SEPARATION AND PRECONCENTRATION OF PLATINUM GROUP METALS AND GOLD ON MODIFIED SILICA AND XAD SORBENTS IN THE PRESENCE OF CATIONIC SURFACTANTS FOR THEIR DETERMINATION BY ICP-AES

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Various modified silica sorbents and unmodified silica were tested for the separation and preconcentration of 10–200 ng cm^{-3} from 50–1 000 cm^3 sample volume of platinum group metals (PGMs), Pt(IV, II), Pd(II), Ir(IV), Rh(III), Os(VI), Ru(IV) and Au(III) in the form of ion associates of their chloro and bromo complexes with cationic surfactants. [1-(Ethoxy-carbonyl)pentadecyl]trimethylammonium bromide (Septonex®), benzyl(dodecyl)dimethyl-ammonium bromide (Sterinol®), trimethyl(tetradecyl)ammonium bromide or hexadecyl(trimethyl)ammonium chloride and 0.1 M HCl or 0.1 M HBr are suitable for the purpose. 100% recovery for Pd(II), Pt(IV) and Au(III) was obtained with octadecyl silicas Separon™ SGX C18, Separon™ SGX RPS and Phenyl™ silica in the presence of 0.006 M Septonex® or 0.003 M Sterinol®. The retained PGMs and Au(III) were eluted with acetonitrile and determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) after evaporation of organic solvent in the presence of 0.1 M HCl. The enrichment factor on Separon™ SGX RPS reaches 100. A 1 000 : 1 excess of Cl$^-$, NO$_3^-$, SO$_4^{2-}$, Na$^+$, K$^+$, Ca^{2+}, Mg^{2+}, Fe^{3+} or Al^{3+} does not interfere with the preconcentration of PGMs and Au(III) on this sorbent. With the silica-based anion exchanger Separon™ SGX AX, the 100% recovery is observed for Ir(IV), Pd(II), Pt(IV) when the elution is performed with 5 M HCl or 5 M HNO$_3$. Macroporous sorbents Amberlite™ XAD2 and Amberlite™ XAD4 are suitable for the retention of Au(III), Pd(II) and Pt(IV) from 0.1 M HCl and 0.006 M Septonex®. 100% recovery is achieved using acetonitrile as eluent but there is no preference of these sorbents to modified silica. In this way, the recovery of 0.1–0.2 µg cm^{-3} Au(III), Pd(II), Pt(IV) was also successfully tested with spiked matrices of soil extracts, power station dust samples and natural waters.

Keywords: Platinum group metals; Gold; Sorbents; Modified silica; Amberlite XAD2 and XAD4; Quaternary ammonium surfactants; Inductively coupled plasma atomic emission spectrometry (ICP-AES).

Recently, the platinum group metals (PGMs) awoke a considerable interest because of their increased occurrence in the environment. This is due to

their use as industrial and automobile catalysts and application of some platinum(II) complexes as anti-cancer drugs[1]. Thus, microamounts of PGMs are dispersed in the ambient air, airborne dust particles, road dust, soil and plants near the busy highways and waters[1–3]. The platinum content of the airborne dust ranged from 0.6 to 130 ng g^{-1}, in air from 0.02 to 5.10 pg m^{-3} and in motorway soils from 15 to 30 ng g^{-1} (ref.[4]). Platinum has to be monitored in body fluids and tissues in cancer treatment and Pt(II) traces may appear on the furniture in rooms or in waste-waters of some hospitals[5]. Several compounds of Pt(IV) and Pd(II) are gastrointestinal irritants and strong allergens already in the nanogram level for sensitive persons[1,2]. Gold contents in the environment are also low, *i.e.* 0.05 ng cm^{-3} of Au was found in sea-water and 0.09 and 0.2 ng cm^{-3} in river- and spring-water, respectively, but the average concentration in the Earth crust 4 ng g^{-1} was reported[6].

The widely used inductively coupled plasma atomic emission spectrometry (ICP-AES) can be successfully used for simultaneous determination of PGMs and Au in limit concentrations below μg cm^{-3} without preconcentration. Moreover, the accompanying common metals and a large excess of acids and inert salts may interfere[3,7–9].

Modified and unmodified silica coated with more and less strongly retained organic reagents have been already reported for separation of PGMs (ref.[10]). Octadecyl silica was already used for the preconcentration of Pt(IV) in the form of ion associate of hexachloroplatinate with various cationic surfactants, in particular benzyl(dodecyl)dimethylammonium bromide prior to its determination by emission spectrometry in spiked plant ash[11].

Recently, the retention of several PGMs and Au(III) in the form of ion associates of chloro complexes with [1-(ethoxycarbonyl)pentadecyl]trimethylammonium bromide was studied on octadecyl silica only. The recovery of preconcentrated metals was evaluated by ICP-AES and inductively coupled plasma mass spectrometry[12] (ICP-MS). At present, ICP-MS was only suitable for their direct determination in airborne dust particulates, usual soils, waters and plant tissues[8,13–15]. This approach was then used for testing analytical performance characteristics of various types of inductively coupled plasma spectrometers[16]. A selective preconcentration of gold was also described on octadecyl silica in the form of ion associates of Au(III) chloro complex and Au(I) cyano complex with quaternary bases including some cationic surfactants[17].

In this paper, a number of modified silicas, silica-based anion exchangers, Amberlite™ XAD2, XAD4 and LiChrolut™ EN polymers are tested and compared for simple selective separation, preconcentration and recovery of PGMs and Au(III) in the form of ion pairs of chloro and bromo complexes

in the presence of various cationic surfactants. After elution, multicomponent determination follows by ICP-AES.

EXPERIMENTAL

ICP-AES Instrumentation and Operation Conditions

Final measurements were carried out on an echelle-based ICP spectrometer with a prism predisperser IRIS AP™ (Thermo Jarrell Ash, U.S.A.) containing a CID detector with 512×512 pixels for 195–900 nm and axial plasma discharge. The echelle grating contained 54.4 lines mm^{-1}, the plasma source was a generator with 27.12 MHz which operated with a power output of 1.15 kW. The plasma argon flow rate was 12 dm^3 min^{-1}, that of the auxiliary argon was 0.5 dm^3 min^{-1} and carrier 1.0 dm^3 min^{-1}. The signal integration time was 30 s and every result was the average of three measurements. The continuous background correction minimised the noise of the plasma and of solutions with high salt concentrations. The Meinhard nebulizer was fed by a peristaltic pump (flow rate 1.85 cm^3 min^{-1}).

The following spectral lines (nm) in high orders were used for evaluation (orders in parentheses): AuI 242.795 (107), RuII 240.272 (108), RhII 233.477 (111), PdI 340.458 (76), OsII 225.585 (115), IrII 224.268 (116), PtII 214.423 (121). Background-corrected intensities were evaluated for the analysis of samples.

Four-point calibration plots were made for different spectral lines of PGMs and Au in the concentration range 0–2 mg dm^{-3} with correlation coefficients of 0.9998–0.9999. Calibration solution was prepared in 0.1 M HCl and various amounts of surfactants being used, which influenced the plots.

The instrumental detection limits (*cf.* Table I) are based on the 3σ definition[18] and were evaluated from 10 measurements of the blank solutions containing 0.1 M HCl and 0.006 M cationic surfactant Septonex® or 0.003 M Sterinol®.

Sorbents

The following modified silica sorbents were used in plastic cartridges 20×9 mm with sorbent particles of 60 μm size (Tessek, Prague, Czech Republic): octadecyl silica (Separon™

TABLE I
Limits of detection (in μg cm^{-3}) on IRIS AP™ ICP spectrometer[a]

Surfactant	Metal						
	Au	Ir	Os	Pd	Pt	Rh	Ru
Septonex	0.0026	0.0073	0.0019	0.0066	0.0053	0.0062	0.0035
Sterinol	0.0034	0.0050	0.0038	0.0065	0.0043	0.0102	0.0041

[a] Average values for blank solutions containing 0.1 M HCl and 0.006 M Septonex® or 0.003 M Sterinol®.

SGX C18 and Separon™ SGX RPS), octyl silica (Separon™ SGX C8), cyanoethyl silica (Separon™ SGX CN), phenyl silica (Separon™ SGX Phenyl), aminopropyl silica (Separon™ SGX NH$_2$), silica (Separon™ SGX), a strong basic anion exchanger (Separon™ SGX AX).

Modified-silica-based sorbents LiChrolut™ RP-18, LiChrolut™ RP-18e (particle size 40–60 µm, Merck, Darmstadt), macroporous styrene–divinylbenzene polymers LiChrolut™ EN (particle size 40–120 µm), and Amberlite™ XAD2 and Amberlite™ XAD4 (particle size 0.3–0.9 mm, Merck Darmstadt, Germany) were ground and sieved to 63–100 µm particle size. The last two were filled into 2.5-cm^3 plastic columns of MoBiTec (Göttingen, Germany).

Chemicals and Solutions

A multielement standard stock solution contained 100 mg dm^{-3} of Pt(IV), Rh(III), Ir(IV), Os(IV), Ru(IV), Pd(II) and Au(III) as chloro complexes in 20% HCl (Astasol MIX, Analytica, Prague, Czech Republic). Bromo complexes of platinum metals or gold resulted when solutions of their chloro complexes containing 1 mg of PGMs and Au and 5% HCl were heated for 60 min with 10 ml of 46% HBr almost to the boil. The excess of HBr was removed by partial evaporation. After dilution with water to the final volume, the metal concentration was 8 mg dm^{-3} and the HBr concentration was 0.2 mol dm^{-3}. The transformation of PGM and Au(III) chloro complexes to bromo complexes is assumed to be complete although the presence of some anionic mixed chloro bromo complexes of Pt(IV) and P(II) is possible[19]. The transformation was followed by comparison of absorption spectra[20].

Reduction of PGM and Au(III) with hydrazine hydrate. The standard stock solution in 20% HCl was heated for 30 min with 0.80% hydrazine hydrate. After cooling, the solution was diluted with 4 M HCl to 25 cm^3. It contained 8 mg dm^{-3} of PGMs and Au. In this way, Pt(IV) was reduced to Pt(II), Au(III) to Au(I) and Au(0), and Ir(IV) to Ir(III).

Cationic surfactants. [1-(Ethoxycarbonyl)pentadecyl]trimethylammonium bromide (Septonex®; Farmakon, Olomouc, Czech Republic), benzyl(dodecyl)dimethylammonium bromide (Sterinol®; Galenus, Warsaw, Poland), trimethyl(tetradecyl)ammonium bromide (Merck, Darmstadt, Germany), hexadecyl(trimethyl)ammonium chloride and 1-hexadecyl-pyridinium chloride hydrate (Fluka, Switzerland) were used in 0.1 M stock solutions.

Humic acid 244 MAR was a low-molecular-weight sample of the Research Institute of Inorganic Chemistry (Ústí nad Labem, Czech Republic), prepared from oxyhumolite originating from Bohemian brown coal. The stock solution contained 1 g of humic acid in 500 cm^3. The sample was previously dried over phosphorus pentoxide and finally transformed into the ammonium salt in an exsiccator over concentrated ammonia during 24 h.

All the other used chemicals and solvents were of analytical grade purity from Lachema Brno, Analytika, Ltd. Prague and Aldrich and Fluka companies.

Characteristics of Tested Samples

Three soil extracts in *aqua regia* were samples of the Central Institute for Supervising and Testing in Agriculture (Brno, Czech Republic) containing certified macro- and microelements (S, As, Mo, Zn, Pb, Co, Cd, Ni, V, Be, Cu, Cr, P, Mn, Fe, Mg, Ca, Al, K, Tl).

Power-station fly-ash was a reference material from the Czechoslovak Metrological Institute (Bratislava, Slovakia) certified for main components such as Al, Ca, K, Fe, Mg, Na, Si, Ti and traces of As, Ba, Ce, Co, Cr, Cs, Cu, Eu, La, Mn, Pb, Rb, Th, V, Zn.

Water samples were from a Moravian river (National Park Podyjí) and peat moor water (Velké Dářko).

PGMs and Au(III) were always absent in samples which was confirmed by ICP-MS (ref.[21]). Thus, they were spiked into the samples for testing their recovery in particular matrices by the procedures mentioned below.

Retention and Elution Arrangement

Solutions were simultaneously pumped through repeatedly used plastic cartridges with the sorbents placed in a water-pump-operated vacuum suction device DORCUS™ (Tessek, Prague, Czech Republic). A peristaltic pump UNIPAP 315™ (Poland) was attached with a 3-mm silicone tubing to the cartridges and operated with an optimised solution flow rate of 1 cm^3 min^{-1}. The recovery of PGMs and Au did not depend on the flow rate of sorption from 0.3 to at least 1.5 cm^3 min^{-1}. Higher values were not used[12] to guarantee the highest effectivity of retention.

Sorption and Elution Procedures on Modified Silica and Amberlite™ XAD2 and XAD4 Sorbents

A cartridge with the sorbent was first washed with 10 cm^3 of 96% ethanol and then conditioned with 10 cm^3 of surfactant solution with selected concentration. Optimisation studies were carried out with 50 cm^3 of a sample solution containing 20 μg of PGMs and Au(III) as chloro or bromo complexes, 0.1 M HCl and a surfactant at a selected concentration. 0.1 M HCl is an optimum since higher concentrations decrease the sorption efficiency by partial damage of the hydrophobic sorbent surface. Lower contents of the acid cause losses of PGMs and Au(III) on the surface of dishes. The metal species were eluted from the sorbents with 10 cm^3 of CH_3CN. An amount of 1 cm^3 of 0.1 M HCl was added to the eluate and the solution evaporated in a suitable Teflon™ dish to 1 cm^3, the residue was diluted to 10 cm^3 in a volumetric flask and analysed by ICP-AES. For sorbents Amberlite™ XAD2 and XAD4, new cartridges must be always used.

The cartridges with Separon™ SGX AX in the DORCUS™ arrangement were washed with 10 cm^3 of distilled water and the retention was studied from 50 cm^3 of a sample containing 20 μg PGMs and Au(III), 0.1 M HCl or 0.1 M HBr. Sodium perchlorate and mineral acids of various concentrations were used for elution.

The recovery was always calculated from the known amount of PGMs and Au(III) in the used dilute standard solution and the evaluated value in the eluate. The confidence interval of mean recovery resulted from 3 or 6 independent retentions and elutions. The span between the lowest and highest values of the variation interval of parallel experiments was used for the statistical evaluation of recovery[22].

RESULTS AND DISCUSSION

Effect of Solvents

A number of solvents were tested as eluents (*cf.* Table II) with a similar effect for Au(III), Pd(II), Pt(IV), Os(VI), Ir(IV) but acetonitrile is recommended

because of 100% recovery for Au(III), Pt(IV) and Pd(II) and 80–90% recovery for Ir(IV) and Os(VI).

Effect of Surfactant

The effect of Septonex®, Sterinol®, trimethyl(tetradecyl)ammonium bromide, hexadecyl(trimethyl)ammonium chloride and 1-hexadecylpyridinium chloride was studied in the 0–0.01 M concentration interval after sorption and desorption of PGMs and Au(III) on Separon™ SGX C18. Similar plots were obtained for the other kinds of modified silica used. The kind of surfactant and its concentration in solution significantly influences the sorption of PGMs and Au(III). For 0.006 M Septonex® and 0.003 M Sterinol®, the recovery is nearly 100% from 0.1 M HCl for Au(III), Pd(II) and Pt(IV), 85–90% for Os(VI) and Ir(IV); however, the sorption of Rh(III) and Ru(IV) are far from being quantitative. The 0.006 M trimethyl(tetradecyl)ammonium chloride and hexadecyl(trimethyl)ammonium chloride are suitable for the recovery of Au(III) and Pd(II) but not suitable for Pt(IV). 1-Hexadecylpyridinium chloride should not be used for the sorption under above conditions since the ion associates of the chloro complexes of PGMs and Au(III) are strongly bonded to the sorbent. The elution efficiency is low for all PGMs when 10 cm^3 of acetonitrile, ethanol, methanol, propan-2-ol, acetone or even 0.5 M thiourea in acid solution were used as eluents.

TABLE II
Average recovery (in %) of PGMs and Au(III) after elution with various solvents from Separon™ SGX C18[a]

Eluent	Metal						
	Au	Ir	Os	Pd	Pt	Rh	Ru
Ethanol	100	88	90	100	101	6	25
Methanol	100	95	86	96	100	12	60
Propan-2-ol	100	87	68	101	97	12	60
Acetone	96	95	76	101	97	11	60
Acetonitrile	101	89	91	101	99	13	68

[a] PGMs and Au(III) (20 μg) were retained as chloro complexes from 50 cm^3 solution in the presence of 0.006 M Septonex® and 0.1 M HCl. Average recoveries were calculated from 3 independent experiments.

The formation of micelles in solutions with surfactant concentrations ≥ 0.008 mol dm^{-3} for all the used surfactants competes with the sorption of chloro complexes of PGMs and Au(III) (*cf.* Fig. 1). More than 0.01 M surfactant in solution also interferes by clogging the columns.
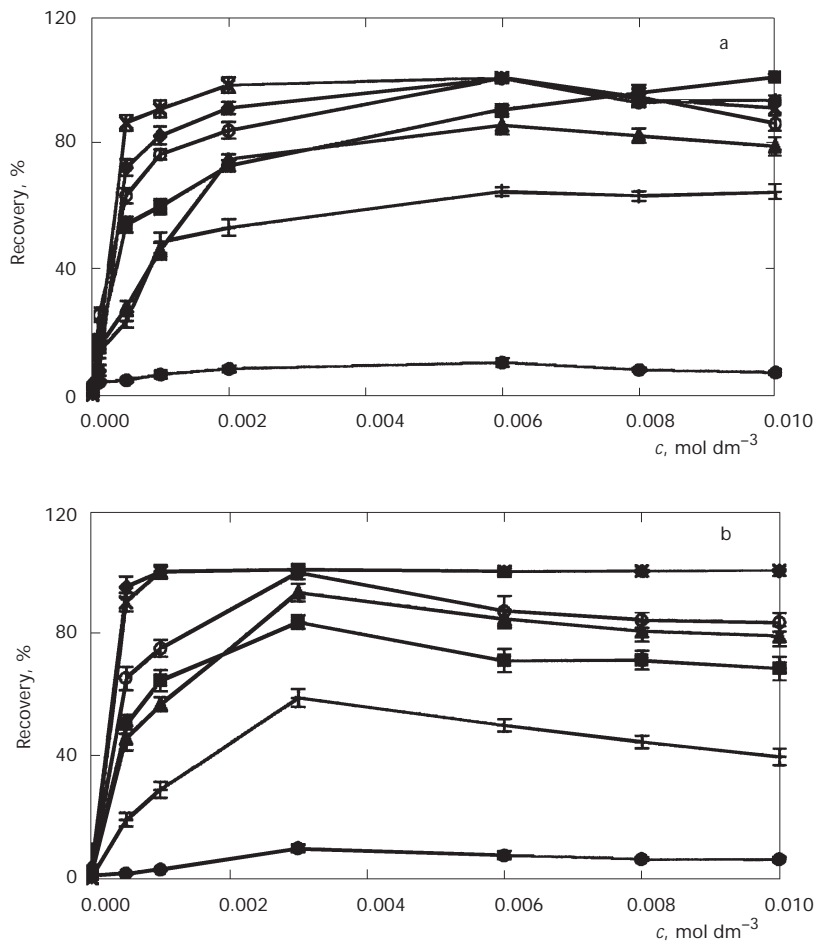

FIG. 1
Effect of concentration of Septonex® (a) and Sterinol® (b) on the recovery of PGMs and Au(III) on Separon™ SGX C18. An amount of 50 cm^3 from a sample solution containing 20 μg of PGMs and Au(III), 0.1 M HCl and surfactant of a selected concentration was applied onto Separon™ SGX C18; elution was carried out with 10 cm^3 of acetonitrile. The segments correspond with the confidence interval from 3 experimental values. ◆ Au, ■ Ir, ▲ Os, × Pd, ○ Pt, ● Rh, + Ru

Effect of Various Modified Silica Gel Sorbents

100% recovery resulted for Au(III), Pd(II) and Pt(IV) on conditioned Separon™ SGX C18, Separon™ SGX RPS, Separon™ SGX C8, Separon™ SGX Phenyl and Separon™ SGX CN sorbents (*cf.* Fig. 2) when 50 cm³ of sample solutions containing 20 μg of PGMs and Au(III), 0.1 M HCl and the optimum 0.006 M Septonex®, trimethyl(tetradecyl)ammonium bromide, hexadecyl(trimethyl)ammonium chloride or 0.003 M Sterinol® were used for the retention and 10 cm³ of acetonitrile for elution. A low recovery was observed for Rh(III) and Ru(IV) for all the tested sorbents and surfactants. The phenyl silica Separon™ SGX Phenyl (*cf.* Table III) and Separon™ SGX C18 are most suitable for the sorption of Ir(IV) and Os(VI) in the presence of Sterinol® or Septonex®. Sorbents Separon™ SGX and SGX NH₂ are unsuitable since no retention of metal complexes resulted even when the column was conditioned by the surfactant. The behaviour of silica, Separon™ SGX, proves the necessity of hydrophobic surface of the sorbent but the processes on modified hydrophobic silica may be complex. The dynamic retention of the surfactant is assumed to proceed on the sorbent surface, as
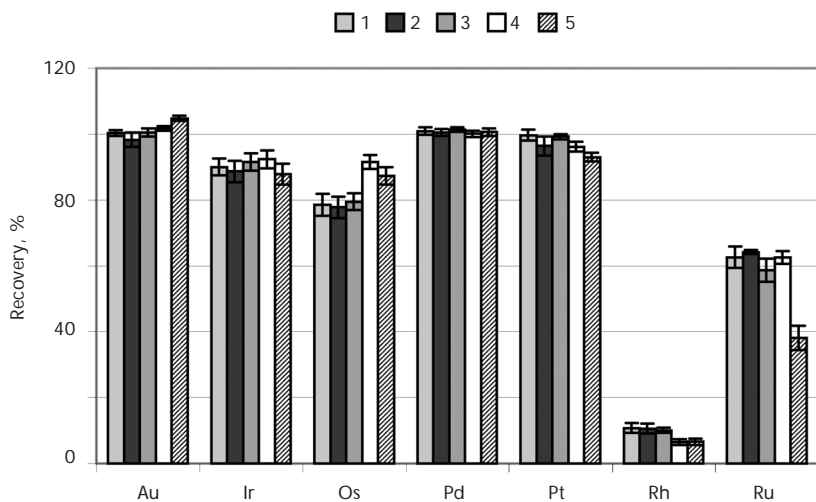

Fig. 2

Recovery of PGMs and Au(III) after sorption on various sorbents. An amount of 50 cm³ from a sample solution containing 20 μg of chloro complexes of PGMs and Au(III), 0.006 M Septonex® and 0.1 M HCl was applied onto Separon™ SGX C18 (1), Separon™ SGX C8 (2), Separon™ SGX RPS (3), Separon™ SGX Phenyl (4) and Separon™ SGX CN (5). The segments correspond with the confidence interval from 3 experimental values

far as the sorbent surface has been previously saturated with the surfactant. The anionic PGMs and Au halo complexes are then retained on the sorbent surface. Such process, however, may be accompanied by the direct bonding of the ion associate on the column because the ion association between large anionic halo complexes and cationic agents is commonly assumed to occur in solution during extraction processes.

No retention of PGMs and Au(III) was observed in the absence of cationic surfactant in solution and without previous conditioning of the sorbents with the surfactant. In addition, no retention took place when non-ionic surfactant such as Triton X-100™ was used in concentrations of 0.01–0.006 mol dm^{-3}.

The low retention efficiency and recovery of Rh(III) and Ru(IV) is caused by a complex equilibrium in 0.1 M HCl containing partial aquation and hydrolysis of chloro complexes to monomeric and oligomeric species[19,23–25] without or with different charges whose tendency to form ion associates with cationic surfactants decreased. The incomplete retention of Ir(IV), Os(VI), Rh(III) and Ru(IV) was also proved by analysis of effluents from the column after sorption which contained the rest of the PGMs (*cf.* Table IV).

Separon™ SGX NH$_2$ gives a very low sorption efficiency for PGMs and Au(III) under all tested conditions even in the presence of surfactant on the

TABLE III
Average recovery (in %) of PGMs and Au(III) from Separon™ SGX Phenyl and Separon™ SGX RPS in the presence of various cationic surfactants[a]

Surfactant	Metal						
	Au	Ir	Os	Pd	Pt	Rh	Ru
6 mM Septonex[b]	98.9 ± 1.0	92.8 ± 1.2	82.3 ± 1.3	100.9 ± 0.8	98.4 ± 1.4	12.2 ± 1.1	58.8 ± 0.9
6 mM Septonex	100.7 ± 0.7	92.3 ± 1.4	91.5 ± 2.1	100.1 ± 0.9	96.2 ± 1.5	6.6 ± 0.9	62.5 ± 1.9
3 mM Sterinol[b]	98.5 ± 1.7	78.2 ± 1.8	79.6 ± 1.9	99.8 ± 0.9	97.9 ± 3.7	15.9 ± 1.3	56.8 ± 1.6
3 mM Sterinol	100.3 ± 0.4	98.3 ± 2.5	83.3 ± 1.4	100.3 ± 0.6	100.8 ± 0.6	17.0 ± 0.9	49.5 ± 1.8
6 mM TTAB	98.8 ± 2.4	53.0 ± 3.0	39.8 ± 2.1	100.3 ± 0.8	56.7 ± 3.1	17.3 ± 1.1	39.0 ± 2.6
6 mM CTAC	100.5 ± 1.9	49.4 ± 3.6	53.2 ± 3.8	100.3 ± 0.7	67.3 ± 1.3	4.2 ± 0.5	26.2 ± 2.3

[a] PGMs and Au(III) (20 μg) were retained as chloro complexes from 50 cm^3 solution in the presence of surfactant and 0.1 M HCl. Confidence intervals were calculated at the level of significance α = 0.05 from 3 independent repetitions. [b] Separon™ SGX RPS, confidence intervals were calculated from 6 independent repetitions.

sorbent and in the solution. This is surprising since this sorbent should behave as weak anion exchanger.

After heating the sample with 0.8% hydrazine hydrate solution in 20% HCl, Pt(IV) is reduced to Pt(II) which is also retained. The recovery of 20 μg of PGMs with Separon™ SGX C18 from 50 cm^3 of a solution containing 0.1 M HCl and 0.006 M Septonex® remains nearly 100% for Pd(II), Pt(II) and Ir(III), that of Os(III) and Ru(III) increases in comparison with Os(VI) and Ru(IV) in solution without reductant but is not quantitative. The extremely low sorption efficiency of gold is due to Au(I) and Au(0) formed in reduction.

The sorption efficiency of analogous LiChrolut™ RP-18 and LiChrolut™ RP-18e is comparable with previous sorbents under analogous optimum conditions. Polymer LiChrolut™ EN, however, is not suitable for the retention because of its very low sorption efficiency for the metals (Fig. 3).

Effect of Sample Volume and PGMs and Au(III) Contents

The sorption efficiency for 10–200 ng cm^{-3} of Au(III), Pd(II) and Pt(IV) on silica Separon™ SGX RPS little depends on the sample volume between 50 and 1 000 cm^3 as well as on the common limit of determination by inductively coupled plasma atomic emission spectrometry, which corresponds to the enrichment factor up to 100. The solutions contain the standard stock solution of PGMs and Au(III), 3 cm^3 of 0.1 M Sterinol® or 6 cm^3 of 0.1 M Septonex® and 0.1 M HCl; acetonitrile was the eluent. For Ir(IV), Os(VI), Rh(III), Ru(IV), the sorption efficiency rapidly decreased with increasing sample volume (Table V).

TABLE IV
Retention of PGMs and Au(III) on Separon™ SGX C18[a]

Retention	Metal						
	Au	Ir	Os	Pd	Pt	Rh	Ru
Retained, %	100	93	83	101	100	10	61
Passed, %	0	7	17	0	0	90	39

[a] PGMs and Au(III) (20 μg) were retained as chloro complexes from 50 cm^3 solution in the presence of 0.006 M Septonex® and 0.1 M HCl. Average recoveries were calculated from 3 independent experiments.

Similarly, no effect of metal concentration on the sorption efficiency was observed for 10–200 ng cm^{-3} of Au(III), Pd(II) and Pt(IV) when sorbed from 100 cm^3 of a solution containing 0.006 M Septonex® or 0.003 M Sterinol® and 0.1 M HCl, but a considerable sorption efficiency decrease was again observed with Ru(IV), Os(VI), Ir(IV), Rh(III) from solutions containing less than 50 ng cm^{-3}. No washing-out effect was observed for the retained ion associate for ≥10 ng cm^{-3} Pt(IV), Pd(II) and Au(III) in 50–1 000 cm^3 sample volumes in the presence of Septonex® or Sterinol® surfactants (*cf.* Table V). Similarly, the recovery higher than 90% was earlier reported for Au(III) under similar conditions[17].

Effect of Foreign Ions

No interference of 0.02–1 mol dm^{-3} of chloride, nitrate, sulfate or 200 mg dm^{-3} of Fe(III), Ca^{2+}, Mg^{2+}, Na$^+$, K$^+$ and 1 000 mg dm^{-3} of Al(III) was observed, when 10–20 µg of PGMs and Au(III) were retained on Separon™ SGX RPS
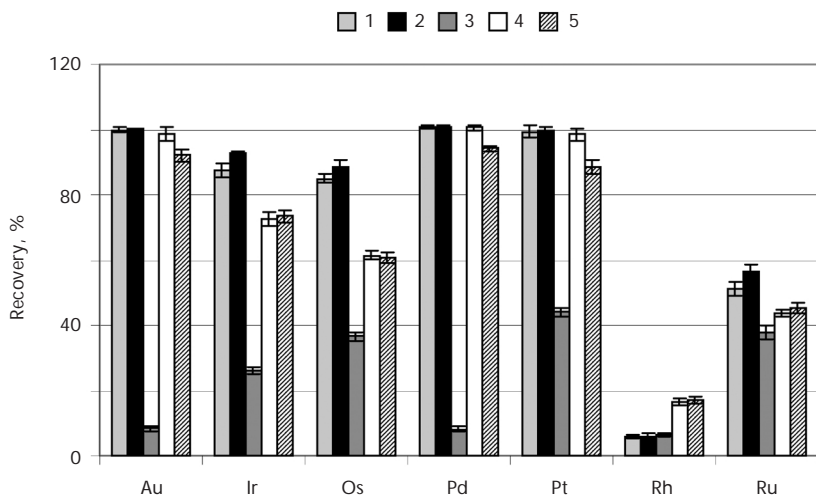

Fɪɢ. 3

Comparison of the recovery of PGMs and Au(III) after sorption on various sorbents in the presence of cationic surfactant Septonex®. An amount of 20 µg of PGMs and Au(III) was sorbed from 50 cm^3 solution containing 0.1 M HCl and 0.006 M Septonex® on LiChrolut™ RP-18 (1), LiChrolut™ RP-18e (2), LiChrolut™ EN (3), Amberlite™ XAD4 (4) and Amberlite™ XAD2 (5). An amount of 10 cm^3 acetonitrile was used for elution. The segments correspond with the confidence interval from 3 experimental values

from 50 cm^3 of a sample solution containing 0.1 M HCl and 0.006 M Septonex®.

Preconcentration of PGM and Au from Their Bromo Complexes

Similar results to the recovery of chloro complexes of PGMs and Au(III) were obtained for bromo complexes under analogous conditions. 0.006 M Septonex® and 0.1 M HBr were optimum concentrations for the sorption of 20 µg of bromo complexes of PGMs and Au on Separon™ SGX C18 from 50 cm^3 of a sample solution (Table VI). There is no preference of bromo complexes to chloro complexes of PGMs and Au for the retention.

In fact, bromo complexes of some PGMs were successively used for the separation and determination of µg cm^{-3} concentrations of Pt(II), Pt(IV), Pd(II) and Au(III) by reverse phase HPLC on octadecyl silica in the form of bromo complex associates with selected cationic surfactants[20,26]. The sorption of Pt(IV) in the form of some kind of bromo complex on octadecyl silica Separon™ SGX RPS at pH 3 is effective even for the concentration of

TABLE V
Average recovery (in %) of PGMs and Au(III) after sorption on Separon™ SGX RPS from various sample volumes[a]

Volume cm^3	Surfactant	ng cm^{-3} PGMs	Au	Ir	Os	Pd	Pt	Rh	Ru
50	A	200	100	99	75	100	99	11	23
	B	200	99	84	95	98	96	10	54
100	A	100	101	92	68	100	98	8	23
	B	100	102	79	88	100	98	5	54
250	A	40	101	89	63	100	96	2	19
	B	40	102	68	64	101	89	2	49
500	A	20	99	84	58	100	96	1	9
	B	20	102	58	52	101	89	1	45
1 000	A	10	98	73	44	99	96	0	6
	B	10	101	49	49	101	91	1	44

[a] The solution contained 0.1 M HCl and 6 cm^3 of 0.1 M Septonex® (A) or 3 cm^3 of 0.1 M Sterinol® (B). Average recoveries were calculated from 3 independent experiments.

2 ng cm^{-3} from 10–200 cm^3 sample volume[12] but such low amount is not determinable by ICP-AES.

Sorption on Amberlite™ XAD2 and XAD4

Macroporous sorbents Amberlite™ XAD2 and XAD4 strongly bind PGMs and Au(III) from their chloro complexes in solutions containing 0.1 M HCl and 0.006 M Septonex® and their desorption is difficult with ethanol, 0.5 M thiourea in 0.2 M HNO$_3$ or 0.2–5 M HNO$_3$. Acetonitrile remains the most effective eluent for Au(III), Pd(II) and Pt(IV) which leads to nearly 100% recoveries. There is, however, no preference of these sorbents to modified silica for the previous separation of PGMs and Au(III) (Fig. 3). On the contrary, no retention of PGMs and Au was observed when no cationic surfactant was used with this kind of sorbents.

Retention of PGMs and Au(III) Chloro and Bromo Complexes on Silica-Based Anion Exchanger in the Absence of Surfactant

For elution of PGMs and Au(III) from silica-based anion exchanger Separon™ SGX AX, sodium perchlorate and mineral acids were used. Recoveries for various eluents are summarised in Table VII. An amount of 2–4 cm^3 of 0.5–1 M NaClO$_4$ leads to a quantitative elution of Pd(II). 5 M HNO$_3$ is the optimum agent for the elution of chloro complexes of Ir(IV), Pd(II) and Pt(IV). Decreased recoveries for Au(III), Os(VI) and Ru(IV) correspond with the strong retention on the sorbent. No difference is observed in the behaviour of PGMs and Au(III) bromo complexes under similar conditions.

TABLE VI
The sorption efficiency of bromo complexes of PGMs and Au(III) on Separon™ SGX C18[a]

Metal	Au	Ir	Os	Pd	Pt	Rh	Ru
Recovery, %	101.6 ± 1.2	92.5 ± 2.1	75.7 ± 2.0	100.6 ± 2.4	98.4 ± 1.8	27.7 ± 3.1	76.9 ± 2.5

[a] PGMs and Au(III) (20 μg) were retained on Separon™ SGX C18 from 50 cm^3 solution in the presence of 0.006 M Septonex® and 0.1 M HBr. Confidence intervals were calculated at the level of significance α = 0.05 from 6 independent repetitions.

Effect of Humic Acid

The sorption efficiency for Pt(IV), Pd(II) and Au(III) on modified silica sorbents was tested in the presence of various amounts of standard humic acid 244 MAR; the results are collected in Table VIII. The anion exchanger Separon™ SGX AX is more effective for the preconcentration of Pt(IV) and Pd(II) from humic acid-containing waters. Increased amounts of humic acids negatively influence their retention from natural waters when octadecyl silica has been used as sorbent. Moreover, the acids are partly cosorbed under above conditions and finally eluted with the used eluents.

Determination of Pt(IV), Pd(II) and Au(III) in Spiked Soil Extracts, Power Station Dust and Natural Waters Using Octadecyl Silica and Septonex® prior to ICP-AES

Spikes of PGMs and Au(III) solutions were added to 75 cm^3 of soil extracts in *aqua regia* to reach the final concentration of 0.1 mg dm^{-3} and the solutions were equilibrated for 24 h. The spiked extracts (75 cm^3) with 0.1 M Septonex® were diluted to 200 cm^3. Three aliquots of 50 cm^3 of this solution containing 0.006 M Septonex® were applied onto a cartridge with Separon™ SGX RPS and the metals were eluted with 10 cm^3 of acetonitrile and analysed by ICP-AES after solvent evaporation in the presence of 0.1 M

TABLE VII
Average recovery (in %) of PGMs and Au(III) from Separon™ SGX AX after elution with various eluents[a]

Eluent	Metal						
	Au	Ir	Os	Pd	Pt	Rh	Ru
0.5 M NaClO$_4$	21.1 ± 2.2	86.3 ± 1.8	51.3 ± 1.8	100.2 ± 1.8	86.4 ± 2.1	31.1 ± 1.7	40.2 ± 2.2
1 M NaClO$_4$	18.9 ± 1.7	87.1 ± 1.5	55.0 ± 3.1	100.0 ± 1.5	83.1 ± 2.4	31.9 ± 1.5	37.7 ± 2.1
1 M HCl	42.2 ± 2.6	100.3 ± 1.2	51.2 ± 3.3	100.1 ± 0.6	99.7 ± 1.2	25.5 ± 1.8	61.8 ± 2.2
5 M HCl	40.5 ± 2.2	100.9 ± 0.9	52.3 ± 1.6	101.2 ± 1.0	100.9 ± 0.9	26.2 ± 2.3	64.0 ± 2.2
5 M HNO$_3$[b]	70.5 ± 1.1	100.2 ± 1.2	73.5 ± 1.1	100.5 ± 0.7	100.3 ± 1.2	41.3 ± 1.1	58.4 ± 0.8
5 M HNO$_3$[b,c]	70.9 ± 1.9	98.5 ± 2.3	72.2 ± 1.8	100.1 ± 1.0	100.4 ± 1.7	40.2 ± 2.8	65.2 ± 1.4

[a] Sample solution (50 cm^3) contained 20 μg of PGMs and Au(III) as chloro or bromo complexes and 0.1 M HCl (HBr). Confidence intervals were calculated at the level of significance $\alpha = 0.05$ from 3 independent repetitions. [b] Confidence intervals were calculated from 6 independent repetitions. [c] Bromo complexes.

HCl (Table IX). It was observed that the twice or three times diluted *aqua regia* does not negatively influence the sorption efficiency of the sorbent for PGMs and Au but the lifetime of column filling is decreased.

For power station dust, four aliquots of a 0.2500-g sample were spiked with dilute standard solutions to contain 5 µg of PGMs and Au(III). The mixture was homogenised, dried, ignited and leached with 12 cm^3 of *aqua regia* by boiling under reflux for 1 h. After evaporating excess of acids and cooling, the mixture was filtered with a cellulose filter into a 50-cm^3 volumetric flask, the Septonex® solution was added to the final concentration of 0.006 mol dm^{-3}, filled with distilled water up to the mark and transferred onto a modified silica Separon™ SGX RPS column. The eluate in acetonitrile was analysed by ICP spectrometry after removing the solvent. The recoveries of PGMs and Au agree with those of pure dilute standard solutions. The results are collected in Table IX.

Two procedures were used for river- and humic acid-containing waters, (i) 50 cm^3 aliquots of river- or peat moor-water containing humic acid were spiked with 10 µg of PGMs and Au(III), 0.003 M Sterinol® and 0.1 M HCl and the solutions obtained were treated with Separon™ SGX RPS, eluted

TABLE VIII
Sorption efficiency (in %) on Separon™ SGX RPS and Separon™ SGX AX in the presence of humic acid 244 MAR

Sorbent	Humic acid mg dm^{-3}	Metal		
		Au	Pd	Pt
Separon™ SGX RPS[a]	10	101.0 ± 0.5	100.6 ± 0.4	98.9 ± 1.9
	50	100.2 ± 0.4	98.5 ± 1.7	97.1 ± 1.7
	100	92.3 ± 1.9	91.2 ± 2.6	88.8 ± 1.7
Separon™ SGX AX[b]	10	70.1 ± 1.5	100.3 ± 0.8	100.2 ± 2.3
	50	65.1 ± 1.3	100.1 ± 1.9	100.0 ± 1.0
	100	67.2 ± 1.3	99.9 ± 1.1	98.9 ± 1.7

[a] Pt(IV), Pd(II) and Au(III) (20 µg) were retained from 50 cm^3 solution in the presence of 0.003 M Sterinol®, 0.1 M HCl and humic acid. An amount of 10 cm^3 of ethanol was used for elution. [b] Pt(IV), Pd(II) and Au(III) (20 µg) were retained from 50 cm^3 solution in the presence of 0.1 M HCl and humic acid. An amount of 10 cm^3 of 5 M HNO$_3$ was used for elution. Confidence intervals were calculated at the level of significance α = 0.05 from 3 independent repetitions.

with 10 cm^3 of ethanol and analysed on an ICP spectrometer after removal of solvent by evaporation with 0.1 M HCl, or (ii) the Separon™ SGX AX anion exchanger was used for 50-cm^3 samples of river- or peat moor-water with 10 µg PGMs and Au(III) spikes in 0.1 M HCl. The elution followed with 10 cm^3 of 5 M HNO$_3$ and the eluate was analysed by ICP-AES after removing excess of acid by evaporation. The results are given in Table IX.

TABLE IX
Recoveries (in %) of Au(III), Pd(II) and Pt(IV) from spiked soil extracts, power station dust and river-water after retention on Separon™ SGX RPS or Separon™ SGX AX

Sample	Sorbent[a]	Metal		
		Au	Pd	Pt
Soil extract	A	101.0 ± 1.3	95.8 ± 1.5	101.7 ± 1.2
Power station dust	A	98.8 ± 1.9	100.2 ± 0.5	99.1 ± 0.9
River water	A	98.1 ± 1.3	97.9 ± 0.6	100.7 ± 1.1
River water	B	70.3 ± 1.6	100.2 ± 1.5	100.0 ± 1.0
Humic water	A	93.0 ± 0.6	90.4 ± 1.3	88.2 ± 2.2
Humic water	B	68.5 ± 1.0	100.7 ± 0.9	98.8 ± 0.7

[a] Separon™ SGX RPS (A), Separon™ SGX AX (B). Confidence intervals were calculated at the level of significance $\alpha = 0.05$ from 3 independent repetitions.

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