

On the Underestimated Factors Influencing the Accuracy of Determination of Pt and Pd by Electrothermal Atomic Absorption Spectrometry in Road Dust Samples

Barbara Leśniewska, Sylwia Sawicka
and Beata Godlewska-Żyłkiewicz

Abstract The accurate determination of Pt and Pd in environmental samples requires application of sensitive analytical technique as well as the separation/preconcentration of analytes from complex matrix of such samples. The careful optimization of sample pre-treatment procedure is also essential, but often certain steps of optimization process are neglected. The solid phase extraction procedure based on separation/preconcentration of Pt and Pd on immobilized biomass of fungi *Aspergillus* sp. and determination of analytes by ETAAS was chosen as an example for discussion. The most critical aspects of sample pre-treatment procedure, that affect the accuracy of determination of Pt and Pd in road dust, such as sample storage, sample digestion, transformation of analyte into adequate form, and separation of analytes from interfering matrix are discussed in this chapter. The optimized procedure was applied to the determination of Pt and Pd in road dust collected in Białystok (Poland). The content of Pt in road dust increased from $93 \mu\text{g kg}^{-1}$ in 2000 to $263 \mu\text{g kg}^{-1}$ in 2011, while the content of Pd increased from $43 \mu\text{g kg}^{-1}$ in 2000 to $328 \mu\text{g kg}^{-1}$ in 2011.

1 Introduction

The elevated content of Pt and Pd in the urban and roadside environment, which significantly exceeds the geochemical background (1 ng g^{-1}), is mainly connected with emission of these metals from industrial and transport sources. The biological processes occurring in various compartments of environment can lead to the transformation of platinum group elements (PGE) into forms available to plants and

B. Leśniewska · S. Sawicka · B. Godlewska-Żyłkiewicz (✉)
Institute of Chemistry, University of Białystok, Hurtowa 1, 15-399 Białystok, Poland
e-mail: bgodlew@uwb.edu.pl

other living organisms. In the last decade the studies related to emission, occurrence, toxicity, transformation and determination of Pt and Pd in the environment were undertaken (Kalavrouziotis and Koukoulakis 2009; Spada et al. 2012; Zereini et al. 2012). In the near future regular monitoring of these metals in the environment will be probably compulsory.

The determination of Pt and Pd in environmental samples is still a challenging task as a content of these analytes is at a level of ng g^{-1} . The application of sensitive analytical technique, such as inductively coupled plasma mass spectrometry (ICP-MS) (Gomez et al. 2003; Shinotsuka and Suzuki 2007), inductively coupled plasma optical emission spectrometry (ICP-OES) (Herincs et al. 2013), electrothermal atomic absorption spectrometry (ETAAS) (Schuster and Schwarzer 1996; Boch et al. 2002), chemiluminescence (CL) (Malejko et al. 2012) or adsorptive stripping voltammetry (AdVS) (Zimmermann et al. 2003), and careful optimization of sample analytical procedure are necessary to obtain reliable results of analysis. Generally, for elimination of interference arising from complex matrix of samples the application of separation/preconcentration procedure is essential. For this purpose classical methods of separation, such as precipitation and liquid-liquid extraction have been developed. Co-precipitation of Pt with tellurium (Gomez et al. 2003) and Pd with mercury (Zimmermann et al. 2003) was successfully applied for separation of analytes from environmental samples. A variety of dispersive liquid-liquid microextraction (Liang and Zhao 2011) and cloud point microextraction methods (Meeravali et al. 2008) have been used as well. Among other methods, the solid phase extraction (SPE) is most widely recommended (Godlewska-Żyłkiewicz 2004; Myasoedova et al. 2007). The retention mechanism of analytes on solid sorbents include adsorption (Schuster and Schwarzer 1996; Ebrahimzadeh et al. 2010; Rastegarzadeh et al. 2010; Leśniewska et al. 2005; Bagheri et al. 2012), chelation (Rojas et al. 2006, 2009), ion-exchange (Shinotsuka and Suzuki 2007; Nakajima et al. 2009; Krishna et al. 2009; Herincs et al. 2013) and ion-pair formation. Biosorbents, including free and immobilized biomass such as algae *Chlorella vulgaris* (Dziwulska et al. 2004), yeast *Saccharomyces cerevisiae* (Godlewska-Żyłkiewicz and Kozłowska 2005) and fungi *Aspergillus* sp. (Woińska and Godlewska-Żyłkiewicz 2011; Malejko et al. 2012), have proved to be an attractive alternative to traditional, commercially available sorbents. The biosorption process has been successfully applied for separation of PGE from environmental samples and their determination by ETAAS.

Even if it is widely recognized that the sample pre-treatment procedure is a main source of errors in the analytical process, certain factors are still underestimated by some analysts. The most critical aspects of the sample pre-treatment procedure, that affect the accuracy of the results, such as sample digestion and separation of analytes from interfering matrix before determination of Pt and Pd in road dust samples by ETAAS technique, will be discussed in detail in this chapter. As an example, the procedure based on separation of Pt and Pd on immobilized biomass of fungi *Aspergillus* sp. (Woińska and Godlewska-Żyłkiewicz 2011), has been chosen.

The analysed samples of road dust were collected from the main intersection located in the centre of Białystok (Poland) in the period from 2000 to 2011. The fraction of size <0.075 mm was taken for analysis.

2 Digestion Procedure for Road Dust Samples

Inhomogeneous distribution of PGE in road dust and their resistance to various chemicals, complex matrix of such samples often induce problems with complete transfer of the analytes into solution (Balcerzak 2002; Godlewska-Żyłkiewicz 2004). The selected digestion procedure must provide quantitative dissolution of analytes and their transformation into chemical forms suitable for a further pre-treatment step.

Pt and Pd of anthropogenic origin are mainly emitted to the environment in elemental (nano-metallic) and oxide forms (Merget and Rosner 2001). Wet chemical digestions utilizing various mineral acids (HCl, HNO₃, HClO₄, HF) in open (Chwastowska et al. 2004) or closed systems heated in convection or microwave ovens are commonly proposed for decomposition of road/tunnel dust or soil (Table 1) (Boch et al. 2002; Limbeck et al. 2003; Matusiewicz and Lesiński 2001; Tsogas et al. 2008). The necessity of using HF for digestion of samples containing silicate matrix was discussed in the literature (Balcerzak 2002; Boch et al. 2002; Leśniewska et al. 2005). According to some authors (Boch et al. 2002; Tsogas et al. 2008) Pd is strongly bound to silicate matrix of dust and ceramic particles emitted to environment from automotive catalysts, therefore its quantitative releasing into solution arises after total digestion of the sample matrix. However, the addition of concentrated HF to the sample induces some analytical problems. The larger amount of dissolved metal ions from silicates or aluminosilicates, e.g. Al(III), Fe(III), Pb(II), Ni(II), Co(II), Cu(II) in the final solution may cause spectral interference in the detection step (Brzezicka and Szmyd 1999; Brzezicka and Baranowska 2001; Godlewska-Żyłkiewicz and Leśniewska 2006, 2010) or problems with efficient separation of matrix.

The removal of these heavy metals from the digested solutions is difficult, because in the presence of HF negatively charged fluoride complexes are formed, which cannot be separated from anionic chlorocomplexes of Pt and Pd, and often are simultaneously enriched on anion-exchange columns (Brzezicka and Baranowska 2001; Godlewska-Żyłkiewicz and Leśniewska 2006). The excess of HF in the analysed solutions might also cause serious damage to the column packing used for the separation of the matrix, e.g. silica gel (Boch et al. 2002). To avoid these adverse effects the evaporation of excess of HF (Limbeck et al. 2003) or masking of fluoride ions with H₃BO₃ (Boch et al. 2002; Tsogas et al. 2008) have been proposed. Some examples of successful application of alone *aqua regia* for digestion of road dust (Rauch et al. 2000; Müller and Heumann 2000) and BCR 723 (Leśniewska et al. 2005; Godlewska-Żyłkiewicz and Leśniewska 2006; Wońska and Godlewska-Żyłkiewicz 2011) for determination of PGE show that addition of HF to such samples is not essential.

Table 1 Digestion procedures for the determination of Pt and Pd by ETAAS in environmental samples

Sample	Digestion procedure	Evaporation of excess of acids	Separation of analytes	References
Road dust, soil	I step: dry ashing at 400 °C for 1 h;	Evaporation of acids with 2 mL of HCl (2x); residue was dissolved in 3 mol L ⁻¹ HCl	Polymethacrylic ester modified with dithizone	Chwastowska et al. (2004)
	II step: digestion with <i>aqua regia</i> in open vessels			
Urban aerosol	I step: MW digestion with HNO ₃	Evaporation of acids near to dryness; dilution in 1.2 mol L ⁻¹ HCl	Silica gel (C18) modified with DEBT	Limbeck et al. (2003)
	II step: digestion with HF: HClO ₄ (2:1) in open vessels			
Tunnel dust	I step: MW digestion with HNO ₃ :H ₂ O ₂ (5:2);	Dilution in water	Silica gel (C18) modified with DEBT	Boch et al. (2002)
	II step: HF addition;			
	III step: H ₃ BO ₃ addition			
Road dust CW-7	MW digestion with HNO ₃ : HF:HClO ₄ (1:1:1)		Electrochemical preconcentration on graphite tube	Matusiewicz and Lesiński (2001)
Road dust BCR-723	I step: MW digestion with HNO ₃ :HF (2:3)	Evaporation to dryness; dissolution of residue in 1 mol L ⁻¹ HNO ₃		Tsogas et al. (2008)
	II step: H ₃ BO ₃ addition			
Road dust	MW digestion with <i>aqua regia</i>	Evaporation near to dryness with 1 mL HCl (2x); dilution in water	Yeast <i>Saccharomyces cerevisiae</i> immobilized in calcium alginate	Godlewska-Żyłkiewicz and Kozłowska (2005)
Road dust	MW digestion with <i>aqua regia</i>	Evaporation with 2 mL HCl (3x); dilution with water	Fungi immobilized on Cellex-T	Woińska and Godlewska-Żyłkiewicz (2011)

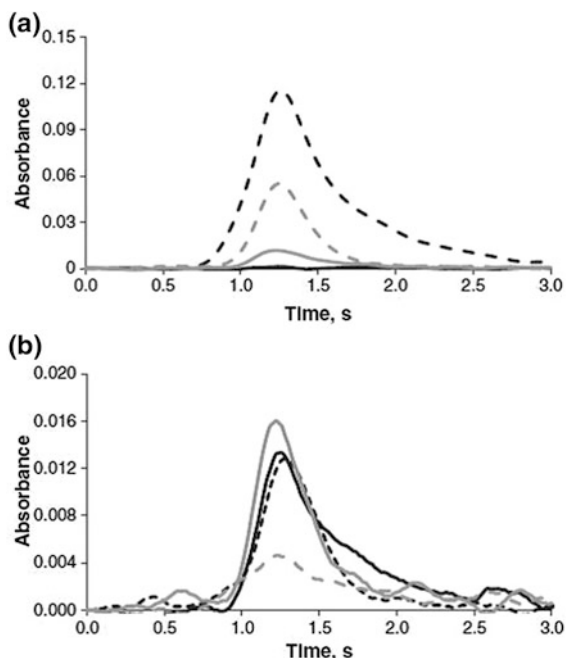
MW—microwave assisted digestion, DEBT—N,N-diethyl-N'-benzoylthiourea

It must be also considered that during storage and pre-treatment of samples, the specific problems connected with chemical reactions and physical processes taking place in solutions or at the phase boundary, e.g. adsorption of analytes on the vessel's surface or changes in the oxidation state may occur. The type of vessels used for preparation and storage of standard and sample solutions (Godlewska-Żyłkiewicz 2002; Cobelo-Garcia et al. 2007), and the roughness of their surface have also an effect on the accuracy of analysis. The memory effect cannot be neglected as well (Kowalska et al. 2005). The storage of Pt solutions in quartz vessels and Pt solutions in glass vessels is recommended, because in this way the adsorption effect is diminished. Efficient cleaning of laboratory ware is possible with solutions containing chemical agents complexing Pt and Pd, such as acidic solutions of thiourea (Godlewska-Żyłkiewicz 2002; Cobelo-Garcia et al. 2007). The crucibles of unknown history should be cleaned before use in concentrated acids, e.g. in a mixture of HCl, HNO₃ and HClO₄, HCl or *aqua regia*.

Due to the variety of chemical forms of Pt and Pd in solutions obtained after digestion of samples and various stability of the species, the special treatment of samples should be performed in order to transform the analytes into the form suitable for separation step. A high amounts of chloride and nitrate(V) ions are often added during sample preparation procedure, e.g. during leaching of PGE from road dust with *aqua regia*. It was found that the presence of hydrochloric acid (0.5–4.0 mol L⁻¹) and nitric(V) acid (0.5–2.0 mol L⁻¹) cause increase of the analytical signal of Pt by 20–50 % and the signal of Pd by 30–60 % measured by ETAAS (Godlewska-Żyłkiewicz and Leśniewska 2010). The possibility of formation of stable nitrosyl and/or hydroxynitrate compounds of some PGE (Pt, Ru, Pd) must be carefully considered during sample preparation procedure. The excess of acids should be removed from a digested sample while different species of analytes should be transferred into stable chlorocomplexes. The repeated evaporations of the solution in the presence of concentrated HCl is recommended to that end. It must be stressed that this stage may seriously influence the accuracy of results. On the one hand, the complete evaporation of the solution can lead to the irreversible adsorption of the analyte on the surface of the vessel. On the other hand, often the non-quantitative conversion of analytes takes place as the efficiency of the conversion reaction depends on the number of evaporation steps and the volume of HCl used. Therefore, this step should be optimized experimentally, depending on the type and amount of the digested sample matrix.

In this work the effect of sample pre-treatment step on the accuracy of determination of Pt by ETAAS in road dust was studied in detail. The recovery of Pt from BCR-723 and road dust samples spiked with 20–30 ng of analyte was controlled after variable number of evaporation steps performed with addition of different volumes of concentrated HCl. Such pretreated samples were next loaded on the columns filled with immobilized fungi *Aspergillus* sp. The proper evaporation procedure was chosen on the basis of recovery data and the shape of absorbance signals of the analyte registered from column eluate (Fig. 1). Initially, the digested sample was evaporated two times, almost to dryness, in cleaned quartz crucibles with addition of 1 mL of HCl. However, the repeatability of Pt determination was low (>15 %). Furthermore, a high signal of background was also registered.

Fig. 1 Atomization signals of Pt from BCR-723 (road dust) (taken from Woińska and Godlewska Żyłkiewicz 2011, with Elsevier permission); **a** — Pt in digested sample; ---- sample background; Pt in eluent (sample evaporated 2 times with 1 mL HCl); eluent background; **b** — Pt in eluent (sample evaporated 4 x with 1 mL HCl); ---- eluent background; Pt in eluent (sample evaporated 3 times with 2 mL HCl); eluent background



When road dust sample was evaporated four times with addition of 1 mL of HCl, the recovery of Pt decreased to 80 %. When samples were evaporated three times with 2 mL of HCl the recovery of Pt from road dust reached 105 %, and from BCR-723 was equal to 107 %. It was confirmed that this procedure provides acceptable recovery of the analyte as well as the efficient elimination of the background signal. For comparison, the atomization signal of Pt obtained from directly injected digested sample is also shown in Fig. 1a.

3 Separation and Determination of PGE

For separation of trace amounts of Pt and Pd from road dust the SPE technique based on biosorption process on various microorganisms was developed (see chap. “Appraisal of Biosorption for Recovery, Separation and Determination of Platinum, Palladium and Rhodium in Environmental Samples”). It was found that fungi *Aspergillus* sp. immobilized on Cellex-T resin were very efficient in terms of selectivity and reproducibility (Woińska and Godlewska-Żyłkiewicz 2011). The analytes were efficiently retained from standard solutions on this biosorbent at pH range from 1 to 4 and quantitatively eluted from the column with thiourea solutions (0.25 mol L^{-1}) prepared in HCl (0.3 mol L^{-1}). However, in order to apply the developed procedure to analysis of road dust samples some further optimization of the procedure had to be done.

Generally, the large content of transition metal ions in the solution obtained after evaporation of digested road dust sample may influence the recovery of the analyte from biosorbent. The retention of the analyte may be diminished due to the competition of the analyte and interfering ions for active sites of sorbent or overloading sorption capacity of the used sorbent. The signals of the analytes registered from eluates are decreased due to interferences from foreign ions co-eluted together with the analytes, and this effect influences their recoveries. Therefore, in many cases the analytical procedure should be completed with additional step of column rinsing before elution of the analyte. The addition of acids, bases and buffering agents used for adjusting of sample pH to the value required to efficient separation as well as reagents used for elution can influence the analytical signal of analytes measured by ETAAS.

The retention of palladium and platinum on the fungi *Aspergillus* sp. immobilized on Cellex-T was not diminished in the presence of high excess of transition metal ions (10 mg L^{-1} - 10 g L^{-1} of Al(III), Cr(III), Co(II), Fe(III), Ni(II), and Pb(II)) (Woińska and Godlewska-Żyłkiewicz 2011). However, their presence considerably influenced the recovery of analytes. The strongest decrease of platinum and palladium recoveries (to 46.5 and 56.2 %, respectively) was observed in the presence of Co(II) ions (10 mg L^{-1}). The significant background signals registered from eluate solutions indicate that transition metal ions nonspecifically retained on the low mass of sorbent were co-eluted together with the analytes. Removing of matrix ions retained on the sorbent was performed by rinsing the column before the elution step with water or nitric acid of different concentrations. The example below shows the process of optimization of rinsing procedure, which had been used for the elimination of negative effect of Co(II) ions (10 mg L^{-1}) on the recovery of Pt ($50 \text{ } \mu\text{g L}^{-1}$) from the column (Fig. 2). As mentioned above the recovery of Pt from such solution was only 46.5 %. Rinsing the column with 3, 5 or 20 mL of water resulted in significant reduction of the background signal and increase of Pt recovery to 55, 64 and 78 %, respectively (Fig. 2a). Because the recovery of Pt was not quantitative, solutions of nitric acid of various concentrations (0.001 – 0.1 mol L^{-1}) were tested for removal of Co(II) ions from the column. As can be seen in Fig. 2b, the use of 3 and 5 mL of $0.001 \text{ mol L}^{-1} \text{ HNO}_3$ resulted in 51 and 83 % recovery of Pt. The recovery equals 79 % was obtained using for this purpose of 3 mL of $0.05 \text{ mol L}^{-1} \text{ HNO}_3$. Accurate results of the analysis (recovery: $93.2 \pm 2.0 \%$, $n = 3$) and the total elimination of the background signal was obtained when column was rinsed with 5 mL of $0.05 \text{ mol L}^{-1} \text{ HNO}_3$. The small losses of Pt (recovery: 86 %) with rinsing solution were observed when higher concentration of nitric acid ($>0.1 \text{ mol L}^{-1}$) was used. The effectiveness of the developed procedure was proved by analysis of standard Pt solutions ($50 \text{ } \mu\text{g L}^{-1}$) containing a high concentrations of foreign ions, namely a mixture of Al(III), Cr(III) and Co(II) ions of total concentration from 30 mg L^{-1} to $2,608 \text{ mg L}^{-1}$. The recovery of Pt from such solutions was in the range from $101.7 \pm 2.3 \%$ to $106.8 \pm 5.2 \%$ ($n = 4$). The recovery of platinum decreased to $60.3 \pm 0.4 \%$ ($n = 3$), when the solution contained as much as 10 g L^{-1} of Al(III), 400 mg L^{-1} of Cr(III) and 30 mg L^{-1} of Co(II). In the same way the procedure of column rinsing was optimized for Pd determination. The recovery of Pd ($50 \text{ } \mu\text{g L}^{-1}$) from the column in the presence of other

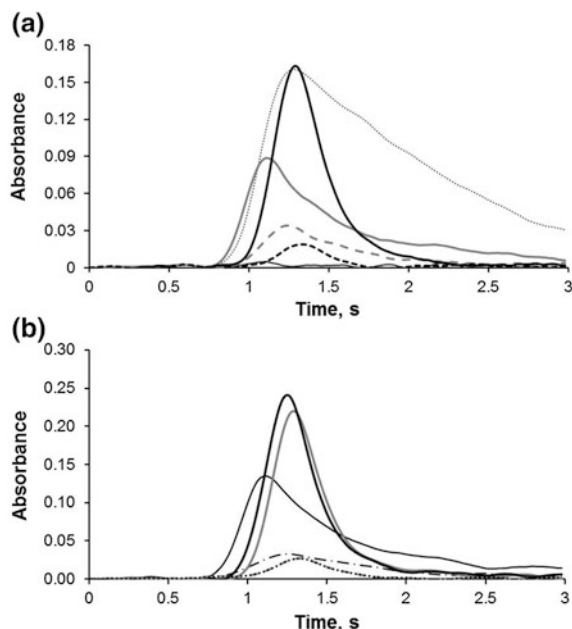


Fig. 2 Atomization signals of Pt from solutions containing $50 \mu\text{g L}^{-1}$ Pt + 10mg L^{-1} Co after separation on fungi *Aspergillus* sp immobilized on Cellex-T: **a** — Pt signal in sample solution; sample background; Pt signal in eluent, column rinsed with: — 3 mL of H₂O, 20 mL of H₂O; eluent background, column rinsed with: --- 3 mL of H₂O, ---- 20 mL of H₂O; **b** Pt signal in eluent, column rinsed with: — 3 mL 0.001 mol L⁻¹ HNO₃, — 5 mL 0.001 mol L⁻¹ HNO₃, 5 mL 0.05 mol L⁻¹ HNO₃; eluent background, column rinsed with: --- 3 mL 0.001 mol L⁻¹ HNO₃, ---- 5 mL 0.001 mol L⁻¹ HNO₃, 5 mL 0.05 mol L⁻¹ HNO₃

ions (2.5g L^{-1} of Fe(III), 500mg L^{-1} of Ni(II), 9mg L^{-1} of Co(II) and 6mg L^{-1} of Pb(II)) amounted to $100.3 \pm 0.4 \%$ ($n = 4$). Finally, it was found that using of 5 mL of 0.05mol L^{-1} HNO₃ for column rinsing in case of Pt determination, or 5 mL of 0.1mol L^{-1} HNO₃ in the case of Pd determination, allows for quantitative recovery of analytes and significant elimination of interferences even in the presence of 50,000–60,000-fold excess of other ions.

4 Analysis of Road Dust Samples

The content of Pt and Pd in road dust samples collected in the center of Białystok (300,000 inhabitants, main intersection of urban roads, sampling at the distance of 2 meters from a footpath with traffic lights) was determined using a developed procedure consisting of digestion of samples in *aqua regia*, evaporation of samples with concentrated HCl, separation of analytes on fungi *Aspergillus* sp. immobilized on Cellex-T and their determination by ETAAS. The obtained results are presented in

Fig. 3 Pt and Pd content in road dust collected in years 2000-2011 from main intersection in Białystok

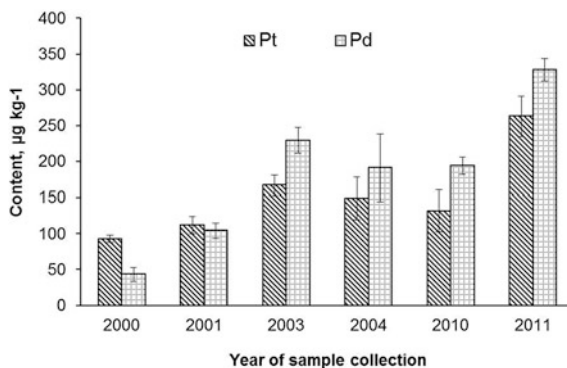


Fig. 3. The content of Pt in road dust increased from $93 \mu\text{g kg}^{-1}$ in 2000 to $263 \mu\text{g kg}^{-1}$ in 2011, while the content of Pd increased from $43 \mu\text{g kg}^{-1}$ in 2000 to $328 \mu\text{g kg}^{-1}$ in 2011. These values are significantly higher than background values, which suggest the input of PGE to the environment from automobile catalyst systems. The rapid increase of content of PGE in road dust is probably an effect of 140 % increasing of the number of cars registered in Białystok within this period (according to the Department of Inhabitants Service, City Office, Białystok from 58,000 in 2001 to 138,407 in 2011). The increase of Pd content in road dust was more rapid than the increase of Pt, which can be related to the changes in composition of catalytic converters introduced at the beginning of 2000, when Pt was replaced by Pd due to its high price. Since 2003 almost constant ratio of content of Pt to Pd in collected road dust has been observed ($\text{Pt}_{\text{content}}/\text{Pd}_{\text{content}} = 0.746 \pm 0.055$).

The obtained values of Pt and Pd content in road dust in Białystok are similar to the results obtained in the UK (Prichard et al. 2009), Spain (Simitchiev et al. 2008), the USA (Spada et al. 2012) or Greece (Tsogas et al. 2008) (Fig. 4) in road dust collected from the places with high traffic. The traffic intensity, the speed of cars and driving conditions influence the emission rate of PGE. The emission is also higher during continued stop/start cycles as well as during engine's ignition (Tsogas et al. 2008), what often happens at traffic lights. The content of PGE in samples collected in Białystok is quite high, which can be explained by the sampling place situated close to traffic lights. The content of Pt and Pd in samples collected in 2009 from ring road of the city was much lower, namely 48 and $97 \mu\text{g kg}^{-1}$. The content of PGE in tunnel dust (the USA) is among highest values.

The PGE content in road dust obtained in Hong Kong and Macao (China) is also comparable to our results, as in those cities catalytic converters were applied to vehicles as early as in European countries (Pan et al. 2013). In Beijing and Shanghai (China) the PGE content in road dust samples is relatively lower, what was explained by considerable dilution of dust due to engineering (road) construction in the sampling time of 2007. The lower content of PGE in road dust in Kolkata (India), Qingdao and Wuhan (China), and Seoul (Korea) (Lee et al. 2012) can be connected with shorter time period when vehicles have been equipped with catalytic converters.

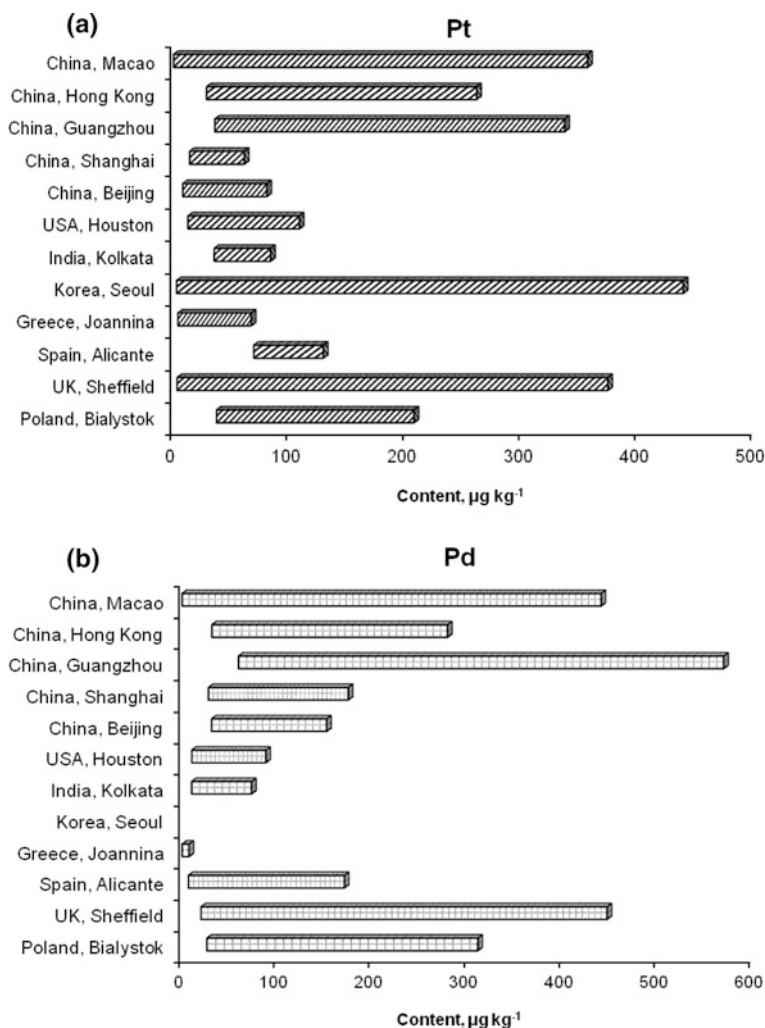


Fig. 4 Ranges of Pt (a) and Pd (b) content in road dust in different countries (Pan et al. 2013; Spada et al. 2012; Lee et al. 2012; Tsogas et al. 2008; Smitchiev et al. 2008; Prichard et al. 2009, this work)

5 Conclusions

It is of key importance that the reliable determination of Pt and Pd in road dust by spectrometric techniques (e.g. ETAAS) requires careful optimization of sample pre-treatment procedure. The steps, which seems to be less important, as evaporation of acids from digested samples or rinsing of column after separation of analytes, have

the significant effect on the final result, what was described in this chapter. Therefore, all steps of procedure should be optimized experimentally using samples of similar matrices or certified reference materials.

References

- Bagheri A, Taghizadeh M, Behbahani M, Asgharinezhad AA, Salarian M, Dehghani A, Ebrahimzadeh H, Amini MM (2012) Synthesis and characterization of magnetic metal-organic framework (MOF) as a novel sorbent, and its optimization by experimental design methodology for determination of palladium in environmental samples. *Talanta* 99:132–139
- Balcerzak M (2002) Sample digestion methods for the determination of trace of precious metals by spectrometric techniques. *Anal Sci* 18:737–750
- Boch K, Schuster M, Risse G, Schwarzer M (2002) Microwave-assisted digestion procedure for the determination of palladium in road dust. *Anal Chim Acta* 459:257–265
- Brzezicka M, Baranowska I (2001) Methods for separation of trace amounts of platinum and investigation of the influence of interfering elements during platinum determination in copper ores and copper concentrates by graphite furnace atomic absorption spectrometry. *Spectrochim Acta* 56B:2513–2520
- Brzezicka M, Szmyd E (1999) Investigation of the influence of interfering elements on the determination of palladium in copper ores by graphite furnace atomic absorption spectrometry. *Spectrochim Acta* 54B:883–889
- Chwastowska J, Skwara W, Sterlińska E, Pszonicki L (2004) Determination of platinum and palladium in environmental samples by graphite furnace atomic absorption spectrometry after separation on dithizone sorbent. *Talanta* 64:224–229
- Cobelo-Garcia A, Turner A, Millward GE, Couceiro F (2007) Behaviour of palladium(II), platinum(IV), and rhodium(III) in artificial and natural waters: influence of reactor surface and geochemistry on metal recovery. *Anal Chim Acta* 585:202–210
- Dziwulska U, Bajguz A, Godlewska-Żyłkiewicz B (2004) The use of algae *Chlorella vulgaris* immobilized on Cellex-T support for separation/preconcentration of trace amounts of platinum and palladium before GFAAS determination. *Anal Lett* 37:2189–2203
- Ebrahimzadeh H, Tavassoli N, Amini MM, Fazaeli Y, Abedi H (2010) Determination of very low levels of gold and palladium in wastewater and soil samples by atomic absorption after preconcentration on modified MCM-48 and MCM-41 silica. *Talanta* 81:1183–1188
- Godlewska-Żyłkiewicz (2002) Hazards of error in the palladium storage and determination by GFAAS. *Anal Bioanal Chem* 372:593–596
- Godlewska-Żyłkiewicz B (2004) Preconcentration and separation procedures for the spectrochemical determination of platinum and palladium. *Microchim Acta* 147:189–210
- Godlewska-Żyłkiewicz B, Kozłowska M (2005) Solid phase extraction using immobilized yeast *Saccharomyces cerevisiae* for determination of palladium in road dust. *Anal Chim Acta* 539:61–67
- Godlewska-Żyłkiewicz B, Leśniewska B (2006) Sources of error and their elimination for spectrometric determination of palladium in environmental samples. In: Zereini F, Alt F (eds) *Palladium emission in the environment*. Springer, Berlin Heidelberg, pp 97–109
- Godlewska-Żyłkiewicz B, Leśniewska B (2010) Analysis of road dust: determination of platinum and palladium by GFAAS and ICP MS techniques. In: Żyrnicki W, Borkowska-Burnecka J, Bulska E, Szmyd E (eds) *Methods of analytical atomic spectrometry. Theory and practice*. Malamut, Warsaw, pp 375–384 (in Polish)
- Gomez MB, Gomez MM, Palacios MA (2003) ICP-MS determination of Pt, Pd and Rh in airborne and road dust after tellurium coprecipitation. *J Anal At Spectrom* 18:80–83

- Herincs E, Puschenreiter M, Wenzel W, Limbeck A (2013) A novel flow-injection method for simultaneous measurement of platinum (Pt), palladium (Pd) and rhodium (Rh) in aqueous soil extracts of contaminated soil by ICP-OES. *J Anal Atom Spectrom* 28:354–363
- Kalavrouziotis IK, Koukoulakis PH (2009) The environmental impact of the platinum group elements (Pt, Pd, Rh) emitted by the automobile catalyst converters. *Water Air Soil Pollut* 196:393–402
- Kowalska J, Asztomborska M, Godlewska-Żyłkiewicz B, Golimowski J (2005) Systematic errors in the determination of trace metals, Part II. Memory effects of quartz vessels used for samples preparation in the determination of ultra-trace levels of platinum. *Microchim Acta* 150:55–58
- Krishna MVB, Ranjit M, Chandrasekaran K, Karunasagar D (2009) On-line preconcentration and recovery of palladium from waters using polyaniline (PANI) loaded in mini-column and determination by ICP-MS; elimination of spectral interferences. *Talanta* 79:1454–1463
- Lee HY, Chon HT, Sager M, Marton L (2012) Platinum pollution in road dusts, roadside soils, and tree barks in Seoul, Korea. *Environ Geochem Health* 34:5–12
- Leśniewska B, Godlewska-Żyłkiewicz B, Hulanicki A (2005) The effect of hydrofluoric acid on determination of platinum and palladium in road dust applying inductively coupled plasma mass spectrometry. *Anal Chem (Warsaw)* 50:945–950
- Liang P, Zhao E (2011) Determination of trace palladium in complicated matrices by displacement dispersive liquid-liquid microextraction and graphite furnace atomic absorption spectrometry. *Microchim Acta* 174:153–158
- Limbeck A, Rendl J, Puxbaum H (2003) ETAAS determination of palladium in environmental samples with on-line preconcentration and matrix separation. *J Anal At Spectrom* 18:161–165
- Malejko J, Szygałowicz M, Godlewska-Żyłkiewicz B, Kojło A (2012) Sorption of platinum on immobilized microorganisms for its on-line preconcentration and chemiluminescent determination in water samples. *Microchim Acta* 176:429–435
- Matusiewicz H, Lesiński M (2001) Electrodeposition sample introduction for ultra trace determinations of platinum group elements (Pt, Pd, Rh, Ru) in road dust by electrothermal atomic absorption spectrometry. *Int J Environ Anal Chem* 82:207–223
- Merget R, Rosner G (2001) Evaluation of the health risk of platinum group metals emitted from automotive catalytic converters. *Sci Total Environ* 270:165–173
- Meeravali NN, Kumar SJ, Jiang SJ (2008) Interference free ultra trace determination of Pt, Pd and Au in geological and environmental samples by inductively coupled plasma quadrupole mass spectrometry after a cloud point extraction. *J Anal At Spectrom* 23:854–860
- Müller M, Heumann KG (2000) Isotope dilution inductively coupled plasma quadrupole mass spectrometry in connection with a chromatographic separation for ultra trace determinations of platinum group elements (Pt, Pd, Ru, Ir) in environmental samples. *Fresenius J Anal Chem* 368:109–115
- Myasoedova GV, Mokhodoeva OB, Kubrakova IV (2007) Trends in sorption preconcentration combined with noble metal determination. *Anal Sci* 23:1031–1039
- Nakajima J, Ohno M, Chikama K, Seki T, Oguma K (2009) Determination of trace of palladium in stream sediment and auto catalyst by FI-ICP-OES using on-line separation and preconcentration with QuadraSil TA. *Talanta* 79:1050–1054
- Pan S, Sun Y, Zhang G, Chakraborty P (2013) Spatial distributions and characteristics of platinum group elements (PGEs) in urban dusts from China and India. *J Geochem Explor* 128:153–157
- Prichard HM, Sampson J, Jackson M (2009) A further discussion of the factors controlling the distribution of Pt, Pd, Rh and Au in road dust, gullies, road sweeper and gully flusher sediment in the city of Sheffield, UK. *Sci Total Environ* 407:1715–1725
- Rastegarzadeh S, Pourreza N, Kiasat AR, Yahyavi H (2010) Selective solid phase extraction of palladium by adsorption of its 5(p-dimethylaminobenzylidene)rhodanine complex on silica-PEG as a new adsorbent. *Microchim Acta* 170:135–140
- Rauch S, Motelica-Heino M, Morrison GM, Donard OFX (2000) Critical assessment of platinum element determination in road and urban river sediments using ultrasonic nebulisation and high resolution ICP-MS. *J Anal At Spectrom* 15:329–334

- Rojas FS, Ojeda CB, Pavón JMC (2006) Automated on-line separation preconcentration system for palladium determination by graphite furnace atomic absorption spectrometry and its application to palladium determination in environmental and food samples. *Talanta* 70:979–983
- Rojas FS, Ojeda CB, Pavón JMC (2009) Simultaneous determination of palladium and rhodium using on-line column enrichment and electrothermal atomic absorption spectrometric detection. *J Anal Chem* 64:241–246
- Schuster M, Schwarzer M (1996) Selective determination of palladium by on-line column preconcentration and graphite furnace atomic absorption spectrometry. *Anal Chim Acta* 328:1–11
- Shinotsuka K, Suzuki K (2007) Simultaneous determination of platinum group elements and rhenium in rock samples using isotope dilution inductively coupled plasma mass spectrometry after cation exchange separation followed by solvent extraction. *Anal Chim Acta* 603:129–139
- Simitchiev K, Stefanova V, Kmetov V, Andreev G, Sanchez A, Canals A (2008) Investigation of ICP-MS spectral interferences in the determination of Rh, Pd and Pt in road dust: assessment of correction algorithms via uncertainty budget analysis and interference alleviation by preliminary acid leaching. *Talanta* 77:889–896
- Spada N, Bozlaker A, Chellam S (2012) Multi-elemental characterization of tunnel and road dusts in Houston, Texas using dynamic reaction cell-quadrupole inductively coupled plasma-mass spectrometry: evidence for the release of platinum group and anthropogenic metals from motor vehicles. *Anal Chim Acta* 735:1–8
- Tsogas GZ, Giokas DL, Vlessidis AG, Evmiridis NP (2008) On the re-assessment of the optimum conditions for the determination of platinum, palladium and rhodium in environmental samples by electrothermal atomic absorption spectrometry and microwave digestion. *Talanta* 76:635–641
- Woińska S, Godlewska-Żyłkiewicz B (2011) Determination of platinum and palladium in road dust after their separation on immobilized fungus by electrothermal atomic absorption spectrometry. *Spectrochim Acta, Part B* 66:522–528
- Zereini F, Alsenz H, Wiseman CLS, Püttmann W, Reimer E, Schleyer R, Bieber E, Wallasch M (2012) Platinum group elements (Pt, Pd, Rh) in airborne particulate matter in rural versus urban areas of Germany: Concentrations and spatial patterns of distribution. *Sci Total Environ* 416:261–268
- Zimmermann S, Messerschmidt J, van Bohlen A, Sures B (2003) Determination of Pt, Pd and Rh in biological samples by electrothermal atomic absorption spectrometry as compared with adsorptive cathodic stripping voltammetry and total reflection X-ray fluorescence analysis. *Anal Chim Acta* 498:93–104