Solid Phase Extraction and Preconcentration for the Determination of Trace Amounts of Platinum Group Metals in Environmental and Biotic Material
A Critical Review

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Approaches to preconcentration, separation, and determination of platinum group metals, especially platinum, in environmental and biotic material are reviewed and critically commented.

Nowadays a great attention is paid to the analytical chemistry of platinum group metals (PGM), especially platinum [1—3], for several deciding reasons.

a) A massive introduction of automobile catalytic converters on the basis of PGM (Pt, Pd, Rh) to remove toxic components of spark ignition engines. During this process microamounts of PGM are released into the exhaust and spread into the ambient air, airborn dust particles, road dust, soil and plants near to frequented highways and tunnels.

b) Several compounds of Pt(IV) and Pd(II) are nephrotoxic, gastrointestinal irritants and strong allergens already in ng-level against sensitized persons [4—6]. Pt(II) compounds may have mutagenic, genotoxic or carcinogenic properties. No comprehensive data about toxicity of other PGM are available till now.

c) Selected Pt(II) complex species are effective cytostatics being used in the therapy of some forms of cancer [7] and Pt(II) traces may appear on the equipment, in the rooms, ambient air or waste waters of some hospitals.

d) The need of determination of "ng- to subng-" levels of Pt and other PGM in environmental and biotic samples or when monitoring platinum in food chains. Several problems may appear when looking for certified reference materials or standards of environmental and biotic origin for extreme trace concentration range.

Abundance of Pt and Other PGM in the Environment or Body Fluids and their Determination

Detailed data for the environmental material and human body are available for platinum coming from the anthropogenic activity, *e.g.* in river and sea waters and their biotics [8—11], ambient air [8, 12, 13], airborn particles, road and tunnel dust [12, 14—17, 55, 56], plants near motorways [8, 18, 19], body fluids of exposed persons [12, 20—28]. The contents of Pd are usually considerably lower but may sometimes increase [8]. In the engine catalyst exhaust, platinum is mainly generated in elementary state and bound in the form of clusters to common metal oxide particles depending on the particle size [12, 14]. The heterogeneity with respect to Pt content in dust particles may cause serious incertainty and errors of analytical results for road dust, collected airborn dust particles, engine soot, and soil samples. A part of Pt is, however, in soluble state, penetrates into the soil and is uptaken by the plants growing around the motorways [18]. Soluble Pt can also be extracted from the road sediments [29].

When Pt is metabolized in plants, 90 % is bound to low-molecular species, such as methionine or dimethionine or peptide glutathione. The rest of platinum is fixed to high-molecular phytochelatines or to polygalacturonic acid behaving as ion exchanger [5, 18].

For monitoring the increase of platinum and other

PGM content in the environment and human body, the knowledge of the natural PGM background values is necessary. For their determination, extremely sensitive analytical methods are, however, necessary. Some average contents for platinum in rocky crust, sediments, sea waters, fresh air, biotics, and blood are mentioned in literature [4]. Some problems with their estimation are discussed by *Alt et al.* [30].

ET-AAS [19, 23, 31—33], ICP-AES [31, 32, 34—36], ICP-MS [19, 24, 37], adsorption voltamperometry [11, 21, 29, 38, 39], and neutron activation [13, 40] are considered as sensitive and selective methods for the determination of platinum and some other PGM in environmental and biotic matrices. The first three, however, are most easily applicable for the determination of "ng- and subng-" levels of platinum and other PGM in complicated matrices of the real world after separation and preconcentration of PGM.

For the ET-AAS in graphite cuvettes, detection limits ($3s_B$) among 0.5—6 μg dm^{-3} [41] or 3 μg dm^{-3} [42] are given for PGM in pure solutions depending on the conditions used. Drawbacks are coming from the little volatility of PGM and their tendency to form thermostable carbides, which requires a previous treatment of the cuvettes, platforms or the presence of modifiers. Common matrix elements interfere with the atomization process and must often be removed. The sensitivity and detection limits may be enhanced by slurry techniques [43, 44] or various kinds of preconcentrations or by the presence of oxygen in argon. High background levels especially for biotic samples and interferences from common metals and inert salts are observed [43].

ICP-AES of PGM in argon with determination limits 300—30 μg dm^{-3} [41] or 10.0—2.0 μg dm^{-3} [45] is less sensitive with classical nebulizers but advantageous because of little spectral interferences and broad linear calibration functions. Chemical interferences may be, however, serious in the presence of increased amounts of inert salts and common metal ions. Organic solvents of low polarity may also interfere.

ICP-MS is the most suitable method with the highest detection power and large dynamic concentration interval for PGM when internal standards or isotopic dilution [10] is used for quantitative evaluation. A variety of sample introduction modes into ICP, such as current or ultrasonic nebulization, thermospray nebulization, electrothermal vaporization [10, 25, 46—48], slurry technique in the presence of nonionic surfactants [46] or direct injection have been used. The method is, however, not free of serious limitation by matrix elements and components, mutual influence of PGM metals and acids in solution. This is often connected with the limited resolution of the attached mass spectrometer [41, 49]. Detection limits of PGM for pure solutions have been compared for ET-AAS, ICP-AES, and ICP-MS [41].

The application of on-line flow systems with hyphenated techniques containing separation columns is often hindered by the slow kinetics in connection with the formation of PGM chelates or ion associates during the separation and preconcentration or has some drawbacks if microvolumes are sampled in the ET-AAS.

Values for the platinum content in the environment obtained by ET-AAS and ICP-MS from several laboratories were tested with respect of the rules of quality assurance and quality control including sampling and sample decomposition. Considerable differences have been observed among the results [50].

HPLC may be used with advantage for the separation and evaluation of low-molecular platinum species in biotic and soil samples [51]. A hyphenated combination of HPLC-ICP-MS is readily suitable when hydrophobic derivatized silica gel, the gradient elution on the basis of CH_3CN, and ICP-MS attached through an ultrasonic cross flow nebulizer and membrane desolvator are used [52].

The separation of PGM in "ng- and subng-" levels from the matrix components is obligatory after the sample decomposition prior to the application of all the above methods because of serious interferences of matrix components in real samples. For the precedent separation and preconcentration, the electrodeposition on carbonaceous material [16], anion exchangers and especially the SPE by hydrophobic bare, derived or modified sorbents, fibres and sorbent powder—fibres mixtures are used and the retained PGM species are then eluted for final determination.

Decomposition of Samples

Dust filters with airborn particulates of metrologic stations could be successfully leached with HNO_3 and H_2O_2, samples of engine soot were decomposed in low-pressure oxygen high-frequency plasma [45] prior to analysis by ICP-AES or ICP-MS. Mixtures of HCl, HNO_3, and HF are suitable for the decomposition of road dust or soil using microwave oven with pressurized or open air vessels [10, 20] but high-pressure PTFE bombs [51] or high-pressure ashers [12, 53] can also be used with success. Biotic samples or body fluids are decomposed in microwave oven with mixtures of acids and H_2O_2 or directly analyzed after dilution with ET-AAS or ICP-MS [54]. Excess of acids such as HCl [41] and HNO_3 [45] interferes and must be removed by evaporation in the presence of repeated portions of HCl or HNO_3, respectively.

Preconcentration of PGM by Solid Phase Extraction (SPE)

A variety of sorbents are suitable for the preconcentration and separation of PGM from the inorganic or organic matrix after mineralization. Several com-

mon elements do not interfere under validated conditions. Complexes, chelates or ion associates are retained on filled columns of various lengths or short prefabricated cartridges in home-made or commercial arrangement. The elution of the particular PGM species follows with a limited volume of eluent and the elements are determined *via* instrumental methods, especially by GF-AAS, ICP-AES or ICP-MS in off-line or on-line mode. The recovery of element nearly 100 % for a large concentration level, a high enrichment factor with respect to the volume of the primary solution and the increased selectivity for PGM are demanded. The sample solution is sucked under validated conditions *in vacuo* or pushed by a peristaltic pump through the column.

After sample decomposition, the PGM come usually in the form of inert halogenide complexes and the formation of chelates with particular organic reagent, except those of Pd(II) is slow enough or kinetically hindered at room temperature in contrast to the formation of ion associates with cationic species. The formation of retaining PGM species is usually demanded in solutions prior to the interaction with the sorbent. Complexing agents forming water-soluble complexes are more suitable because of not causing clogging of the sorbent column. PGM chelates are often more rapidly formed at elevated temperature in sulfuric or perchloric acid medium containing acetic acid as catalyst or in the presence of nonaqueous solvents. Batch procedures are sometimes preferred for reaching formation equilibrium of kinetically inert PGM chelates but the use of sorbent columns is more advantageous for the practice.

An early review on preconcentration of noble metals and Ag by coprecipitation on inorganic and organic collectors and some complexing sorbents on the basis of polymers, fibres, and cellulose-containing guanidine, rhodanine, alkylpyrazole or 8-sulfanylquinoline groups is only available [56].

Hydrophobic Sorbents with Surface-Immobilized Reagents. PGM Complexes, Chelates or Ion Associates Are Retained

Bare derivatized silica or coated with more or less strongly retained reagent is often used. Octadecyl silica gel in 3 cm cartridges (particle size 7 μm), was suitable for the almost quantitative preconcentration of 2—20 μg of platinum(IV) as hexachloroplatinate from 0.1 M-HCl in the presence of cationic surfactant dimethyllaurylbenzylammonium bromide. 96 % ethanol was a suitable eluent of the $PtCl_6^{2-}$ ion associate. Cetylpyridinium bromide behaves similarly but the elution of the Pt(IV) ion associate from the column demands higher volumes of ethanol which may interfere with the subsequent ICP-AES. The recovery for platinum was 86—110 % [42] and the sample volume and concentrations of PGM do

not influence the recovery of PGM in a limited interval.

Satisfying results for preconcentration of PGM were obtained when ion associates of their chloro complexes with the N-[1-(ethoxycarbonyl)pentadecyl]-trimethylammonium bromide (Septonex®) were used. Samples containing 0.1 M-HCl, 0.006 M surfactant and 1—20 μg of PGM were pumped (1 cm³ min⁻¹) through the octadecyl silica gel column (1 cm³ of sorbent, particle size 60 μm). The eluate with 96 % ethanol was evaporated in the presence of 0.1 M-HCl and the aqueous solution of the residue was analyzed with ICP-AES and ICP-MS. The recoveries were (100 ± 3) % and (100 ± 1) % for 1—20 μg Pt and Pd from 50 cm³ of pure solutions. Os and Ir were retained by 90 %. Very poor recoveries were observed for Ru(IV) and Rh(III). The retention decreases with increasing sample volume and in the presence of common metal ions excess, NO_3^- interferes [45]. At present, the sorption of ion associates of PGM chloride, bromide or thiocyanate complexes with a variety of cationic surfactants on various derivatized silica gels is being studied and validated [57].

Aminopropyl and sulfanyl substituted ligands were also immobilized on silica gel. The dynamic capacities of each gel were evaluated for Pd(II) or Rh(III). The retention of Ag(I), Au(III), Ir(III), Os(IV), Pd(II), Pt(IV), Rh(III), and Ru(III) was evaluated in a batch procedure by ICP-AES. Finally metal ions were retained on columns and eluted at different pH [58].

Silica gel derivatized by phenyl- and benzoylthiourea was also successfully used. Distribution coefficients for noble metals 10^2—10^5 cm³ g⁻¹ have been mentioned. Pt(II), Pd(II), and Au(III) were eluted by thiourea solutions in the form of their stable chelates and could be determined by atomic spectrometry [59].

Silica gels C18 and C8 covered with N,N'-dialkyl-N'-benzylthiourea retain Pd(II) quantitatively in the form of a complex from 1—2 M-HCl. The column was rinsed with diluted HNO_3 and Pd(II) finally eluted from the column with ethanol into the GF of AA-spectrometer [60].

The retention of Ir(IV), Rh(III), Pt(IV), Ru(IV), Os(VIII), Pd(II), and Au(III) from aqueous solutions by silica gel modified with nitrogen-containing organic ligands from diluted hydrochloric acid has also been recommended. The interaction of noble metal complexes with the sorbent-containing monoamine groups seems to run *via* complexation at pH > 1, but at pH < 1 according to anion-exchange mechanism. Especially silica gels containing aliphatic mono- and polyamines have a high sorption rate for noble metals. The desorption of the noble metal ions was, however, a complicated process and the authors preferred the final determination by X-ray fluorescence and emission spectrometry of the sorbent phase [61]. The retention of Pt(II), Pd(II), Au(III), Ag(I), Cd(II), and Hg(II) on silica gel containing N-propyl-N'-

[1-(2-sulfanylbenzthiazolyl)-2,2,2-trichloroethyl]urea (TBTS) was also suitable [62].

Silica gel modified by aminopropylbenzoylazo-1-(2-pyridylazo)-2-naphthol was used for the separation and preconcentration of 20 μg of Pd(II) or Pt(IV) in the form of chelates from 0.1 M-HCl and in the presence of 200 μg of La(III), Cu(II), and Ni(II), 170 μg of Hf(IV), and 500 μg of Cr(III) and Zr(IV). Pd(II) and Pt(II) were successively eluted with a solution of 0.03 M thiourea in 0.1 M-HCl and determined by spectrophotometry. The recoveries for Pd and Pt were 98 % and 96 % and the enrichment factor was 143. The modified sorbent is stable from 6 M-HCl to pH 6 and can be repeatedly used [63]. Silica gels containing adsorbed dithizone, 4,4-bis(dimethylamino)thiobenzophenone or 4-(2-thiazolylazo)naphthol from their solutions in hexane are also suitable to retain Pt(II) and Au(I) [64] but no details are available.

Bis(carboxymethyl)dithiocarbamidate (CMDTC), bis (2-hydroxyethyl)dithiocarbamidate (HEDTC) but also N-methylfurohydroxamate (N-MFHA) and N-(dithiocarboxy)sarcosine (DTCS) give chelates with heavy metal ions and some PGM which may be readily retained on XAD-Amberlite® sorbents. Pt(II), Rh(III), Pd(II) are successfully retained as CMDTC chelates from 1—3 M-HCl solutions in the presence of SnCl$_2$ and reagent excess on microcolumns of XAD-4 macroporous resin (particle size 50—100 μm), later eluted with 5 M-NH$_3$ or 0.5 M-NH$_3$ and on-line determined with GF-AAS or ICP-AES using a segmentation technique for the continuous flow. The previous formation of PGM chelates in solutions is completed after 60 min. The retention of PGM chelates is partly hindered by the presence of heavy metal ions, such as Fe(III) or Cu(II). Os and Ir have not been retained under such conditions. With the AAS detection, detection limits 0.03 ng, 0.1 ng, and 0.01 ng for Pd(II), Pt(II), and Rh(III) were given [33], respectively. The Pt(II) chelates with CMDTC obtained from Pt(IV) by the reduction with SnCl$_2$ are adsorbed on Amberlite XAD-4 resin and may also be back-eluted with ethanol. The ethanol was evaporated and the residue was dissolved in 0.14 M-HNO$_3$. In this way Pt is separated from most matrix elements. Recoveries for Pt were 62—102 % and the detection limit was 1 pg [47]. The commonly used pyrrolidinecarbodithioate on C18 bonded silica gel may also be used for the preconcentration of PGM [65].

Pd(II) and Au(III) are rapidly retained from a medium containing 0.4 M-NaBr, 0.01 M-KSCN, and 0.05 M-HNO$_3$ on the macroporous sorbent XAD-7 (0.18—0.25 mm) at flow rates 8—10 cm^3 min^{-1} The retained metals were eluted with acetone, the eluate evaporated and the residue dissolved by 0.4 M-NaBr in 0.05 M-HNO$_3$. The absorbance was measured at λ = 377.4 nm and 332.7 nm for the determination of Au and Pd, respectively [66]. Moreover, the retention also

follows in the presence of 3 M-HCl, 25 % KSCN, and 20 % SnCl$_2$. After elution of PGM with acetone, evaporation of the organic solvent and dilution with 25 % KSCN, 20 % SnCl$_2$, and 3 M-HCl the absorbance was measured at 400 nm [67].

Silica gel (S-120, fraction 0.2—0.35 mm) was modified by some organic azo dyes, namely PAN, PAR, TAN, TAR for the retention of Pd(II) besides of Co(II) in the form of chelates and the metals were determined by spectrophotometry after elution [68]. The reaction of heterocyclic hydroxy-substituted azo dyes (HCA) with most PGM is kinetically hindered and chelates are often formed at elevated temperature only. The chelate formation, however, does not take place in the HCl medium from inert PGM halogenide complexes. The reaction is improved from PGM sulfates or perchlorates or in the presence of dioxane or dimethylformamide. The conversion of PGM halogenide complexes to sulfate succeeds during heating the solution with sulfuric acid and acetate. Pd(II) chelates with HCA are formed most easily in perchlorate medium but excess of chloride also interferes strongly.

By using ethylenediamine modified poly(vinyl chloride) (particle size 0.32—1.25 mm) Pd(IV), Pt(IV), Ir(IV) have been surprisingly retained from waste waters. Pd(II) and Au(III) were eluted with 10 M-HCl containing 2 % thiourea, Pt(IV) with a mixture of 10 M-HCl and concentrated HBr and Ir(IV) with a mixture of NaNO$_2$, NH$_4$I, and KI solutions. The recoveries were 93.3—100 % and metals were finally determined by ICP-AES [69].

Polyurethane foam is a suitable sorbent for inorganic species from solutions containing metal halogenide and thiocyanate complexes in sulfuric, nitric, and hydrochloric acid media [70]. The retention is influenced by the properties of the retained complex species as well as by the solution composition [71]. Pt(IV), Pd(II), Au(III) and other metal ions were successfully retained on polyurethane foam coated by immobilized 4-adamantyl-2-(2-hydroxy-1-naphthyl)thiazole (AOT) [62]. Complicated ternary species of PGM in the presence of 50 % KI, 0.5 M-SnCl$_2$ in 2.4 M-HCl and 1.2 M-HCl are also retained on cubes of polyurethane foam. After preconcentration the metal contents were determined by flame AAS or ICP-AES. Recoveries/% were 99.2; 98.6; 97.8; 98 or 97.8 for Pt, Pd, Rh, Ir, Au, respectively [72].

Complexing or Chelating Sorbents

Sorbents have also been synthesized and the chelating functional analytical group covalently incorporated in the sorbent skeleton of various origin.

A macroporous chelating resin containing thiosemicarbazide (TSC) is suitable for the preconcentration of Pt(IV), Pd(II), and Au(III) from 1.5 M-HCl. The elution of the elements was followed by 5 % thiourea

solution with a 97—107 % recovery and metals were determined by AAS [73].

Noble metal ions, especially Pd(II) and Pt(IV) may also be retained at pH 1—7 on a chelating resin prepared by the reaction of dithizone with a chloromethylated poly(vinyl pyridine) resin. Pd and Pt were desorbed from the resin with 1 % or 5 % thiourea in 0.1 M-HCl [74].

The chelating macroporous resin containing imidazolinylethylamino functional groups retains chloride complexes of Pt(IV) and Pd(II) from diluted HCl. The retained species were quantitatively desorbed with 4 % thiourea in 0.25 M-H_2SO_4 with a 90—110 % recovery and finally determined by ICP-MS [75].

A macroporous resin with poly(vinylaminoacetone) chelating groups (PVAA) can be synthesized readily. This resin is suitable for preconcentration and separation of traces of Au(III), Pd(IV), Rh(III), and Ru(III) under solutions flow rate 1.5 cm^3 min^{-1} After elution from the column by mixed 6 M hydrochloric acid and 3 % thiourea solution, traces of Au, Pd, Rh, and Ru were determined by ICP-AES. Interferences by common metals were not observed in real samples. Recoveries of these elements in nonferrous matrices were above 95 % with the RSD between 2.0 % and 4.0 % [76].

A spherical macroporous epoxy-imidazole complexing resin has been found suitable for preconcentration and separation of traces of Pd(IV), Ru(III), and Au(III) from diluted HNO_3 and HCl solutions in dependence on pH as well as the subsequent elution by 5—6 M-HCl containing thiourea. The metals were finally determined by ICP-AES. A 100-fold excess of common metal ions causes little interferences [77].

Similarly a macroporous poly(vinylthiopropionamide) resin retained Pt(IV), Pd(II), and Ir(III) from solutions at different pH. The elution of PGM followed by 6 % thiourea in 1 M-HCl and 6 M-HCl for Ir(III) respectively and the metals were determined by ICP-AES. Traces of Pt(IV) and Pd(II) were enriched quantitatively in the range of 5 M-HCl to pH 9. Recoveries were higher than 96 %, for traces of Ir > 93 % between pH 1—9. The retention of Ru(III) or Rh(III) at pH 3—6 was incomplete [78].

A chelating resin containing 2-aminopyridine functional groups was recommended for the retention of Rh(III), Ir(III), Pt(II), and Pd(II). Common metal ions were eluted by 0.5 M-HCl and finally the PGM with a mixture of 4 M-HCl and 2 M-$HClO_4$. Their final determination has been carried out with ICP-AES [79]. An on-line flow system with a microcolumn of ion exchanger resin containing 2-aminopyridine has been described for the retention of Pd(II), Pt(IV), and Ir(III) [80]. The column was successfully rinsed with 6 M-HCl, H_2O, 6 M-NaOH, and water and the PGM eluted by a mixture of 0.5 M-HCl, 0.5 M-$HClO_4$, and 0.5 M-$MgCl_2$ and determined with FAAS in acetylene—air flames [80].

A resin containing polydithiocarbamate retains Pt(II) and Pd(II) besides of Au(III) and Ag(I). The solution was passed through a small column of poly(dithiocarbamate) resin (0.16—0.25 mm). The resin was then dried at 80 °C and decomposed with 50 % H_2O_2 at 230 °C for 4 h. After evaporation, the resin residue was dissolved in 2 cm^3 of 1 M-HNO_3 and the noble metals were determined by ICP-AES. The recoveries were 93—99 % [81].

2-Methyl-1,3,5-oxathiazepine-4-thione, a homopolymer of 2-(vinyloxy)ethylisothiocyanate, and a homopolymer of N,N'-bis(vinyloxyethyl)thiuramdisulfide were synthesized and studied with respect to the sorption ability towards Pt-metals, Au, Ag, and Hg. All compounds retain metal ions in 1—6 M acid solutions. Under these conditions, the separation of PGM, Au, Ag, and Hg is possible from large amounts of Fe, Cu, Ni, Co, Zn. The retention of PGM depends on concentration and nature of acid and the nature of complexes in solution [82].

A chelating resin YPA-4 (no information about its structure) is described to retain PGM from 2.5 M-HCl. After careful rinsing, the resin was ashed after addition of graphite. The residue was vaporized by laser ablation into ICP atomic emission spectrometer. Detection limits were 0.7 ng g^{-1} for Pd, Pt, Rh, and Ru and 0.6 ng g^{-1} for Ir and Os [83].

Russian chelating sorbents POLYORGS on the basis of styrene copolymers, glycidyl derivatives, alkylated cellulose, aminopolystyrene, and fibrous acrylonitrile containing pyrazole, imidazole, amidoxime, 2-sulfanylbenzothiazole, thioglycolanilide or bisazo dyes with characteristic function-analytical groups as components show increased selectivity for heavy metal ions, lanthanoids, and noble metals. They are suitable for the preconcentration of metals during the analysis of ores, rocks, waters, and industrial products. After preconcentration in batch or column procedures the metal species are eluted or the sorbent decomposed by acid ashing with graphite or applied in suspension in DMF and the metal traces determined by GF-AAS, AES, ICP-AES or X-rays emission spectrometry. Especially POLYORGS with 3,5-dimethyl- or 5-methylpyrazolone, pyrazolazo and benzimidazole components are suitable for the preconcentration of PGM and Au, Ag from 50—300 cm^3 of 0.1—2 M hydrochloric acid at room temperature or in microwave oven at 100 °C, using 0.1—0.2 g of the sorbent [34, 84].

The metals were also concentrated on POLYORGS sorbent based on the copolymer glycidylmethacrylate—ethylene—dimethacrylate [85, 86] by shaking with 1 M hydrochloric acid containing 0.01—1 μg cm^{-3} of the metals for 1 h. The sorbent was filtered off and decomposed by 10—15 min heating with 1 M-HCl at 80 °C and the solution analyzed by ET-AAS. Pd, Pt, and Rh were determined spectrophotometrically at λ = 244.8 nm, 265.9 nm, and 343.5 nm, respectively.

The limits of detection were 80 pg of Pt, 26 pg of Pd, and 18 pg of Rh [85].

A chelating resin containing N,N'-dialkylbenzoyl-thiourea has increased affinity towards Pd(II), Pt(IV), Ru(III), Ir(III) but lowered affinity against heavy common metal ions which is advantageous for the separation of PGM. The elution is carried out by 0.2 M thiourea in 0.1 M-HCl with a high recovery [87].

Similarly chelating resins containing SH groups are suitable for the preconcentration of Pd(II), Pt(IV), and Au(III) from aquatic medium. Contamined ions were rapidly eluted with 0.1—0.2 M-KCN but the elution of adsorbed Os(VIII) and Ir(IV) was difficult [88].

In addition, PGM metals are recovered by sorbents with aliphatic or heterocyclic amino groups from hydrochloric acid solutions ($c_{HCl} > 1$ mol dm^{-3}) due to the interaction with protonated positively charged sorbent amino groups. The most effective recovery of platinum metals was obtained on the sorbent based on weakly cross-linked polystyrene containing diethylene-triamine groups [89—91]. Under these conditions, the 95—99 % recoveries of Ru(IV), Rh(III), Pd(II), Ir(III, IV), Pt(IV) were obtained even in the presence of 10^6—10^7 amounts of Cr(III), Fe(III), Ni(II), Cu(II) and sulfate. The PGM were finally determined by ET-AAS. Platinum metals were also retained from chloride solutions by solid extraction of hydrophobic ion associates of anionic chloride complexes with protonated N'-(dodecyl)diethylenetriamine containing sorbent [43, 92].

Silica gels modified with amine, ammonium, guanidinium, morpholinium or triphenylphosphonium groups are also suitable for the preconcentration of chloride complexes of PGM and Au. Equilibrium was reached after shaking for 10 min. After separation of the sorbent, the noble metals were determined by ICP-AES or by luminescence with 1,10-phenanthroline in the case of Os. All five derived sorbents exhibited high distribution ratios for all metals [93].

Fibrous Complexing Sorbents

Chelating sorbents may be used in the form of granules, powders, and fibres. Fibrous complexing sorbents possess essential advantages for preconcentration with respect to increased speed of sorption and suitability of preconcentration procedure. Fibrous complexing sorbents were synthesized with different functional groups on the base of polyacrylonitrile, poly(vinyl alcohol) or cellulose. Sorbents containing amine, heterocyclic amine, and 2-mercaptobenzothiazole groups are suitable for the preconcentration of noble metals.

A special kind of fibrous sorbents are those filled with a complexing ion exchangers. Thus, filled materials consist of two polymers, in the fibrous and powdered forms. The powdered polymer is well retained in the fibre and has a good contact with solution. PGM retained by fibrous complexing sorbents are finally determined by means of AAS, ICP-AES, XRF [95].

By using polyacrylacylisothiourea chelating fibres, Au(III), Pd(IV), and Ru(III) are satisfactorily enriched and separated from samples with satisfactory results and determined by ICP-AES [96].

A poly(acrylamidrazone-hydrazide) chelating fibre packed in a glass column has also been used to retain PGM from sample solutions adjusted to pH 2—4. The elution of PGM was effected with a mixture of 6 % H$_2$SO$_4$, 2.5 % thiourea and Au and Pd were determined by ICP-AES. The fibres gave recoveries of > 95 % and were regenerated by washing with 12 M-HCl or 15 M-HNO$_3$ followed by dilute NH$_3$ solution and water [97].

Fibres of the copolymer of acrylonitrile with 2-methyl-5-vinylpyridine were also chosen for preconcentration and separation of platinum metals and gold. Pyridine groups in the sorbent phase cause anion-exchange properties of the fibre [98].

Columns with activated carbon fibre (ACF) were used for the quantitative preconcentration of Pd(II) from solutions with pH 3.0. The elution followed by 1—1.5 % thiourea in 1 M-HCl with a recovery 103—107 % for Pd. The final determination was carried out by ET-AAS or ICP-MS [99].

Grain and fibre carbon materials were found to be selective to micropreconcentration of Pd(II), Rh(III), Ru(IV), and Ir(III) after separation from 100—1000-fold excess of common metals (Cu, Zn, Al, Cr, Mn, Fe, Co, Ni) in technological samples. The final determinations of PGM were carried out after elution by selective kinetic or spectral procedures [100].

PGM, especially Pt(IV) or Pd(II), may also be effectively retained on activated carbon from water acidified with 12 M-HCl during a batch procedure. After filtration, the carbon containing the PGM was ashed at 650 °C, the ash dissolved in aqua regia and the solution analyzed by ICP-MS. Detection limits for Pd and Pt were 0.8 ng dm^{-3} and 0.4 ng dm^{-3} and the enrichment factor was 200 for 1 dm^3 sample volume [48].

Sorbents Coated with Liquid Anion Exchanger and Extracting Agents

Extraction on columns with hydrophobic or inert sorbents is suitable for the separation or preconcentration of elements with similar properties, *i.e.* similar distribution coefficients or stability constants of their complexes. The repeated extraction act on the column is advantageous for the retaining of metal traces in the presence of excess of macrocomponent. The inert sorbent is previously coated by the ion-pairing or chelating agent in low-polar solvent whereas the mobile phase is the aqueous metal solution. This procedure is rather limited for PGM because of the slow formation of PGM chelates.

Rh(III), Ru(IV), Pd(II), Pt(IV), Ir(III), Os(IV), and Au(III) may be extracted with trioctylamine coated on hydrophobic teflon. The particular metal species were then reextracted from the sorbent by mixtures of 1—6 M-HNO$_3$ and HCl or by 5 % thiourea—1 M-HCl mixture. The recoveries for PGM were 92.5—99 % and the final determination was carried out by AAS or ICP-MS [104]. For preconcentration of Pd, tribenzylamine was also used [105].

Silica gel C18 covered by methyltricaprylammonium chloride (Aliquat 336) retains platinum. The platinum species were eluted from the column by a mixture of 1 M-HCl—0.1 M-HClO$_4$ and directly sampled into the nebulizer of the ICP-MS. Such procedure was used for the determination of Pt in tunnel dust after its decomposition by aqua regia and H$_2$O$_2$ in a microwave oven. The detection limit was 0.17 ng Pt [106].

Synthetic samples containing 21 basic metals and 5 noble metals were dissolved and the solutions diluted with 1 M-HCl. A portion of the solution was shaken for 1 h at 25 °C with 0.2 g of trioctylamine containing resin as a group reagent. The solid substance was filtered off and boiled gently to dissolve in 8 cm^3 of HClO$_4$—HNO$_3$ ($\varphi_r = 1$ 1). PGM were determined by ICP-AES. The recovery of PGM has been 90—102 % [94].

Pd(II) is retained on PTFE columns by PAN solution in CHCl$_3$ at pH 2—3 or isopentanol solution at pH 2.5—3.5 or their mixture ($\varphi_r = 1$ 1) from the sulfate and acetate containing mobile phase. The enrichment factor is about 100 [101, 102]. For other PGM such as Pt(II) or Rh(III), a heating of the column to 85 °C and a low flow rate of the aqueous solution of PGM are necessary for the successful retention. At room temperature the separation of Pd from other PGM is only possible. Several common metal ions have been screened by EDTA [103].

Pd(II), Pt(II), and Rh(III) were also retained from their sulfate solutions (pH 3.0 to 3.8) containing Na acetate and 1 M-H$_2$SO$_4$ at 85 °C by a column of PTFE carrying 4-(2-pyridilazo) resorcinol (PAR) in isopentanol and the chelates were reextracted from the cooled column with CHCl$_3$—isopentanol ($\varphi_r = 2$

1). The three components in the eluate can be determined spectrophotochemically in the form of their PAR chelates or separated by HPLC on a column of polar silica gel (Silasorb 600$^®$) with benzene—propan-2-ol ($\varphi_r = 9$ 1) as mobile phase and detected at 440 nm. The enrichment factor was nearly 100 in this way [107].

Pt(II), Pd(II), Rh(III), Ir(III) chelates are also extracted with 1-(2-pyridylazo)-2-naphthol (PAN) in isoamyl alcohol coated on Teflon$^®$ (particle size 0.1—0.2 mm) from sulfate medium at pH 3.0—3.8 [108, 109].

Solid-supported liquid membranes containing liquid anion exchanger as a carrier are now more frequently used for selective transport of PGM from sample solutions.

A PTFE membrane impregnated with trioctylamine in kerosene was modified with octan-1-ol for extraction of Pt(IV), Pd(IV), and Au(III) species from the outer solution containing HCl. The noble metals were stripped into 1 M-HClO$_4$ placed in the inner compartment of a polypropylene device. The transport across the membrane for Pt(IV) and Pd(IV) was enhanced by higher trioctylamine concentrations [110]. A liquid kerosene membrane containing tridecanol and 7-dodecenyl-8-quinolinol enhanced the transport of Pt(IV) from diluted HCl or H$_2$SO$_4$. On the other hand, Pd(II) was retained in the membrane if transported from H$_2$SO$_4$ or HNO$_3$ solutions [124]. The separation and enrichment of traces of Pd(II) (as PdCl$_4^{2-}$) from aqueous solution was performed by means of emulsion membrane. The composition of the organic phase in the membrane was 5 % trioctylamine, 10 % monobutanediimide, 10 % liquid paraffin oil as membrane modifier, and 75 % kerosene as membrane solvent. The 5-fold excess of aqueous phase consisted of 11 % NH$_3$, and the optimal volume proportion of organic and aqueous phase was 2 1. Pd was finally determined by flame AAS. Best recoveries for Pd by 96 % with RSD of 1.1 % were from a sample solution containing 1 μg cm^{-3} Pd, 1 mM-NaCl and 0.1 M-HCl. Large excess of common metal ions only interferes [111]. Similarly IrCl$_6^{2-}$ could be transported through a supported liquid membrane from diluted HCl into small volume of 1 M-HClO$_4$ [125]. A microporous polydifluoroethylene film was impregnated with Aliquat 336 and used to separate mixtures of Rh, Pd, and Pt. A feed solution containing 10 mg dm^{-3} of each Rh, Pd, and Pt and 1 mM-SCN$^-$ was extracted and Pt and Pd were transported into the stripping solution while Rh remained in the feed solution because Rh(SCN)$_6^{3-}$ had not been formed [112].

Common Basic Anion Exchangers

Common strongly basic anion exchangers Dowex 1 based on the styrene—divinylbenzene copolymer strongly retain PGM from solutions containing chloride and thiocyanate complexes in the presence of diluted HCl. The separation and preconcentration of PGM in the form of inert chloride complexes on basic anion exchanger has been frequently used [44, 113—119]. The retention has been performed from hydrochloric acid solutions or mixtures of diluted HCl, HNO$_3$, and HF. Common matrix metal ions can be previously eluted, for the strongly retained PGM anions 11 M-HCl or 13.5 M-HNO$_3$ for Ru, Pd, Pt, Ir [118], hot 6 M-HCl for Rh and diluted NH$_3$ for Pd and Pt(IV) [117], 0.3 M thiourea with 0.1 M-HCl for Ru, Pd, Pt, and part of Rh and 12 M-HCl for Ir(IV) and the rest of Rh [116], and 0.5 M-NaClO$_4$ for Pt(IV) [119] have also been used. The strongly acid

cation exchanger Amberlite CG-120® is more suitable for the retention of PGM from 0.2 M-HCl. The recovery > 95 % results for Pd(II), Ru(IV), Rh(III), Ir(III), Pt(IV), and Au(III) after elution with 2.5 M-HCl [113].

Amberlite IRA 416® and Amberlite IRA 910® type anion exchangers were also suitable for the retention of chloro complexes of gold(III) and palladium(II) in hydrochloric acid media. A good separation of Au and Pd chloro complexes can be achieved in spite of the small selectivity of this kind of resins [121]. Increased amounts of eluting agents and salts interfere with the subsequent spectrochemical methods and must be previously removed.

For analysis of dust, ion-exchange separation was used after digesting samples in pressurized vessels of microwave oven. The residue after evaporation was dissolved and submitted to the ion exchanger column in 0.5—0.3 M-HCl. Pt(IV) retained on the column was eluted with nitric acid at 90 °C and analyzed by isotope dilution ICP-MS. The recovery for 10 ng of Pt was > 60 % and the detection limit 1.4 ng g^{-1} [120].

A column packed with a Chinese HHY-10A macropore anionic resin has been used for the retention and desorption of ^{199}Au and ^{195m}Pt from 0.5 M-HCl. The column was washed with 0.1 M-HCl and the radioisotopes eluted with 2 % thiourea. Under optimal conditions, the recoveries were (92.3 ± 2.6) % for Au and (97.7 ± 0.9) % for Pt [122].

Aluminium oxide activated with 0.1 M-HNO$_3$ also retains PtCl$_6^{2-}$ from pH 2.5 and HCl medium with surprisingly 100 % efficiency under optimized conditions. The elution took place with 2 M-NH$_3$. Excess of inert salts and chlorides considerably interferes [123].

CONCLUSION

Most convenient methods for the determination of platinum and other PGM metals in environmental and biotic material are usually ET-AAS, ICP-AES, and ICP-MS which show sufficient sensitivity and detection power but precedent separation and preconcentration of PGM must be carried out. For this purpose solid phase extraction (SPE) may be used with advantage. The retention of ion associates of PGM halogenide complexes with cationic surfactants such as N-[1-(ethoxycarbonyl)pentadecyl]trimethylammonium bromide (Septonex®) on columns with bonded C18 or C8 silica gel and coated with the surfactant is highly efficient from hydrochloric acid medium. The formation of ion associates is fast enough and the retention as well as the elution with ethanol proceeds rapidly and is quantitative for Pt(IV), Pd(II), Au(III). A drawback is the interference of HNO$_3$ in solution which must be removed by repeated evaporation with HCl prior to the application of surfactant and interaction with the column. Strongly basic anion exchangers firmly retain PGM as halogenide complexes from HCl

medium but there is no selectivity for PGM. Moreover, the elution of PGM from the column is difficult and hot diluted HNO$_3$, high concentrations of mineral acids, complexing agents or 0.5 M-NaClO$_4$ must be used. The excess of inert salts or complexing agent in the eluate usually interfere with the final ICP-AES or ICP-MS.

The interaction of halogenide complexes of PGM with complexing sorbents or those being modified by coated chelating reagents is kinetically hindered at room temperature with the exception of Pd(II). Thus, the retention of PGM on sorbent columns during the dynamic mode is often insufficient. In such a case the previous formation of PGM chelates in solution is recommended or the previous conversion of PGM halogenides into sulfates in the presence of acetic acid as coordination catalyst at elevated temperature. The highest affinity towards PGM in low valency numbers, especially Pd(II) and Pt(II) is shown by the complexing reagents containing sulfur or nitrogen in the function – analytical group, e.g. dithiocarbamidate or thiourea derivatives.

REFERENCES

1. Yi Biu Qu, *Analyst 121*, 139 (1996).
2. Balcerzak, M., *Analyst 122*, 67R (1997).
3. Pyrzynska, K., *Talanta 47*, 841 (1998).
4. *Platinum, Environmental Health Criteria 125.* World Health Organization, Geneva, 1991.
5. Klueppel, D., Jakubowski, N., Messerschmidt, J. Stuewer, D., and Klockow, D., *European Winter Conference on Plasma Spectrochemistry*, 12—17 January, 1997, University of Gent, Gent, Belgium, 1997.
6. Redijk, J., *Pure Appl. Chem. 59*, 181 (1987).
7. Abrams, M. J. and Murrer, B. A., *Science 261*, 726 (1993).
8. Hodge, V F. and Stallard, M. O., *Environ. Sci. Technol. 20*, 1058 (1986).
9. Eller, R., Alt, F., Tölg, G., and Tobschall, H. J., *Fresenius' J. Anal. Chem. 334*, 723 (1989).
10. Colodner, D. C., Boyle, E. A., and Edmond, J. M., *Anal. Chem. 65*, 1419 (1993).
11. Georgieva, M. and Pihlar, B., *Anal. Lab. 4*, 224 (1995).
12. Alt, F., Bambauer, A., Hoppstock, K., Mergler, B., and Tölg, G., *Fresenius' J. Anal. Chem. 346*, 693 (1993).
13. Wildhagen, D. and Krivan, V., *Anal. Chim. Acta 274*, 257 (1993).
14. Schlögl, R., Indlekofer, G., and Oelhafen, P *Angew. Chem. 99*, 312 (1987).
15. Farago, M. L., Kavanagh, P. Blank, R., Kelly, J. Kazantzis, G., Thorton, I., Simpson, P R., Cook, J. M., Parny, S., and Hall, G. M., *Fresenius' J. Anal. Chem. 354*, 660 (1996).
16. Beinrohr, E., Lee, M. L., Tschöpel, P., and Tölg, G., *Fresenius' J. Anal. Chem. 346*, 689 (1993).
17. Schramel, P. Wendler, I., and Lustig, S., *Fresenius' J. Anal. Chem. 353*, 115 (1995).
18. Messerschmidt, J., Alt, F., and Tölg, G., *Anal. Chim. Acta 291*, 161 (1994).

19. Hall, G. E., Pelchat, J. C., and Dunn, C. E., *J. Geochem. Explor. 37*, 1 (1990).
20. Begerow, J., Turfeld, M., and Dunemann, L., *Anal. Chim. Acta 340*, 277 (1997).
21. Kolpakova, N. A., Antipov, S. A., and Kaminskaya, O. V., *International Congress on Analytical Chemistry*, Moscow, Russia, June 15—21, 1997, Abstract G-27.
22. Begerow, J. and Dunemann, L., *J. Anal. At. Spectrom. 11*, 303 (1996).
23. Einhäuser, T. J. Galanski, M., and Keppler, B. K., *J. Anal. At. Spectrom. 11*, 747 (1996).
24. Balcerzak, M. and Donard, O. F. X., *International Congress on Analytical Chemistry*, Moscow, Russia, June 15—21, 1997, Abstract N-18.
25. Matusiewicz, H. and Barnes, R. M., *Acta Chim. Hung. 125*, 777 (1988).
26. Nyrgen, O., Vaughan, G. T., Florence, T. M., Morrison, G. M. P., Warner, I. M., and Dale, L. S., *Anal. Chem. 62*, 1637 (1990).
27. Casetta, B., Roncadin, M., Montanari, G., and Furlanut, M., *At. Spectrosc. 12*, 81 (1991).
28. Van Warmerdam, L. J. C., Van Tellingen, O., Maes, R. A. A., and Beijnen, J. H., *Fresenius' J. Anal. Chem. 351*, 777 (1995).
29. Wei, Ch. and Morrison, G. M., *Anal. Chim. Acta 284*, 587 (1994).
30. Alt, F., Eschnauer, H. R., Mergler, B., Messerschmidt, J., and Tölg, G., *Fresenius' J. Anal. Chem. 357*, 1013 (1997).
31. Korda, T. Buchbinder, G., Kalish, N. and Torgov, V., *International Congress on Analytical Chemistry*, Moscow, Russia, June 15—21, 1997, Abstract O-20.
32. Torgov, T., Demidova, M., Korda, T., Kalish, N., and Shulman, R., *Analyst 121*, 489 (1996).
33. Lee, M. L., Tölg, G., Beinrohr, E., and Tschöpel, P. *Anal. Chim. Acta 272*, 193 (1993).
34. Kuz'min, N. M., Kubrakova, I. V., Pukhovskaya, V. M., and Kudinova, T. F., *J. Anal. Chem. 49*, 182 (1994).
35. Calmotti, S., Dossi, C., Recchia, S., and Zanderighi, G. M., *Spectrosc. Eur. 8*, 18 (1996).
36. Watson, A. E., Russell, G. M., Middleton, H. R., and Davenport, F. F., *Rep. MINTEK M81*, 13 (1983).
37. Graham, S. M. and Robert, R. V. D., *Talanta 41*, 1369 (1994).
38. Hoppstock, K., Alt, F., Cammann, K., and Weber, G., *Fresenius' J. Anal. Chem. 335*, 813 (1989).
39. Ulakhovich, N. A., Budnikov, G. K., and Medyantseva, E. P *Zh. Anal. Khim. 47*, 1546 (1992).
40. Rietz, B. and Heydron, K., *J. Radioanal. Nucl. Chem. 174*, 49 (1993).
41. Paukert, T., *Chem. Listy 87*, 8 (1993).
42. Otruba, V., Strnadová, M., and Skalníková, B., *Talanta 40*, 221 (1993).
43. Kubrakova, I. V. Kudinova, T. F., Kuz'min, N. M., Kovalev, I. A., Tsysin, G. I., and Zolotov, Yu. A., *Anal. Chim. Acta 334*, 167 (1996).
44. Hodge, V., Stallard, M., Koide, M., and Goldberg, E. D., *Anal. Chem. 58*, 616 (1986).
45. Vlašánková, R., Otruba, V., Bendl, J., Fišera, M., and Kanický, V., *Talanta 48*, 839 (1999).
46. Totland, M., Javis, I., and Jarvis, R. E., *Chem. Geol. 104*, 175 (1993).
47. Parent, M., Vanhoe, H., Moeus, L., and Dams, R., *Fresenius' J. Anal. Chem. 354*, 664 (1996).
48. Hall, G. E. and Pelchat, J. C., *J. Anal. At. Spectrom. 8*, 1059 (1993).
49. Dams, R. F. J., Goossens, J. and Moens, L., *Mikrochim. Acta 119*, 277 (1995).
50. Wegscheinder, W. and Zischka, M., *Fresenius' J. Anal. Chem. 346*, 525 (1993).
51. Jerono, U. Alt, F., Messerschmidt, J., and Tölg, G., *Mikrochim. Acta 108*, 221 (1992).
52. Lustig, S., Michalke, B., Beck, W., and Schramel, P *Fresenius' J. Anal. Chem. 360*, 18 (1998).
53. Alt, F., Jerono, U., Messerschmidt, J., and Tölg, G. *Mikrochim. Acta III, 1988*, 299.
54. Di Noto, V., Ni, D., Dalla Via, L., Scomazzon, F., and Vidali, M., *Analyst 120*, 1669 (1995).
55. Mukai, H., Ambe, Y., and Morita, M., *J. Anal. At. Spectrom. 5*, 75 (1990).
56. Myasoedova, G. V. and Malofeeva, G. I., *Zh. Anal. Khim. 34*, 1626 (1979).
57 Vlašánková, R. and Sommer, L., to be published.
58. Schilling, T., Schramel, P., Michalke, B., and Knapp, G., *Mikrochim. Acta 116*, 83 (1994).
59. Losev, V., Bakhvalova, I., Volkova, G., Mazniak, N., and Trofimchuk, A., *International Congress on Analytical Chemistry*, Moscow, Russia, June 15—21, 1997, Abstract C-26.
60. Schuster, M. and Schwarzer, M., *Anal. Chim. Acta 328*, 1 (1996).
61. Tikhomirova, T. I., Fadeeva, V. I., Kudryavtsev, G. V., Nesterenko, P N., Ivanov, V. M., Savitchev, A. T., and Smirnova, N. S., *Talanta 38*, 267 (1991).
62. Dyachenko, N. A., Karetnikova, E. A., Trofimchuk, A. K., and Sukhan, V V., *International Congress on Analytical Chemistry*, Moscow, Russia, June 15—21, 1997, Abstract C-54.
63. Liu, F., Li, K. A., Wu, Y. S., Wang, X., and Tong, S. Y., *Microchem. J. 52*, 274 (1995).
64. Zaporozhets, O., Petruniok, N., and Sukhan, V., *International Congress on Analytical Chemistry*, Moscow, Russia, June 15—21, 1997, Abstract D-26.
65. Shah, N. K. and Wei, C. M., *J. Radioanal. Nucl. Chem. 130*, 451 (1989).
66. Elci, L., Isildar, S., and Dogan, M., *Anal. Chim. Acta 293*, 319 (1994).
67 Soylak, M., Elci, L., and Dogan, M., *Fresenius' J. Anal. Chem. 351*, 308 (1995).
68. Kuznetsova, O. V. and Ivanov, V. M., *International Congress on Analytical Chemistry*, Moscow, Russia, June 15—21, 1997, Abstract L-104.
69. Chang, X., Su, Z., Zhan, G., Luo, X., and Xu, Z., *Huaxue Xuebao 48*, 157 (1990).
70. Nabivanets, B., Gorlach, V., and Lysenko, E., *International Congress on Analytical Chemistry*, Moscow, Russia, June 15—21, 1997, Abstract C-52.
71. Dmitrienko, S., Pyatkova, L., Myshak, E., Goncharova, L., Gurary, E., and Runov, V., *International Congress on Analytical Chemistry*, Moscow, Russia, June 15—21, 1997, Abstract C-53.
72. Wu, L. S. and Zhao, M. Z., *Fenxi Huaxue 22*, 877 (1994); *Anal. Abstr. 57*, 3D156 (1995).
73. Yu, Z., Wang, H., Li, C., and Wei, X., *Yangkuang Ceshi 10*, 9 (1991); *Anal. Abstr. 54*, 7E42 (1992).

74. Shah, R. and Devi, S., *Anal. Chim. Acta 341*, 217 (1997).
75. Zu, Z. X., Pu, Q. S., Luo, X. Y., Chang, X. J. Zhan, G. Y., and Ren, F. Z., *Talanta 42*, 1127 (1995).
76. Chang, X., Luo, X., Zhan, G., and Su, Z., *Talanta 39*, 937 (1992).
77. Chang, X. J., Su, Z. X., Yang, D., Gong, B., Pu, Q. S., and Li, S. K., *Anal. Chim. Acta 354*, 143 (1997).
78. Su, Z., Chang, X., Xu, K., Luo, X., and Zhan, G., *Anal. Chim. Acta 268*, 323 (1992).
79. Li, L., Ma, J., and Chen, L., *Gaodeng Xuexiao Huaxue Xuebao 10*, 531 (1989).
80. Di, P and Davey D. E., *Talanta 42*, 685 (1995).
81. Chung, Y. S. and Barnes, R. M., *J. Anal. At. Spectrom. 3*, 1079 (1988).
82. Shaulina, L. P., Golentovskaya, I. P., and Smagunova, M. I., *International Congress on Analytical Chemistry*, Moscow, Russia, June 15—21, 1997, Abstract C-68.
83. Duan, Y. R., Li, W. H., and Xu, Y. W., *Fenxi Huaxue 22*, 366 (1994).
84. Myasoedova, G. V., *Fresenius' J. Anal. Chem. 341*, 586 (1991).
85. Stavnivenko, E. B. and Kuz'min, N. M., *Zh. Anal. Khim. 50*, 1243 (1995).
86. Krioukov, S. V., Gabdullin, M. G., Zakharov, S. V. and Garifzianov, A. R., *International Congress on Analytical Chemistry*, Moscow, Russia, June 15—21, 1997, Abstract L-55.
87. Szczepanik, W., *Chem. Anal.* (Warsaw) *37*, 257 (1992); *Anal. Abstr. 55*, 7D116 (1993).
88. Egawa, H., Jyo, A., and Ochiai, K., *Nippon Kagaku Kaishi 4*, 359 (1994); *Anal. Abstr. 56*, 11D150 (1994).
89. Kovalev, I. A., Tsysin, G. I., Formanovski, A. A., Kubrakova, I. V., Zakharov, V. N., Aslanov, L. A., and Zolotov, Yu. A., *Zh. Anal. Khim. 40*, 828 (1995).
90. Kovalev, I. A., Tsysin, G. I., Formanovski, A. A., Evtikova, G. A., Marov, I. N., Zakharov, V N. Aslanov, L. A., and Zolotov, Yu. A., *Zh. Anal. Khim. 40*, 55 (1995).
91. Kovalev, I. A., Tsysin, G. I., and Zolotov, Yu. A., *Mendeleev Commun. 1995*, 111.
92. Kovalev, I. A., Tsysin, G. I., Kubrakova, I. V., and Zolotov, Yu. A., *International Congress on Analytical Chemistry*, Moscow, Russia, June 15—21, 1997, Abstract C-29.
93. Runov, V. K., Strepetova, T. V., Pukhovskaya, V. M., Trofimchuk, A. K., and Kuz'min, N. M., *Zh. Anal. Khim. 48*, 43 (1993).
94. Li, L., Su, X., An, Y., Ma, J., and Yu, S., *Fenxi Shiyanshi 8*, 1 (1989).
95. Shcherbinina, N. I. and Myasoedova, G. V., *International Congress on Analytical Chemistry*, Moscow, Russia, June 15—21, 1997, Abstract C-5.
96. Chan, G. X., Su, Z. X., Zhan, G. Y., Luo X. Y., and Gao, W. Y., *Analyst 119*, 1445 (1994).
97. Chang, X. J., Zhan, G. Y., Luo, X. Y., and Su, Z. X., *Mikrochim. Acta 112*, 245 (1994).
98. Khmelyov, S. S., Mushtakova, S. P., and Simanova, S. A., *International Congress on Analytical Chemistry*, Moscow, Russia, June 15—21, 1997, Abstract C-27.
99. Lin, S. L., Zheng, C. S., and Yun, G. Z., *Talanta 42*, 921 (1995).
100. Tarkovskaya, I. A., Tikhonova, L. P., Rosokha, S. V Korovin, Yu. F., Komarov, V. P., and Kadochnikov, V. A., *International Congress on Analytical Chemistry*, Moscow, Russia, June 15—21, 1997, Abstract C-25.
101. Bolshova, T. A., Morozova, N. B., and Ivanov, V M., *Zh. Anal. Khim. 40*, 1394 (1985).
102. Figurovskaya, O. N., Busev, A. I., and Ivanov, V M., *Zavod. Lab. 39*, 132 (1973).
103. Alimarin, I. P Ivanov, V M. Bolshova, T. A., and Basova, E. M. *Fresenius' J. Anal. Chem. 335*, 63 (1989).
104. Li, L., Xu, X., An, Y. and Ma, J., *Fenxi Huaxue 18*, 195 (1990).
105. Tang, F., Mao, X., Wu, G., and Zhang, Y. *Gaodeng Xuexiao Huaxue Xuebao 14*, 271 (1993); *Anal. Abstr. 55*, 10D217 (1993).
106. Akatsuka, K., Hoshi, S., Katoh, T., Willie, S. N., and McLaren, J. W., *Chem. Lett. 9*, 817 (1995); *Anal. Abstr. 58*, 4H23 (1996).
107 Basova, E. M., Ivanov, V. M., Bolshova, T. A., and Babkova, N. A., *Zh. Anal. Khim. 45*, 671 (1990).
108. Timerbaev, A. R., Tsoi, I. G., and Petrukhin, V M., *J. Chromatogr. 448*, 337 (1990).
109. Ivanov, V M., *Geterotsiklicheskie azosoderzhashchie azosoedineniya*, p. 151. Nauka, Moscow, 1982.
110. Fu, J., Nakamura, S., and Akiba, K., *Anal. Sci. 11*, 149 (1995).
111. Wang, Z. X., Li, Y. M., Li, Y. T. and Guo, Y *Anal. Lett. 27*, 957 (1994).
112. Fontas, C., Antico, E., Salvado, V., Valiente, M. and Hidalgo, M., *Anal. Chim. Acta 346*, 199 (1997).
113. Chen, Z., Fryer, B. J. Longerich, H. P., and Jackson, S. E., *J. Anal. At. Spectrom. 11*, 805 (1996).
114. Colodner, P., Boyele, E. A., and Edmond, J. M., *Anal. Chem. 65*, 1419 (1993).
115. Al-Bari, S. J. and Chow, A., *Talanta 31*, 815 (1984).
116. Jarvis, M. M., Totland, M. M., and Jarvis, K. E., *Analyst 122*, 19 (1997).
117. Gaita, R. and Al-Bari, S. J., *Talanta 42*, 249 (1995).
118. Rehkämper, M. and Halliday, A. N. *Talanta 44*, 663 (1997).
119. Krásenský, P and Kanický, V., *Šcr. Fac. Sci. Nat. Univ. Mas. Brun. 27—28*, 75 (1997—1998).
120. Akatsuka, K., Hoshi, S., McLaren, J. W., and Berman, S. S., *Bunseki Kagaku 43*, 61 (1994); *Anal. Abstr. 56*, 8H26 (1994).
121. Sanchez, J. M., Antico, E., Hidalgo, M., Valiente, M., and Salvado V *International Congress on Analytical Chemistry*, Moscow, Russia, June 15—21, 1997, Abstract C-46.
122. Li, C. S., Chai, C. F., Yang, X. F., Hou, X. L., and Mao, X. Y., *Talanta 44*, 1313 (1997).
123. Putnova, P. and Otruba, V., private communication.
124. Fu, J., Nakamura, S., and Akiba, K., *J. Membr. Sci. 107*, 283 (1995).
125. Fu, J., Nakamura, S., and Akiba, K., *Sep. Sci. Technol. 30*, 3821 (1995).