentration factors of 416 (Pt), 503 (Pd), 423 (Rh) and 46 (Ru) were obtained.

Application to Other Tunnel Dust Sample

The applicability of the present electrodeposition technique was proven by analyses of the tunnel dust sample. Table VI shows results for determinations of PGEs in this sample. In all cases, calibration was achieved using the method of standard additions. Results were compared to those obtained by a number of other laboratories [2,5,9,35] and the effectiveness of this digestion-and-analysis method is demonstrated by the reasonable agreement between the results achieved. However, the Pd contents published for the tunnel dust sample [9,35] are somewhat lower. A drawback that remains is the limited sample size that can be digested with the microwave digestion system. The final results cannot be disclosed in forms of concentration values at present due to lack of certified reference material(s) with complex matrices and environmentally relevant PGE concentrations.

Generally, under optimum conditions, the entire procedure including microwave-assisted digestion (including heating and cooling steps) and measurement of atomic absorption signal took about 80 min.

TABLE VI ET-AAS results of the determination of PGEs (concentrations in ng/g ± SD of three parallel analyses) for a tunnel dust sample after electrolytic preconcentrations

Element	*This work*	*Literature data*		
		[2,5]	[9]	[35]
Pt	82.8 ± 28.4	av. 60	62.5 ± 3.8	47.0 ± 4.0
			62.9 ± 4.2	47.0 ± 3.1
			60.1 ± 3.9	69.9 ± 14.8
Pd	61.3 ± 13.4		17.4 ± 2.3	3.2 ± 0.4
Rh	19.6 ± 10.4		9.4 ± 0.8	
Ru	< LOD[a]			2.0 ± 0.2
				1.9 ± 1.0
				4.99 ± 0.90

[a] Below the limit of detection.

CONCLUSIONS

The combination of an acid digestion with *in situ* electrodeposition method in a flow-through graphite tube cell for ET-AAS has been evaluated for analytical application to environmental samples. By this approach, analytes can be removed from their matrix so that possible matrix effects from real samples can be substantially reduced. At the same time, it enables the preconcentration of these analytes, leading to corresponding improvements in detection limits compared with direct sampling of solution. On the other hand, the present method is time consuming in comparison with direct instrumental techniques. The use of HNO_3–HF–$HClO_3$/$HClO_4$ mixtures allows the determination of the total content of the elements analyzed in both road dusts and automobile exhausts. It was shown that the digestion time, acid mixtures and working pressure play a significant role in the efficiency of digestion. The main limit encountered was that the relatively small (about 100 mg) sample masses used in our procedures necessitate a very high degree of homogenization and careful subsampling during the earlier stages of sample preparation. In addition, care should be taken with the blank. The estimation of measurement uncertainty for the determination of the noble metals Pt, Pd, Rh and Ru by use of acid digestion as a sample preparation technique with subsequent analysis by ET-AAS, the contributions of the individual steps of the combined analytical methods give overall standard uncertainties of about 10–30%, depending on the analyte and the matrix used.

It should be stressed that the results of this study show that, considering the high requirements dictated by the demand to be able to determine with good accuracy low concentrations of PGEs in various environmental samples, there is still a need to further improve the analytical methodology for this purpose.

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