Development of sensitive determination method for platinum in geological materials by carbon slurry sampling graphite furnace atomic absorption spectrometry

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ABSTRACT

A simple and cost effective preconcentration method based on modified activated carbon is proposed for the determination of traces of platinum (Pt) in geological samples by the carbon slurry sampling technique for graphite furnace atomic absorption spectrometry (GFAAS). The basic parameters affecting the adsorption capacity of Pt(IV) ions on modified activated carbon were studied and the effect of activated carbon modification has been determined by studying the initial runs of adsorption isotherms. The influence of chlorides and nitrates on adsorption ability of Pt(IV) ions onto the modified activated carbon for diluted aqueous solution was also studied in detail in respect to the determination of platinum in solid materials following digestion steps as outlined in the analytical procedure, which usually involves the application of aqua regia. The XPS studies confirmed that not only the surface reduction of Pt(IV) ions into Pt(II) is the main platinum adsorption mechanism on the activated carbon. Determination of platinum after its preconcentration on the modified activated carbon was tested and validated by applying certified reference materials. The proposed method has been successfully applied for the determination of Pt in real samples using the standard calibration method.

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1. Introduction

Platinum — one of the six platinum group-elements, designated PGEs — is widely used in automobile exhaust catalytic converters and as a catalyst. It also finds the application in chemical and glass industries, jewelry and medicine. Unfortunately, soluble platinum compounds, which are toxic and their chronic industrial exposure are responsible for the syndrome known as platinosis [1]. The emitted PGEs are generally accumulated in urban soils around roadsides, or are transported by runoff to surface waters and deposited in sediments, where they can be transformed into more reactive and bioavailable species [2]. Hence, there is an increasing interest from the environmental, public health and analytical points of view to develop high sensitivity, simple and economical methodologies for determination of trace amounts of platinum in geological samples.

The determination of trace levels of platinum in geological materials requires the application of very sensitive analytical techniques, such as graphite furnace atomic absorption spectrometry (GFAAS) [3–10], inductively coupled plasma atomic emission spectrometry (ICPOES) [3–5,9,11], inductively coupled plasma-mass spectrometry (ICPMS), neutron activation analysis (NAA) or adsorptive voltammetry (AdV) [3–5]. It is worth mentioning that platinum occurs in geological materials at low concentrations and its distribution is nonhomogeneous [1]. What is more its determination at low concentration levels is still a serious analytical challenge due to the very unfavorable matrix-to-analyte ratios and interference effects. Therefore, much consideration has to be given to the elimination of matrix effects, particularly those coming from common elements present in examined samples, when the AAS detection method is used [12]. For this reason a separation/preconcentration stage is often applied to remove matrix interferences and preconcentrate the analyte to a level at which it can be reliably determined. Various preconcentration approaches, such as: ion exchange [4,6,9,10,13], precipitation and coprecipitation [4,13], extraction techniques [4,13–22] and biosorption [13,23] have been described in the literature for platinum separation from environmental samples. However, one of the most useful preconcentration treatments is adsorption onto solid adsorbents. This treatment also allows for matrix removal from different samples. Furthermore, it is characterized by simplicity, high adsorptive efficiency, cost-effectiveness, lack of harmful byproducts and great regeneration potential [24]. As reported in papers [7,8,22, 25], various sorbents for platinum adsorption have been proposed. Out of these, activated carbon frequently provides the most economical and efficient method for trace element separation and preconcentration from aqueous solutions [11,18]. Activated carbon is characterized by a large surface area, well-developed micro pore structure, high adsorption capacity and high degree of surface reactivity. What is more, the activated carbon surface can be easily modified in several ways to provide

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varying adsorption capacity and selectivity for different ions [26]. The most important phenomena, which affect the ion adsorption capacity, are ion exchange, nonspecific sorption, redox reactions, surface precipitation and formation of surface chelates. These make the desorption a critical step of an analytical procedure, especially when the main mechanism of metal adsorption is its reduction on the activated carbon surface [27]. Hence, concentrated acid application is necessary for an analyte elution, which can cause severe interferences or lead to substantial sample dilution, resulting in the decreasing preconcentration factor. This limitation can be eliminated by the solid sampling technique application, when loaded activated carbons can be directly introduced into the graphite furnace atomic absorption spectrometry in the form of slurry. It is worth noting that, the carbon slurry sampling technique is a very desirable technique when complete desorption of an analyte from the activated carbon is not possible. For this reason, the development and improvement of specific adsorbents should be investigated and proposed [28].

The aim of this study was to develop a new analytical procedure for platinum determination in geological materials using the carbon slurry sampling technique for GFAAS. In order to find the most effective sorbent, modification of powdered activated carbon by treatment with H_2O_2 and concentrated HNO_3 solution was examined. The effects of carbon modification were characterized using various methods, such as XPS and BET analyses. The basic parameters affecting the adsorption capacity of Pt(IV) ions onto each modified activated carbon were studied. Additionally, the influence of chlorides and nitrates, in the residue of digested solid materials, on Pt(IV) adsorption and desorption from the platinum loaded activated carbons using inorganic acids was studied.

2. Experimental

2.1. Reagents and materials

The powdered activated carbon, Medical Carbon (Carbo Medicinalis), was used as the initial adsorbent. This material was produced from charcoal by Gryfskand in Hajnówka, Poland, which — during the production — was leached of organic and inorganic impurities by the extraction with glacial acetic acid. However, to further improve the purity as required in trace analysis, the activated carbon was pretreated with hydrochloric and hydrofluoric acids (POCH, Gliwice, Poland). It was stated experimentally that this pretreatment reduced ash contents in carbon up to 0.01%.

All chemicals used in this work were of the analytical-reagent grade or better and the presence of platinum was not detected in the working range. Throughout all analytical work, high-purity Milli-Q water with a resistivity of 18.2 MΩ cm was used. All glassware and polyethylene bottles were cleaned by soaking in 20% (v/v) HNO_3 (POCH, Gliwice, Poland) and rinsed with Milli-Q water. Standard solutions of Pt(IV) were prepared in 2 mol L^{-1} HCl by dilution of 1000 mg L^{-1} stock standard solutions (Merck, Darmstadt, Germany). The calibration curve was established using the standard solutions prepared in 2 mol L^{-1} HCl by dilution from the stock standard solution. The calibration standards were not subjected to the preconcentration procedure. Hydrochloric acid Suprapure (36%) (Merck, Darmstadt, Germany) and nitric acid Suprapure (65%) (Merck, Darmstadt, Germany) were used in the following procedures. The solutions of interfering ions were prepared by

Table 1
Temperature program for platinum determination by the slurry sampling GFAAS.

Step	Temperature (°C)	Ramp (°C s^{-1})	Hold (s)	Air flow (mL min^{-1})
Drying I	80	20	5	160
Drying II	105	5	35	160
Ashing	1100	200	5	160
Atomization	2600	FP[a]	5	0
Cleaning	2650	1000	2	280

[a] FP — "full power" — maximum of ramp.

Table 2
Basic parameters of modified activated carbons.

Carbon type	A	B	C
S_{BET} [m^2 g^{-1}]	1200	1090	810
Anion exchange capacity [mmol g^{-1}]	0.29	0.26	0.03
Cation exchange capacity [mmol g^{-1}]	0.37	0.60	2.44

dissolving appropriate salts in Milli-Q water (sodium chloride (ACROS Organics, Geel, Belgium)) and potassium nitrate (POCH, Gliwice, Poland). The solutions of NaOH and HCl were used for pH adjustment.

The proposed methodology was validated using certified reference materials and utilized for the platinum determination in magmatic rock samples. The certified reference materials, SARM — 7 and WPR — 1, were purchased from the International Atomic Energy Agency, IAEA (Vienna, Austria) and the Canada Centre for Mineral and Energy Technology, CANMET (Ottawa, Canada), respectively. The samples of magmatic rocks from Tajno (Mazurian District, Poland) were obtained from the Central Laboratory of the Polish Geological Institute in Warsaw. Four magmatic rock samples were taken from drill cores at the different depths (50–200 m).

2.2. Apparatus

Measurements of platinum concentration in the studied adsorption system and Pt determination in geological samples after preconcentration on activated carbon were carried out with an AAS 3 (Carl Zeiss, Jena, Germany) atomic absorption spectrometer equipped with a deuterium-lamp background correction, an EA 3 electrothermal atomizer and a MPE autosampler. A platinum hollow cathode lamp (Varian, Australia) was used at the wavelength 265.9 nm and a 0.2 nm slit was selected. Pyrolytic graphite coated tubes were used in all determinations. The optimized temperature program for the determination of platinum in the samples by the slurry sampling GFAAS is presented in Table 1.

The pH measurements of the initial platinum solutions as well as of carbon suspensions were made using a combination of glass and calomel electrode, GK2302B (Radiometer).

The chemical characterization of the modified activated carbon was obtained by X-ray photoelectron spectroscopy (XPS), using a Multichamber Analytical System (Prevac, Poland) with monochromated K_α-Al radiation (1486.6 eV) (Gammadata Scienta, Sweden) and the X-ray power of 450 W. The binding energy (BE) scale was referenced against $C1s = 284.7$ eV line. The vacuum in the analysis chamber was better than $1.5 \cdot 10^{-7}$ Pa. The high-resolution scans were performed over the 69–80, 193–205, 282–294 and 528–537 eV ranges for Pt4f, Cl2p, C1s and O1s spectra, respectively.
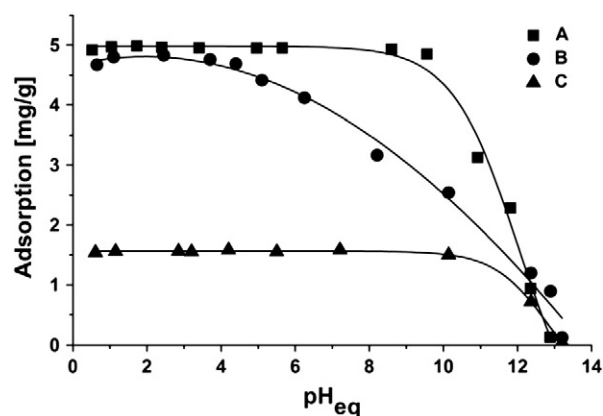

Fig. 1. The pH influence on Pt(IV) adsorption onto activated carbons; m = 0.2 g, V = 50 mL, C_{Pt} = 20 mg L^{-1}, t = 20 min., T = 25 °C.