DETERMINATION OF TRACE AMOUNTS OF PLATINUM GROUP METALS BY INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROMETRY, AFTER SEPARATION AND PRECONCENTRATION, IN ENVIRONMENTAL SAMPLES

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Nowadays a great attention is paid to the analytical chemistry of platinum group metals (PGMs), especially platinum, for several reasons.

(a) A massive introduction of automobile catalytic converters on the basis of PGMs (Pt, Pd, Rh) to remove toxic components of vehicle exhaust gases (carbon monoxide, unburned hydrocarbons and nitrogen oxides). During this process microamounts of PGMs are released into the exhaust gases and spread into the ambient air, airborne dust particles, road dust, soil and plants near to frequented high ways and tunnels. During the use of platinum-containing catalyst in the industry, some platinum may escape into the environment (the loss of platinum from ammonia oxidation gases during nitric acid production). Thus, increased platinum concentrations have been found in environment.

(b) Several compounds of Pt(IV) and Pd(II) are nephrotoxic, gastrointestinal irritants and strong allergens already at the ng-level for sensitised persons. Pt(II) compounds may have mutagenic, genotoxic or carcinogenic properties. No comprehensive data about toxicity of other PGM are available now.

(c) Selected Pt(II) complex species are effective cytostatics used in the therapy of some forms of cancer. Platinum has to be monitored in the body fluids and tissues during cancer treatment and Pt(II) traces may appear on equipment, in rooms or waste waters of hospitals.

In addition, traces of PGMs are in the environment in industrial areas and environmental objects, especially in road and tunnel dust, soil and plants near the frequented highways. In highly industrialised areas, elevated amounts of platinum can be found in river sediments. It is assumed that organic matter, e.g. humic and fulvic acids, binds platinum, aided perhaps by appropriate pH and redox potential conditions in the aquatic environment. In soil, the mobility of platinum depends on the pH, redox potential, chloride concentrations of soil water, and the mode of occurrence of platinum in the primary rock. It is assumed that platinum is mobile only in extremely acid conditions or in soil water with high chloride content.

The widely used multicomponent technique ICP-OES can be successfully used for the simultaneous determination of platinum group metals and gold but the sensitivity of this method is limited and the accompanying common metals and large excess of acids and inert salts interfere. For this purpose, preconcentration and separation of PGMs and Au by solid phase extraction is used with advantage.

A variety of sorbents, such as hydrophilic sorbents with surface-immobilised reagents, complexing or chelating sorbents, fibrous complexing sorbents, sorbents coated with liquid anion exchanger and extracting agents or anion exchangers are suitable for the preconcentration and separation of PGMs from the inorganic matrix or organic matrix after mineralization.

Various sorbents based on modified silicagel (such as Separon SGX C18 (Ref.3,4), Separon SGX C8, Separon SGX RPS, Separon SGX Phenyl and Separon SGX CN) were used for separation and preconcentration of PGMs – Pt(IV, II), Pd(II), Ir(IV), Rh(III), Os(IV), Ru(VI) and Au(III). The preconcentration is based on the sorption of ion associates of halo complexes of PGMs and gold with the cationic surfactants (Septonex – carboxyoxypentadecyltrimethylammonium bromide, Sterinol – dimethylaurylnbenzalammonium bromide, hexadecyltrimethylammonium chloride and tetradecyltrimethylammonium bromide).

Dynamic retention of the surfactant is assumed on the sorbent surface and the subsequent bonding of anionic PGMs and Au(III) halo complexes forming stable ion associates on the sorbent surface. Such process is accompanied by direct bonding of the ion associate formed in solutions containing the cationic surfactant.

The cartridge with the sorbent was washed with ethanol and later conditioned with a surfactant solution. A sample containing PGMs and Au(III), hydrochloric acid and the sodium salt was pumped through this conditioned column. After elution with acetonitrile the eluate was evaporated in the presence of HCl and resulting aqueous solutions were analysed with ICP-OES. The recoveries of 1–20 µg PGMs and Au(III) from 50 ml of synthetic solution, under optimum conditions of sorption, were 100 % for Pt(II), Pd(II, IV) and Au(III) after sorption on octadecylsilica Separon SGX C 18, Separon SGX RPS and the phenylsilica in the presence of 0.006 mol l⁻¹ Septonex or 0.003 mol l⁻¹ Sterinol. The enrichment factor on silica SGX C18 reached 100. The 80–90 % recoveries were obtained for Ir(IV) and Os(VI), 60 % for Ru(VI) and only 10–20 % for Rh(III). Results similar to those obtained for the recoveries of chloro complexes of PGMs and Au(III) were acquired also for bromo complexes under analogous conditions.

The (1000:1) excess of Cl⁻, NO₃⁻, SO₄²⁻, Na⁺, K⁺, Ca²⁺, Mg²⁺, Fe³⁺ and Al³⁺ does not interfere with the sorption and elution of PGMs and Au(III) on the modified silica. The sorption efficiency depends little on the sample volume between 50 and 1000 ml which corresponds with the enrichment factor up to 100. Similarly, no effect on the sorption efficiency was observed for 10 up to 200 µg l⁻¹ of Au(III), Pd(II) and Pt(IV).

Common strongly basic anion exchangers strongly retain platinum and platinum group metals from solutions containing...
their chloride complexes in the presence of dilute HCl. The separation and preconcentration of PGMs in the form of inert chloride complexes on basic anion exchangers has been frequently used.

A basic anion exchanger anchored on the modified silicagel was used for preconcentration of PGMs. The elution was performed with nitric acid of optimum concentrations and eluate was analysed by ICP-OES. The recoveries of PGMs from basic anion exchanger were 100% for Pd(II), Pt(IV) and Ir(IV), 70% for Au(III) and Os(VI) and 50–40% for Rh(III) and Ru(IV).

These two methods of preconcentration of platinum group metals and gold a) sorption of PGMs and Au(III) in the form of ion associates on modified silicagel and b) preconcentration on strongly basic anion exchanger were used for determination of PGMs, in particular platinum, in some environmental samples, especially in soils and waters.

REFERENCES


R. Komendová-Vlašáňková (Institute of Environmental Chemistry and Technology, Faculty of Chemistry, Technical University, Brno, Czech Republic): Determination of Trace Amounts of Platinum Group Metals by Inductively Coupled Plasma Atomic Emission Spectrometry, after Separation and Preconcentration, in Environmental Samples

Platinum metals are toxic and their increasing content in the environment as a consequence of the massive use of automotive catalysts requires extraordinary attention. Significant is also utilization of Pt(II) compounds in medicine as antineoplastic metallopharmaceutics, which get into waste waters of medical facilities. The metals occur in the environment in very low concentrations and hence the use of concentration techniques for their enrichment is necessary. Preconcentrations of platinum metals as ionic associates of their halo complexes with cation-active tensides on modified silica-type sorbents and by sorption of their halo complexes on strongly basic anion exchangers were successfully used for the purpose.