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Determination of platinum and palladium in environmental samples by graphite furnace atomic absorption spectrometry after separation on dithizone sorbent

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Abstract

A graphite furnace atomic absorption method of platinum and palladium determination after their separation from environmental samples has been presented. The samples were digested by aqua regia and the analyte elements were separated on the dithizone sorbent. The procedure of sorbent preparation was described and their properties were established. Two various procedures of elution by thiourea and concentrated nitric acid were described and discussed. The low limit of detection was established as 1 ng g^{-1} for platinum and 0.2 ng g^{-1} for palladium.

There was also investigated the behaviour of platinum and palladium introduced into the soil in various chemical forms.

Keywords: Environmental analysis; Platinum; Palladium; Dithizone sorbent; GF AAS

1. Introduction

Platinum, palladium and rhodium, the noble metals applied in the automobile catalytic converters, are ejected with the exhausted gases, due to the abrasion of the catalytic surface, and contaminate the roads and their surrounding area. The emitted particles have a size distribution with a maximum at 1–2.15 μm. Such small particles (particularly these of sub-μm range) can penetrate deeply in human lungs and are toxicological relevant [1,2]. Platinum and palladium are known as the very potent sensitizers with a high incidence of allergic reactions [3]. Moreover, they are able to form various organo-metalic compounds. In this form they can be solubilised and enter soils, sediments, waters and plants, and in consequence, they can enter the food chain [4]. For platinum compounds of this type, applied as cytotoxic drugs, numerous toxicities are observed, which indicates that the noble metals in this form are not inert against the living organisms [5]. The mentioned facts cause the necessity to check the contamination level of environment by platinum group metals and what is its physiological effect. Therefore, the determination of these metals in soil and plants at a ng g^{-1} concentration level is required.

The contents of platinum and palladium in the catalytic converters of various types is 5–9 times larger than that of rhodium [6]. This proportion varies strongly in the exhausted fumes dependently on the type of the converter [7,8], however, the concentrations of platinum and palladium in the urban aerosol samples [1] and in the environmental silica containing matrices [9] are usually significantly higher than that of rhodium and, therefore, these two elements may be dealt as an indicator of the environment contamination by platinum group metals.

The most suitable analytical methods for the platinum and palladium determination at a such low concentration level are graphite furnace atomic absorption spectrometry (GF AAS), mass spectrometry with the ICP ionisation (ICP-MS), voltammetric methods and neutron activation analysis (NAA) [10,11]. However, the direct determination by all these techniques is restricted owing to interferences caused by environmental sample matrices and, usually, a preliminary platinum and palladium separation and enrichment is required. The application of NAA is restricted additionally by the access to a nuclear reactor. In the last years some authors [9,12–14] present the ICP-MS methods that enables interference-free or almost interference-free

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direct determination of noble metals in the environmental samples, however, up to now they are not verified in the common use. Application of the conventional ICP-MS is limited by the high matrix concentrations in the investigated samples causing the spectral interferences resulted from the limited resolution of the generally applied quadrupole mass spectrometers. Although the GF AAS shows similar shortcomings the equipment for this technique is available in most laboratories and a method basing on it has a chance to be in common use.

The method most frequently used for separation of platinum and other noble metals from matrix components of various samples and for their preconcentration is ion-exchange chromatography in hydrochloric medium [15–19]. In this way, however, they are separated together with the elements forming negatively charged chlorocomplexes. An improvement of selectivity may be achieved by use of the chelating sorbents with dithio and thio functional groups. Usually such agents as bis-(carboxymethyl)-dithiocarbamate [20,21] and dithizone [22] are used for preparation of such sorbents. Also the resins containing nitrogen-heterocyclic groups are mentioned as highly selective for noble metals [23,24].

Although in the literature many GF AAS methods for the determination of a group or individual noble metals in various types of samples may be found and some of them were published in the last time [25–28], their determination on the low trace concentration level in such difficult matrices as environmental samples creates still many problems. The presented work proposes the determination of palladium and platinum in environmental samples (street dust, soil and plants) by graphite furnace atomic absorption spectrometry after their digestion with aqua regia and separation from the matrix elements on the chelating sorbent containing dithizone immobilised on the solid polymeric support. Since both the elements in the environment are effected by various atmospheric, chemical and biological factors and can be transformed in various chemical forms the behaviour of these compounds added to the soil and their recovery after their extraction by various media was also tested. The use of relatively large analytical samples (5 g for soil and street dust and 25 g for plants material) simplifies the preparation of the samples representative for the total bulk of the investigated materials.

2. Experimental

2.1. Apparatus

Thermo Jarrell Ash SH 4000 atomic-absorption spectrometer, equipped with 188 Controlled Furnace Atomizer (CTF 188), Smith–Hieftje background correction system and Visimax II hollow-cathode lamps for platinum and palladium, was used. Pyrolytically coated graphite tubes were used for all measurements.

Glass columns of 4 mm in internal diameter filled with 50 mg of the dithizone sorbent and conditioned with a solution of the suitable acidity. To minimise the dead volume the column was closed down by the tygon tube with the precise screw lock instead of a cock, Ultrasonic bath Sonorex Super RK (Bandelin), Laboratory shaker type WL-1 (Poland).All glassware were cleaned by soaking in 20% nitric acid (48 h) and then rinsed with water.

2.2. Reagents

The water purified by Water Purification System—Milipore, nitric and hydrochloric acids purified by sub-boiling point distillation, dithizone p.a. (Merck), resin Diaion HP-2MG (Supelco), platinum black (Specpure—Johnson Matthey), palladium sponge (Specpure—Johnson Matthey), tin chloride p.a. (POCH), and thiourea p.a. (Fluka) were used.

Platinum stock solution (1 mg ml^{-1}) was prepared by dissolution of 0.05 g platinum black in 20 ml aqua regia, evaporated to wet salts, twice evaporated with concentrated hydrochloric acid and diluted to 50 ml with 1 M hydrochloric acid.

Palladium stock solution (1 mg ml^{-1}) was prepared from the palladium sponge in the same way as platinum stock solution.

Tin chloride solution was prepared by dissolution of 2 g $SnCl_2{\cdot}2H_2O$ in 5 ml concentrated hydrochloric acid and diluted to 10 ml with water.

Dithizone 0.04 M solution was prepared by dissolution of 0.256 g dithizone in 25 ml chloroform. Thiourea 5% solution in 0.05 M hydrochloric acid

2.3. Dithizone sorbent

One gram of Diaion resin (polymethacrylic ester) was placed in a 50 ml separatory funnel and shaken with 25 ml of 0.04 M dithizone solution in chloroform for 1 h. The sorbent was separated by filtration, allowed to dry in air for 12 h and stored in darkness in a refrigerator at 4 °C. Under these conditions it is stable at least 2 months.

2.4. Procedure of platinum and palladium determination

Five grams of road dust and soil samples were preliminary heated in 400 °C during 1 h to remove the organic mater. Twenty-five grams samples of air dry plant materials without preliminary cleaning, e.g., grass, were burnt and heated in the same way. Then the samples were digested with 20 ml of aqua regia heating carefully at the beginning. Then they were heated close to the boiling temperature during 2 h and left for at least 12 h. Next, the solution was diluted with 20 ml of water and filtrated. The residue was washed accurately with few portions of hot water slightly acidified with hydrochloric acid. The filtrate was evaporated to the wet salts and then twice evaporated to dryness

Table 1
Instrumental parameters of determination

Parameter	Pt	Pd
Wavelength (nm)	265.9	247.6
Bandpass (nm)	0.4	0.4
Lamp current (mA)	7	5
Integration time (s)	6	6
Background correction	Smith–Hieftje	
Aliquots of sample (μl)		
Version I	50	20
Version II	10	10

with 2 ml of concentrated hydrochloric acid. The residue was dissolved in 20 ml of 3 M HCl and 1 ml of tin chloride solution was added to reduce Pt(IV) to Pt(II). This sample solution was left for 15 min and, then, it was passed at a rate of 1 ml min^{-1} trough the column filled with 50 mg of the sorbent and conditioned with the solution of suitable acidity.

Platinum and palladium can be desorbed from the column in two different ways: by the thiourea solution (Version I), or by concentrated nitric acid (Version II).

Version I: Ten milliliters of thiourea solution was passed slowly trough the column and the effluent was collected in a 10 ml volumetric flask.

Version II: After sorption process the column was washed with 2 ml of water and then 1 ml of concentrated nitric acid was passed collecting the effluent in a small quartz evaporating disk. Next, 1 ml of concentrated nitric acid was put onto the column and allowed to react with the sorbent for 30 min. Then it was drained off to the same evaporating disc and the column was washed with 2 ml of water. The solution was evaporated to dryness, the residue was dissolved in 2 ml of 1 M hydrochloric acid and this solution was used for determination.

Platinum and palladium were determined by electrothermal atomic absorption spectrometry in the effluent of the column obtained by the elution according to the *Version I* or to *Version II*. The atomisation was carried out in the coated graphite tubes without platform. The integrated absorbance was measured and the Smith–Hieftje background correction was used. The instrumental conditions of the determination are established in Tables 1 and 2. The calibration standard must be prepared on the basis of the *blank* solution prepared in the same way as the analytical samples. Absorbance of the pure *blank* solution (without standard) usually is equal to zero, otherwise its value should be subtracted from all measured analytical signals.

Table 2
Temperature–time program of atomization

Phase	Temperature (°C)	Ramp (s)	Hold (s)	Purge gas
Drying	120	40	20	Low
Pyrolysis I	1200 (Pt) 850 (Pd)	100[a] 10[b]	10	Medium
Pyrolysis II	200	10	5	Medium
Atomization	2550 (Pt) 2500 (Pd)	0	3	Off
Cleaning	2600	–	3	Medium

[a] Version I.
[b] Version II.

3. Results and discussion

3.1. Digestion of environmental samples

It is well known fact that the extraction of the noble metals from the natural samples, particularly geological samples, is very difficult and, usually, it requires the application of fire assay procedure or preliminary dry chlorination procedure [10]. This concerns, however, the compounds formed by the natural geological processes, e.g., alloys, native metals and sulphide minerals placed inside the sample grains. Though the soil is of the same nature as many of geological samples, platinum and palladium of the automobile catalyst origin are introduced into it in an artificial way and, therefore, the extraction into solution of these elements, or their compounds formed under environmental conditions, should be significantly easier.

Some authors investigated the distribution of organic and total platinum between road sediment and urban gullypots [2] or distribution of soluble and total platinum between various fraction of airborne dust [29]. However, the information on the behaviour of platinum and palladium in the soil and on the optimal extraction procedures into solution of their compounds, that can be formed, are limited. Therefore, we investigated the possibility of extraction and recovery of various forms of these metals added to the soil samples.

The investigation of the behaviour of soluble platinum and palladium compounds in the soil and their leaching by water and 0.1 M hydrochloric acid was carried out using natural soil free from the contamination by these metals. The soil samples were spiked with 5 $\mu\text{g g}^{-1}$ of platinum as hexachloroplatinic acid and potassium hexachloroplatinate and 2 $\mu\text{g g}^{-1}$ of palladium as ammonium chloropalladite. All the compounds were added to the soil in the form of small amount (μl) of solution in water, the samples were air dried and homogenised carefully. Directly after that a part of the samples were digested by 10 ml of water or 0.1 M hydrochloric acid on the ultrasonic bath during 20 min, centrifuged and platinum and palladium were determined in the solution as it is given in the proposed analytical procedure. The rest of the samples were leave for 24 or 96 h and after these times they were treated and determined in the same way. The results presented in Table 3 show that even the compounds easy soluble in water are quickly bound by the components of the soil and cannot be leached by water or diluted hydrochloric acid. Platinum was undetectable in the leaching solution after 24 or 96 h, dependently on its form. Palladium was undetectable immediately after preparation

Table 3
Extraction of the soluble compounds of platinum and palladium after various contact time with the soil

Added compounds	Contact time (h)	Extracting agent	Found in the extract	
			Pt (%)	Pd (%)
H_2PtCl_6	0	H_2O	55	–
		0.1 M HCl	50	–
	24	H_2O	15	–
		0.1 M HCl	25	–
	96	H_2O	0	–
		0.1 M HCl	0	–
K_2PtCl_6 and $(NH_4)_2PdCl_4$	0	H_2O	48	15
		0.1 M HCl	50	0
	24	H_2O	0	15
		0.1 M HCl	0	0

of the samples, when leached by diluted acid, or detectable in a minimum amount, about 15%, when leached by water.

The hydrochloric acid medium is the optimal one for separation of platinum and palladium from most components of the matrix on the dithizone sorbent. Since both the metals and some of their compounds are insoluble in this acid, the optimal medium for digestion of the samples seems aqua regia. To check the leaching of various forms of platinum and palladium by this medium another series of soil samples spiked with platinum and palladium, in the same amounts as in the previous series, were prepared. After air drying and homogenisation the samples were heated in 400 °C during 1 h. In this case besides chloroplatinate and chloropalladite also the solutions of both metals in nitric acid and their complexes with thiourea were used. Nitrate compounds were transformed into oxides during the heating of the samples and may simulate the behaviour of the oxides that can be formed in automobile catalysts in a high temperature in the presence of nitrogen oxides. The thiourea complexes of the noble metals are very stable and they may be considered as representative of all other organic complexes those may be formed in the environment.

The samples of this series were leached by aqua regia and the recovery of platinum and palladium was determined in the same way as those of the first series. The obtained results are presented in Table 4. The determined recovery in all cases is close to 100%. The results obtained for the sample spiked with the metals solved in nitric acid solution are particularly important since nitrate salts are transformed in oxides during evaporation and heating in 400 °C. It is known that some oxides of platinum and palladium are insoluble even in aqua regia. The full recovery determined for these samples suggests that the oxides, that may be formed during the work of automobile catalysts or during pre-treatment of samples, are soluble and the total amount of platinum and palladium introduced in the environment can be determined.

3.2. Characteristic of the sorbent

The amount of dithizone loaded on the resin was determined spectrophotometrically at 605 nm after its multiple elution from the sorbent with chloroform. It was found to be about 22 mg g^{-1} (0.1 mmol g^{-1}) and this value was stable at least during two mounts. It should be notice, however, that the sorbent after elution remains greenish. It suggests that dithizone is bonded to the bead in two ways, by the chemical bond and by the surface adsorption. This suggestion seems to be confirmed by the retention capacity of platinum and palladium that is equal to about 0.16 mmol g^{-1}. These amounts are significantly larger than those resulted from the amount of dithizone eluted by chloroform.

In the strong acidic medium dithizone forms stable complexes beside platinum and palladium also with gold, silver and mercury. All these elements may be present in the environmental materials only on a low trace concentration level as impurities. Since the capacity of the sorbent in the column is equal to 0.008 mmol the concentration of the interfering elements in a 5-g samples necessary to prevent the retention of the analyte elements should be equal to 312 μg g^{-1}

Table 4
Recovery of platinum and palladium digested by aqua regia during 24 h

Added compounds	Recovery (%)	
	Pt	Pd
K_2PtCl_6 and $(NH_4)_2PdCl_4$	95–97	96–97
Pt and Pd in HNO_3	100–102	100–101
Pt and Pd thiourea complexes	97–98	100–101

Table 5
Precision of the determination of platinum and palladium in various environmental samples

Samples	Determined mean values (ng g^{-1})		RSD ($n = 7$)	
	Pt	Pd	Pt	Pd
Soil	35	8	0.09	0.06
Street dust	25	7	0.09	0.07
Grass	∼1	< 0.2	∼0.25	–

Table 6
Recovery of platinum and palladium spiked into natural soil samples

Content in the sample* ($ng\,g^{-1}$)		Added* ($ng\,g^{-1}$)		Determined total* ($ng\,g^{-1}$)		Recovery (%)	
Pt	Pd	Pt	Pd	Pt	Pd	Pt	Pd
35	8	40	10	74	17.5	98	95

* Mean values of five determinations

for gold, 174 $\mu g\,g^{-1}$ for silver and 320 $\mu g\,g^{-1}$ for mercury. Such high concentrations of these elements, about 10,000 higher than those of the analytes, cannot be expected in normal environmental samples. The total retention of platinum and palladium on the column in the presence of 1000-fold excess of gold, silver and mercury was confirmed experimentally.

3.3. Elution of platinum and palladium from the column

In the section describing the proposed analytical procedure there are mentioned two versions of the elution of platinum and palladium from the column. The first one using the thiourea solution is very simple and enables direct determination of both the metals in the eluent by GF AAS. However, the large excess of thiourea present in the solution evolves during the pyrolysis a large amount of aggressive vapours causing the corrosion of graphite tubes and some elements of the furnace and, therefore, this method should not be applied for the analysis of large series of samples. Since the complexes of the noble metals with dithizone are stable we did not succeed to find another than thiourea organic agent that enables their elution from the column. Therefore, in the second version it was applied the desorption by concentrated nitric acid that decomposes the complexes with dithizone and elutes platinum and palladium. In this case, however, only palladium can be determined directly in the eluate after its dilution. The signal of platinum is strongly suppressed in the nitric acid medium. For determination both the elements the eluate must be evaporated and the residue must be dissolved in the hydrochloric acid.

3.4. Atomic absorption measurements

Two different ways of the elution of platinum and palladium from the column require different atomization programs. The first one using the thiourea eluent requires a slow heating rate (ramp 100 s) and high pyrolysis temperature (1200 °C) necessary for destruction and removing the excess of thiourea from the graphite tube. Moreover, the measured absorbance signals are relatively low and the large aliquots of eluate must be injected into the tube, e.g., 50 μl for platinum. All these facts and the evolution of the corrosive gases during atomization cause this procedure, although it enables the good results and is simpler in handling, cannot be recommended for the permanent use for analysis of large series of samples. All the observed shortcomings are eliminated when the elution with nitric acid is applied.

The measurement parameters and temperature–time program during atomization are presented in Tables 1 and 2. The coated graphite tubes without platform were used. The relatively slow atomization heating rate of about 900 $°C\,s^{-1}$ and the atomization temperature limited to 2600 °C, characteristic for the applied equipment, precluded using the tube with platform for such refractory elements as platinum and palladium.

3.5. Evaluation of the method

The precision of the method was estimated by analysis of the samples of soil, street dust and grass, seven of each type, collected on/or beside the busy suburban street in Warsaw. The obtained results are presented in Table 5. The detection limit of the method defined as 3 s of background variation was found 1 $ng\,g^{-1}$ for platinum and 0.2 $ng\,g^{-1}$ for palladium.

The accuracy of the method was tested on the natural samples of soil used for the estimation of the precision and spiked with the additional amounts of both the elements in the same way as it was described in section *Digestion of environmental samples*. The results are presented in Table 6.

4. Conclusions

The dithizone sorbent enables the selective separation of platinum and palladium from all components of the soil that can interfere in their determination by graphite tube atomic absorption.

The presented investigations show that total amount of platinum and palladium introduced in various chemical forms into the soil is extracted by aqua regia. This concerns also the oxides, that may be formed by decomposition of nitric compounds during heating of the soil samples up to 400 °C, and the organic compounds, that may be formed in the environment under action of various chemical, physical and biological factors.

The quick and strong bonding of the easy soluble compounds of platinum and palladium by the soil components and impossibility of their extraction neither by water nor diluted acids suggest that the transfer of these elements into the plants and further to the food chain is very limited. Such hypothesis seems to be confirmed by very low concentration of these elements in the grass cut beside the street in comparison to the concentration in soil taken in the same place.

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