2.3　Sources of Error and their Elimination for Spectrometric Determination of Palladium in Environmental Samples

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2.3.1　Introduction

Despite recent advances in instrumental techniques the determination of palladium in environmental samples, such as urban aerosols, road and tunnel dust, is still a difficult task. Among various analytical techniques appropriate for the determination of low concentrations of palladium inductively coupled plasma mass spectrometry (ICP-MS) and graphite furnace atomic absorption spectrometry (GFAAS) are most often used. However, the determination of palladium in environmental samples by spectrometric techniques is strongly hampered by numerous spectral and non-spectral interferences arising from a complicated sample matrix. In order to obtain reliable results it is crucial that all sources of interferences are identified and initial sample pre-treatment steps, such as sample digestion, storage, pre-concentration of analyte, and separation of matrix, are carefully controlled in respect of palladium chemistry and introduction of potential interferences.

This paper deals with critical points in palladium determination by atomic spectrometric techniques, which may obscure receiving accurate results. The advantages and limitations of selected digestion, separation and pre-concentration procedures as well as analytical problems which may occur during preparation and storage of samples for palladium analysis are specially emphasised. The procedures for determination of palladium in environmental samples by GFAAS and ICP-MS developed by authors are also presented.

2.3.2　Limitations of spectrometric techniques (GFAAS, ICP-MS)

The drawbacks of using of GFAAS for the determination of palladium are: detection limit, insufficient for environmental materials, and occurrence of spectral interferences, which are usually caused by incompletely compensated background signal of matrix origin. The presence of Fe, Pb, Ni, Zn, and Co at $\mu g/g$ concentration causes the change in palladium absorbance

signal at λ=247.6 nm in the range from +40% to –50%, depending on the metal concentration (Leśniewska 2004). The increase of pyrolysis temperature or the measurement of palladium signal at alternative lines can partially compensate this effect. Nevertheless, pre-concentration and matrix separation procedures are essential prerequisites for determination of palladium in environmental samples by GFAAS.

The determination of palladium by ICP-MS is disturbed by spectral interferences from isobaric ions formed in plasma by geologically abundant elements such as Cu, Zn, Sr, Y, Cd, Mo, Zr with non-metals. Considering the relatively high Zr, Cd and Y concentrations in environmental samples and the high ability of Zr and Y to form interfering molecules in the plasma, the most serious interferences on ^{105}Pd, ^{106}Pd and ^{108}Pd isotopes are caused by ^{89}Y^{16}O$^+$, ^{106}Cd$^+$, ^{90}Zr^{16}O$^+$, ^{108}Cd$^+$, ^{92}Zr^{16}O$^+$ ions (Bencs et al. 2003). The instruments with a high-resolution (HR) magnetic sector-field (SF) allow often for separation many polyatomic interferences, but the mass resolution required for the elimination of interferences from ^{90}Zr^{16}O$^+$, ^{89}Y^{16}O$^+$ and ^{88}Sr^{17}O$^+$ on ^{105}Pd and ^{106}Pd is, at present, not commercially available.

The methods of overcoming these interferences were discussed in details by Bencs et al. (2003). Basically, in selection of the isotope for measuring, the composition of the sample should be considered. When simple samples are analysed, e.g. polar and alpine snow (Barbante et al. 1999), the most abundant ^{106}Pd isotope is preferred. In analysis of more complex samples, such as soil or road dust, the use of the ^{105}Pd isotope, which is less abundant but also less hampered by the high Cd and Zr concentration, is recommended (Petrucci et al. 2000, Rauch et al. 2000). The careful optimisation of instrumental conditions partially reduces the interferences to the analyte signal. Additional correction procedures as alternative sample introduction systems (ultrasonic nebulization, membrane desolvation units), use of collision cells and dynamic reaction cells, and/or mathematical correction have been also proposed.

Mathematical correction method, based on the evaluation of the actual influence of interferent on analytical signal, may provide accurate results for the determination of palladium in relatively simple matrices, such as urine (Krachler et al. 1998) or polar snow (Barbante et al. 1999). In the case of road dust and sediment samples, very high concentration of Zr and Cd preclude the application of any mathematical correction method for determination of ^{106}Pd and ^{108}Pd. In addition, the enormous interference from ^{89}Y^{16}O+ on ^{105}Pd makes impossible its accurate determination (Djingova et al. 2003).

Application of an ultrasonic nebuliser (USN) coupled to the ICP-SFMS instrument, instead of conventional pneumatic nebuliser, enhances sensitivity and the detection power of palladium in model solution by one order of magnitude, but is not sufficient for the removal of isobaric interferences during palladium determination in environmental samples (Rauch et al. 2000). Combination of the mathematical correction method and USN-ICP-SFMS allow obtaining only indicative values for palladium content in road dust (Petrucci et al. 2000). The membrane desolvation systems used for elimination of spectral interferences formed by oxide and chloride molecular ions are also inefficient for palladium determination (Kanitsar et al. 2003). Coupling of membrane desolvation system with ultrasonic nebuliser and ICP-SFMS instrument and finally with mathematical correction of interferences caused by $^{88}Sr^{16}O^{1}H^{+}$ ions finally made possible accurate determination of palladium in environmental samples (Köllensperger et al. 2000). The presented strategies need advanced technical devices not often available in routine laboratories, therefore for accurate determination of palladium by ICP-MS the chemical separation of analyte from interfering elements is still a method of choice.

2.3.3   Problems connected with chemistry of palladium in solution

Many analytical problems occurring during palladium analysis arise from the complex nature of its solution chemistry. Palladium occurs in numerous oxidation states (I, II, IV) and forms many species in a given oxidation state. As it belongs according to Pearson theory to the "soft" acids it easily forms halides, hydrides, cyanides, and other complexes with ligands containing sulfur and nitrogen donor atoms. The palladium coordination compounds in aqueous solutions have different stability and kinetic properties. Palladium is usually present in solutions as $Pd(H_2O)_4^{2+}$. The formation of $PdOH^+$ and $Pd(OH)_2$ starts at pH above 1 and insoluble $Pd(OH)_2$ precipitates from diluted nitric acid solutions. The evidence of formation of $PdNO_3^+$, $Pd(NO_3)_2$ and $Pd(OH)NO_3$ in nitric acid has been also shown (Camacho Frias et al. 1995). Above pH 2 polynuclear forms have been identified.

The palladium chloride complexes are more stable than nitrate complexes. Different pH and chloride concentration leads to a different distribution of chloro complexes of palladium in aqueous solutions. At pH 1.0 the complex $PdCl_4^{2-}$ is predominant (90-100%), at pH 2.0 the fraction of the complex $Pd(H_2O)Cl_3^-$ reaches a maximum value (30-40%), while at pH 2.3 $Pd(H_2O)_2Cl_2$ becomes more important (>80%) (Iglesias et al. 1999).

However other studies showed that at pH 3 palladium is present in the form of $PdCl_3^-$ in a wide range of chloride concentration. At higher temperatures (55°C) the change of stability constants of chloro complexes of palladium occurs what results in predominance of $PdCl_4^{2-}$ (Pirogov and Havel 1997). Hence, in the digested sample solution, depending on the pH and chloride concentration, different species of palladium can be present.

Compounds of palladium have also the tendency for sorption and reduction of their oxidation state. The interactions between the solution and the surface of laboratory vessels may cause losses of analyte during storage and pre-treatment steps. The properties of the container, such as its chemical composition and surface roughness may influence the process of adsorption. Those effects were only rarely mentioned, in spite of the fact that they may seriously influence the analytical results. The 10% decrease of absorbance was observed when solutions of palladium and other platinum group elements (PGEs) prepared in 1% HNO_3 were left for a few hours in polystyrene autosampler cups. This problem did not occur with solutions prepared in 1% HCl or stored in glassy cups (Byrne et al. 1997). Although containers made of polyethylene and PTFE are most often used in trace analysis the use of quartz vessels provides better stability of dilute palladium solutions and higher values of absorbance measured by GFAAS technique. The studies performed on the stability of Pd(II) standard solutions stored in different containers have shown that the highest losses of analyte were observed in polyethylene and polyethylene-polypropylene vessels (Godlewska-Żyłkiewicz 2002). It should be stressed that for the stabilization of samples containing palladium addition of HCl is recommended (Godlewska-Żyłkiewicz et al. 2000). Large non-polar complexes of palladium with organic ligands, e.g. with dithiocarbamates or thiourea derivatives (Benkhedda et al. 2003) may be easily adsorbed on hydrophobic materials of system manifolds as surface of tubes or columns. The memory effects and/or analyte losses may also occur in such systems.

Losses of palladium were also observed when solution containing known amounts of PGEs was evaporated directly in glassy carbon crucible indicating some physical or chemical reactions occurring between the analyte and the crucible material (Enzweiler et al. 1995). Other investigations had showed that reduction of palladium ions to metallic palladium on the surface of graphite or glassy carbon occurs from diluted nitric acid solutions (Godlewska-Żyłkiewicz and Zaleska 2002, Komarek et al. 1999). The chloro complexes of palladium formed in hydrochloric acid prevent the reduction of palladium on the carbon surface. Application of zirconium crucibles for sample decomposition (alkaline fusion) could lead to low recoveries of palladium (75%) due to its adsorption on hydrated zirconium

dioxide (Enzweiler and Potts 1995). On the other hand zirconium originating from ball mills, borosilicate glass digestion vessels or leached from crucibles significantly interferes in the determination of palladium by ICP-MS.

Although palladium is an element with the lowest abundance in the earth's crust the use of contaminated materials or tools during any step of analysis may introduce significant errors in its determination. Sample preparation steps should be carried out under clean room conditions. The ultrapure reagents and materials (sub-boiled acids, clean resins), appropriate vessels for sample storage and preparation (tubes, crucibles) and tedious cleaning procedures are necessary to avoid contamination of the samples and to reduce a procedural blank.

2.3.4   Sample digestion procedures

When critically assessing digestion technique a number of factors must be considered, as: complete dissolution of analyte, potential loss of analyte during digestion, and final form of analyte in the mineralised solution, which must be suitable for the pre-treatment procedure and detection technique of choice.

Palladium in geological samples may occur in discrete potentially soluble mineral grains, or may be embedded within refractory chromites and/or silicate minerals. Palladium in environmental samples is present mainly in elementary, more accessible, form (Müller and Heumann 2000) since it originates from catalytic converters of motor cars. Different sample decomposition methods such as digestion with mineral acids in open vessels (Benkhedda et al. 2003, Kanitsar et al. 2003, Kovacheva and Djingova 2002, Limbeck et al. 2003), high-pressure ashers (Müller and Heumann 2000), microwave digestions (Boch et al. 2002, Köllensperger et al. 2000) and fusion with sodium peroxide (Enzweiler and Potts 1995) prior to the determination of palladium have been reported. Microwave digestion allows the more rapid dissolution of materials and reduces the amount of reagents required compared with the open acid method. The efficiency of various acid leaching procedures has been studied extensively, but by far the most popular reagent is *aqua regia* (Kovacheva and Djingova 2002, Müller and Heumann 2000). The use of acids with high boiling point e.g. $HClO_4$, accelerates the dissolution of the resistant products containing palladium and oxidation of organic material (Limbeck et al. 2003, Kanitsar et al. 2003). For complete sample digestion the use of *aqua regia* in combination with HF is necessary.

Contradictory reports can be found in the literature on the necessity of using of HF prior to the determination of palladium. It has been reported that palladium strongly binds to silicate matrix of dust or to ceramic particles of the catalyst released to environment (Benkhedda et al. 2003, Kanitsar et al. 2003), so additional HF attack must be employed in the digestion procedure (Köllensperger et al. 2000, Kanitsar et al. 2003, Boch et al. 2002). However, other investigations showed that the application of HF did not cause higher mobilization of palladium from street dust samples (Kovacheva and Djingova 2002, Müller and Heumann 2000). We confirmed that treatment of road dust samples with *aqua regia* let obtain the total recovery of Pd from certified reference material BCR-723. The content of Pd in BCR-723 determined by ICP-MS (7.2 ± 1.0 ng/g) (Leśniewska 2004) agreed well with the certified value (6.0 ± 1.8 ng/g) (Zischka et al. 2002).

The application of HF for digestion has some disadvantages. The presence of HF in digested sample solution may cause the corrosion of sample introduction system in ICP-MS apparatus, or destroy the silica columns used for matrix separation (Boch et al. 2002). Acid attack with HF is usually followed by evaporation step to remove silica and fluoride, as the volatile silicon tetrafluoride, SiF_4. Overheating of the sample for an extended period can result in low yields either through losses of volatile species or enhancement of interferences. In the absence of solvents irreversible adsorption of palladium on the surface of reaction vessel could occur, and the dry residue could be only partially dissolved with diluted HCl. To avoid the evaporation of HF prior to the measurement step the addition of H_3BO_3, for masking of fluoride ions, was proposed. However, this reagent causes interferences during palladium determination by ICP-MS (Köllensperger et al. 2000), and positive results could only be obtained when additional matrix separation step was applied (Boch et al. 2002). The other potential difficulty is that more interfering Zr and other metals are released form soil samples after the total digestion.

It is worthwhile to stress that the chemical forms of the PGEs after digestion of real sample may not be identical to those found in standard solution. Pre-treatment procedure of samples dissolved in *aqua regia* must include elimination of nitrates from the solution, because stable nitrites of platinum and palladium behave differently to chloride complexes. In this case double evaporation with HCl to ensure conversion of palladium into the chloride form is recommended, especially if the latter ion-exchange separation is carried out. As in the presence of HF fluoride complexes of other metals (e.g. YF_4^-) might be formed, they can pass through the cation-exchange column together with the analyte.

2.3.5   Separation/pre-concentration procedures

 Among various procedures used for the pre-concentration/separation of palladium (Godlewska-Żyłkiewicz 2004), solid phase extraction (SPE) based on different interactions between the analyte and the solid sorbent has found one of the most important positions.

 Ion-exchange methods are based on the fact that palladium forms highly stable anionic chloro complexes, while other metals form weaker anionic or stable cationic species. Prior to any ion-exchange separation it is essential that the palladium is fully in a suitable chemical form. The interfering cations are exchanged and adsorbed on the cation-exchange resin, while the analyte is passed through the clean-up column. The efficiency of such separation depends on the kind of resin, acidity of the sample, presence of sufficient amount of chloride ions, size of the column and mesh of the resin, as well as occurrence of other complexing reagents in the sample solution.

 The efficiency of matrix separation by cation exchangers was assessed using Dowex 50WX-2, Dowex HCR-S, Varion KS, Cellex-P and Dowex 50WX-8. The initial investigations have shown, that the latter has the best characteristic (Table 2.3.1). When the concentration of HCl is too low (below 0.05 mol/l), palladium cannot efficiently form complex anions and is adsorbed on the cation-exchange resin. Fig. 2.3.1 shows that small losses of palladium from 0.5 mol/l HCl may also occur on too large columns, and the use of resins of higher mesh (50-100) is preferable as cations are better retained on such resin. Columns that have been used many times before tend to retain more palladium that columns containing new resin.

 Another potential difficulty of using cation-exchangers is passing through the column, together with $PdCl_4^{2-}$, metals which form oxide interferences on the most of palladium isotopes as Zr, Mo and Y. It was found that a significant amount of yttrium was not retained on the column from road dust (25%) and tunnel dust (49%), when samples were digested with

Table 2.3.1.   Recovery of palladium (1 ng) from synthetic solutions by ICP-MS after elimination of interferences on Dowex 50WX-8 (2g, mesh 50-100) (n = 6)

Sample matrix (1 ng Pd)	Pd recovery [%]
0.5 mol/l HCl	94.2 ± 0.4
0.5 mol/l HCl + 0.7 mol/l HNO$_3$	88.4 ± 0.6
0.05 – 2.5 µg Hf, Zr, Y, Sr, Cu, Zn in 0.5 mol/l HCl	89.1 ± 1.7
0.5 – 25 µg Hf, Zr, Y, Sr, Cu, Zn in 0.5 mol/l HCl	89.5 ± 1.0

HF, indicating that neutral or negatively charged fluorocomplexes of yttrium have been formed. Therefore the use of such procedures in connection with isotope dilution (ID) ICP-MS is problematic with respect to elimination of interferences from metals forming polyatomic ions. The quantitative retention of yttrium (99.9%) on Dowex 50WX-8 was observed when samples were digested with *aqua regia*. The content of palladium in road dust BCR-723 determined by ICP-MS after matrix separation on Dowex 50WX-8 was 7.2 ± 1.0 ng/g (Leśniewska 2004), while the certified value is 6.0 ± 1.8 ng/g (Zischka et al. 2002).

The sorption ability of anion-exchange resins is quite different for various species. The higher oxidation states of PGEs are more strongly sorbed by anion resins, whereas lower oxidation states and less charged species are more weakly bound. Formation of hydroxycomplexes of a smaller charge leads to a decrease in the sorption efficiency on such resins. Another problem with strong anion exchangers is that commercially available resins do not selectively adsorb palladium chloro complexes. The elements that form anionic complexes during digestion procedure (Ti, V, Al, Fe, Ce, Pb, Zr, Cu, and Y) can be also enriched on such resins (Kovacheva and Djingova 2002). However the addition of masking agents should be avoided as they can change the chemical form of palladium. In many cases the recovery of noble metals from strong anion-exchange resins is not quantitative. There-
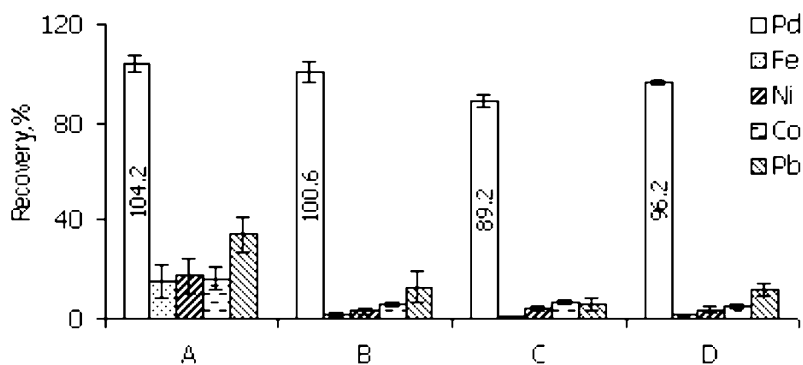
Fig. 2.3.1.   Recovery of Pd (150 ng) and Fe (1 mg), Ni (0.5 mg), Co (0.5 mg), Pb (1 mg) determined by GFAAS from solution passed through cation-exchange resins: A – Dowex 50 WX-8, 20-50 mesh, 2g; B – Dowex 50WX-8, 50-100 mesh, 2g, C - Dowex 50 WX-8, 50-100 mesh, 4g; D – Varion KS, 4g

fore, the ID technique is especially advantageous because partial loss of analyte has no effect on the analytical results (Kanitsar et al. 2003). Since polyatomic interferences on some isotopes may preclude this approach for some sample types, the careful control of isotopic ratios must be performed. The total recovery of palladium has been achieved by digestion of the resin, by elution with large volumes of hot concentrated nitric acid or specific palladium complexing reagents. The main advantage of using weakly basic cellulose exchangers e.g. Cellex-T (containing Quarternary amine functional groups) is a quantitative recovery of palladium retained on the column with relatively small volume (2-5 ml) of diluted thiourea (TU) solution (Godlewska-Żyłkiewicz et al. 2000).

The main limitation in application of anion-exchangers in pre-concentration procedures comes from the fact that environmental samples contain high amounts of inorganic ions which overload the capacity of these sorbents. Therefore the combination of cation and anion-exchangers is proposed.

Because the total retention of palladium on Cellex-T was achieved from solutions of pH>4, to avoid hydrolysis and precipitation of other ions the sample clean-up procedure by means of Dowex 50WX-8 was performed for real samples. The quantitative elution of palladium was obtained for 0.1 mol/l TU in 2 mol/l HCl (Table 2.3.2). The described method was applied for determination of palladium by GFAAS in highly contaminated samples (Pd content > 100 ng/g). When using the evaluated procedure for determination of palladium by ICP-MS unidentified interference occurred, causing the palladium recovery from road dust and BCR-723 above 200%. The low content of yttrium and strontium determined in eluate indicated that these metals can not be a source of such interference. Probably the used eluent partially destroys the resin, and such „particles" introduced into plasma of MS caused interference during palladium measurements. It is worth mentioning that the accurate results were obtained for Pt determination when the described above procedure was applied (Leśniewska 2004).

The pre-concentration based on the biosorption of analyte by micro-organisms is one of the variants of SPE technique. In this case binding of metal ions is attributed to various mechanisms such as ion-exchange, adsorption, complexation, and micro-precipitation depending on kind of used micro-organism and studied metal. The procedures developed for selective accumulation of palladium (together with platinum) on algae *Chlorella vulgaris* immobilized on silica gel (Godlewska-Żyłkiewicz 2003) and Cellex-T resin (Dziwulska et al. 2004) were applied for the determination of palladium in spiked waste water and grass samples by GFAAS.

Table 2.3.2.   Recovery of palladium from road dust after matrix separation on Dowex 50WX-8 (2g, 200-400 mesh) and palladium pre-concentration on Cellex-T (0.2 g)

Sample	Eluent	Eluent volume [ml]	Determination technique	Pd recovery [%]
Road dust*	2 mol/l HCl	4	GFAAS	73.5 ± 4.9
Road dust*	0.25 mol/l TU +1 mol/l HCl	2 + 2 3 + 2 5	GFAAS	80.6 98.3 97.6
Road dust*	0.1 mol/l TU+ 2 mol/l HCl	4	GFAAS	102.9± 4.7
Road dust	0.1 mol/l TU + 1 mol/l HCl	4	ICP-MS	>200
BCR-723	0.1 mol/l TU + 1 mol/l HCl	4	ICP-MS	>200

*spiked with 40 ng of Pd

Using yeast *Saccharomyces cerevisiae* immobilized in calcium alginate results in accurate palladium determination in road dust samples and geological materials (Godlewska-Żyłkiewicz and Kozlowska 2005).

Although the procedures based on SPE concept are still the most popular, alternative methods of palladium separation have been also proposed. The main advantage of separation of palladium by reductive co-precipitation with mercury is that the used collector can be efficiently removed from the sample at 300°C. The procedure followed by total reflection X-ray fluorescence (Messerschmidt et al. 2000) was successfully applied for analysis of road and air dust (Zereini et al. 2004). Electrolytic reduction of palladium at controlled potential on the graphite or glassy carbon electrodes in a flow-through mode was followed by its electrochemical dissolution with the aid of appropriate stripping reagent. The proposed procedure was used for the determination of palladium in road dust samples by GFAAS (Godlewska-Żyłkiewicz and Zaleska 2002).

2.3.6 Conclusions

Accurate determination of trace amounts of palladium by spectrometric methods (GFAAS, ICP-MS) is practically impossible without chemical pre-concentration/separation procedures. The matrix composition and the elements introduced in the course of sample dissolution, also due to contamination, significantly influence the proper choice of the determination technique. Until now the new technical developments, in particular for ICP-MS, not always offer the best way of elimination of the interferences. The use of HF for sample digestion must be critically evaluated, as in some cases it may introduce serious errors. The variety of chemical forms of palladium in the final solution may also affect the results of spectrometric determination. Attention should be paid to the material of the laboratory ware to avoid losses due to adsorption and carryover of the analyte in subsequent analyses. The most reliable way for identification and elimination of errors is always the use of certified reference materials.

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