On-line sorption preconcentration and FIA-FAAS determination of palladium and platinum in solution

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A flow injection flame atomic absorption method for palladium and platinum determination in solution, including sorption preconcentration, has been developed. Preconcentration of platinum metals as ionic associates with n-octyldiethylenetriamine was carried out on 'reversed phase' styrene–divinylbenzene copolymer SSPS. RSD 0.03–0.08, detection limits 5 and 3 μg l^{-1} (Pd and Pt) for 1 min of preconcentration and sampling frequency up to 40 h^{-1} were achieved.

To determine low concentrations of platinum group metals (PGM) in minerals, preconcentration of ores and alloys is often needed. Sorption preconcentration is widely used for this purpose due to the large preconcentration factors obtained and the simplicity of the procedure.[1–5] Dynamic sorption is the most promising method. It does not require phase separation, provides a possibility for automation of the preconcentration process and also for the development of a powerful integrated preconcentration–determination system. However, the variety and remarkable kinetic inertness of PGM complexes in solution complicate their dynamic preconcentration. The distribution coefficients of many metals are rather low and the recovery of PGM is not quantitative. Desorption of PM is slow and difficult; eluents often destroy the sorbent.[1,4,5]

Sorbent extraction combines the benefits of solvent extraction and solid phase preconcentration while eliminating some drawbacks of the two methods. Sorbent extraction applies a solid support of hydrophobic functionality to recover metal hydrophobic complexes, while elution is achieved by reversing the solvent polarity. This allows the use of a wide range of reagents forming even stronger complexes with metals than immobilized functional groups. Elution may be carried out under mild conditions without concentrated acids or other aggressive reagents.[6]

Preconcentration of PGM hydrophobic complexes and ionic associates on reversed-phase sorbents offers new possibilities.[7,8] Desorption of PGM can easily be carried out with polar eluents, providing an opportunity for on-line combination of preconcentration and determination steps. However, the on-line systems including sorption preconcentration previously proposed for the determination of PGM feature low selectivity.[7,9,10] Extraction of PGM anionic chloride complexes was shown to be an effective method for their recovery from complex solutions.[11] Amines and quaternary ammonium reagents are the most promising for extraction of PGM.[11,12] Extraction efficiency was observed to increase from monoamines to triamines. The possible effectiveness of dynamic sorption preconcentration of PGM was also demonstrated on a polystyrene-based sorbent containing immobilized diethylenetriamine groups (DETA-sorbent). Sorption

Table 1 Distribution coefficients of $PdCl_4^{2-}$ ionic associates with amino reagents on 'reversed-phase' sorbents. C_{Pd} = 2 μg ml^{-1}, C_{HCl} = 1 M, C_{reag} = = 5×10^{-3} M, m_{sorb} = 20 mg, V = 50 ml, t_{cont} = 1 h; n = 3, RSD ≤ 3%.

Reagent	Sorbent			
	SSPS	Amberlite XAD-2	Amberlite XAD-8	Silica C_{16}
$C_8H_{17}NH_2$	365	75	247	84
$C_{10}H_{21}NH_2$	960	156	90	145
$NH_2(CH_2)_6NH_2$	150	88	30	62
$CH_3C(CH_2NH_2)_3$	200	20	42	53
$C_8H_{17}N(CH_2CH_2NH_2)_2$	8000	160	350	250
$C_{10}H_{21}N(CH_2CH_2NH_2)_2$	3900	790	246	175
$C_{12}H_{25}N(CH_2CH_2NH_2)_2$[a]	4000	600	90	340

[a] C_{reag} = 5×10^{-4} M.

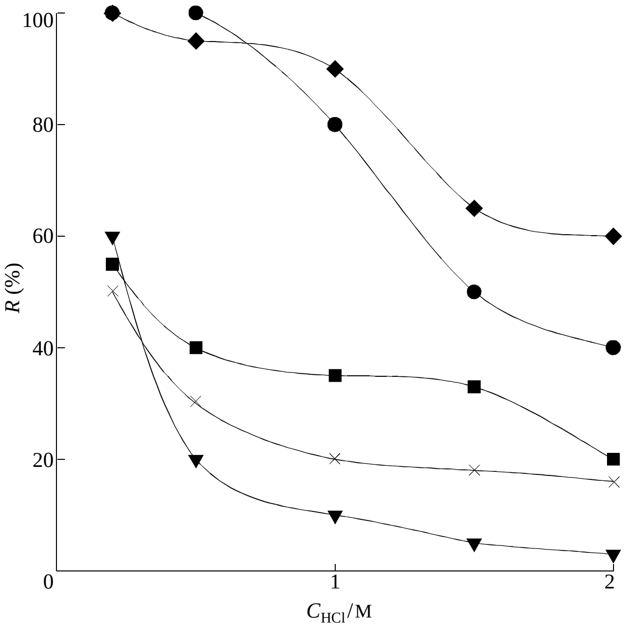

Figure 1 Effect of HCl concentration on the recovery of Pd^{II} on SSPS (circles), silica-C16 (triangles), XAD-2 (squares), XAD-8 (crosses) and Pt^{IV} on SSPS (diamonds). C_{Pd} = 2 μg ml^{-1}, C_{Pt} = 5 μg ml^{-1}, C_{reag} = 5×10^{-3} M, v = 1 ml min^{-1}, V = 10 ml.

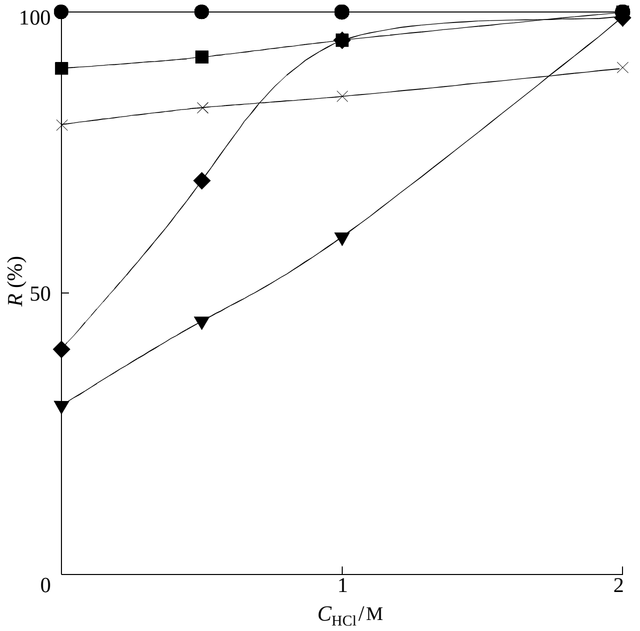

Figure 2 Effect of HCl concentration in eluent on palladium(II) and platinum(IV) desorption. Eluent: methanol (circles for Pd, diamonds for Pt), ethanol (squares for Pd, triangles for Pt), propan-2-ol (crosses for Pd). v = 1 ml min^{-1}, V = 5 ml.

Table 2 Influence of main matrix elements on FIA-FAAS determination of Pd and Pt. $C_{Pd} = 200\ \mu g\ l^{-1}$, $C_{Pt} = 50\ \mu g\ l^{-1}$, $C_{HCl} = 0.5$ M, $C_{reag} = 5\times10^{-3}$ M ($P = 0.95$, $n = 4$).

Matrix element	Matrix element concentration/g l^{-1}	Found Pd/µg l^{-1}	Found Pt/µg l^{-1}
Na	1.0	200±1	51±2
	2.5	200±2	50±3
	5.0	200±2	52±4
	10.0	196±4	41±6
	20.0	148±6	—
	30.0	120±6	—
	40.0	76±8	—
Ca	0.5	200±2	53±2
	1.0	194±2	49±2
	2.0	198±2	55±3
	4.0	199±3	57±5
	10.0	196±4	54±5
	20.0	181±4	53±5
Fe^{III}	1.0	202±2	57±3
	2.0	201±2	53±3
	5.0	200±2	51±3
	10.0	196±3	57±3
	20.0	174±4	45±7
	30.0	—	32±8
Ni^{a}	1.0	51±1	49±2
	2.0	52±2	47±2
	6.0	49±3	42±2
	8.0	50±3	36±5
Cu	1.0	198±1	50±2
	2.0	204±2	53±2
	5.0	180±6	49±1
	10.0	160±8	48±6
	20.0	143±8	40±7
$Cr^{III\ a}$	1.0	52±3	49±2
	5.0	57±9	46±3
	10.0	48±4	44±2
	20.0	23±5	—
	30.0	15±6	—
$Cr^{IV\ b}$	0.1	107±3	50±7
	0.3	101±3	36±5
	0.5	102±4	25±1
	1.0	30±5	—
	1.5	20±5	—
SO_4^{2-}/M^{b}	0.03	—	47±2
	0.05	97±3	63±6
	0.1	101±2	60±4
	0.2	103±6	63±6
	0.4	94±7	—
	0.6	—	65±4

$^{a}C_{pd} = 50\ \mu g\ l^{-1}$. $^{b}C_{pd} = 100\ \mu g\ l^{-1}$.

of PGM from hydrochloric acid solutions on the sorbent is caused by the formation of ionic associates of chloride PGM complexes and the protonated nitrogen of functional groups.[13]

The purpose of this study was to investigate the dynamic preconcentration of palladium and platinum as ionic associates with reagents containing amines (mono-, di-, tri-) and a hydrophobic part on non-polar sorbents and to develop a flow injection–flame atomic absorption (FIA-FAAS) method for the determination of metals in solutions of complicated composition.

Distribution coefficients of ionic associates of $PdCl_4^{2-}$ with various reagents containing amino groups on some reversed-phase sorbents were determined (Table 1). Sorbents Amberlite XAD-2 and XAD-8 (Serva, USA); C_{16}-bonded silica (BioKhimMak, Russia) and SSPS (styrene–divinylbenzene copolymer) (Diapak, Russia) were investigated. The reagents containing a diethylenetriamine part were shown to be essentially more effective than monoamines for recovery of Pd. We suppose that in this case formation of the most hydrophobic species (ionic associates) in solution is caused by binding of a polycharged metal complex with a polycharged protonated molecule of the reagent. The largest distribution coefficient for Pd was achieved with n-octyldiethylenetriamine (Table 1). This reagent was chosen for further investigations.

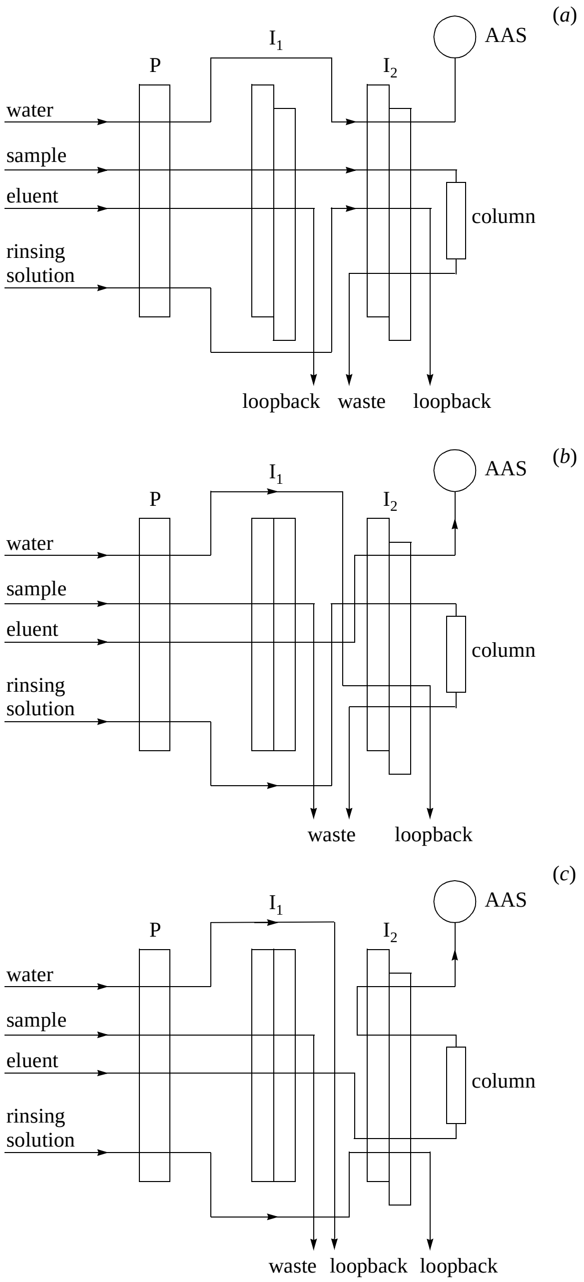

Figure 3 Manifold system for FIA-FAAS determination of Pd and Pt. (*a*) preconcentration, (*b*) rinsing, (*c*) elution; P is a peristaltic pump, I_1 and I_2 are injection valves. Sample is the analysed solution containing of reagent (0.5 M HCl), eluent: 1–2 M HCl in ethanol, rinsing solution: 5×10^{-3} M reagent solution in 0.5 M HCl.

The dependence of Pd and Pt recovery on various sorbents on HCl concentration in solution was studied. The solution was pumped through a sorbent microcolumn (15 mm×2.5 mm i.d.) with a peristaltic pump at a flow rate 1–2 ml min^{-1}. The reagent concentration was 5×10^{-3} M. The recovery of metals was determined by measuring their residual concentrations by FAAS in solution after sorption. Determination of metals was carried out with a Quant-AFA atomic absorption spectrometer (Cortech, Moscow, Russia). Propane–butane–air and acetylene–air flames were applied for the determination of Pd (247.66 nm) and Pt (265.95 nm), respectively. Continuum spectrum D_2–background correction was used. The recovery of Pd and Pt from 0.2–0.5 M HCl is quantitative on SSPS sorbent (Figure 1). The decrease in metal recovery at higher HCl concentrations could be explained by interference from a competitive chloride ion. Quantitative desorption of Pd is achieved with methanol or 1–2 M HCl ethanol solution and for Pt with 1–2 M HCl methanol or ethanol solution (Figure 2).

Table 3 Results of FIA-FAAS determination of Pd and Pt in standard reference materials of alloys and ores (P = 95%, n = 4).

Sample	Pd[a]			Pt[b]		
	Certified/μg g^{-1}	Found/μg g^{-1}	RSD (%)	Certified/μg g^{-1}	Found/μg g^{-1}	RSD (%)
Copper alloy	2900±100	2800±100	3	1000±100	900±100	7
Copper alloy	1000±100	1000±100	6	300±20	310±40	8
VP-2	6.6±0.5	6.3±0.4	4	2.6±0.3	2.5±0.3	8
G-3	5.6±0.3	5.8±0.4	4	1.2±0.1	1.1±0.1	6

[a] Propane–butane–air flame. [b] Acetylene–air flame.

The flow injection–FAAS determination of palladium and platinum was carried out using a commercial automated complex consisting of a Quant-AFA atomic absorption spectrometer, a flow injection device, an IBM compatible computer and the original software. An original manifold system for FIA-FAAS determination of metals including the on-line sorption preconcentration was proposed (Figure 3). The determination cycle consists of preconcentration, rinsing and desorption steps. The solution analysed containing reagent (0.5 M HCl, reagent concentration 5×10^{-3} M), rinsing solution (5×10^{-3} M reagent solution in 0.5 M HCl) and eluent (1–2 M HCl solution in ethanol) were sequentially pumped through a microcolumn. The tubes connecting the FIA device and nebulizer of the spectrometer were filled with eluent simultaneously with the column rinsing. After desorption, metal concentrate in ethanol (methanol) was introduced directly into the detector. The width of the concentrate zone was about 300 μl. Peak area was accepted as a value of the analytical signal. The dependence of the analytical signal on Pd and Pt concentration is linear in the metal concentration range 0–200 μg l^{-1}.

The influence of the main matrix elements on the determination of Pd and Pt was investigated (Table 2). The average concentrations of macrocomponents in the solutions obtained after digestion of alloys and ores are up to 8–10 g l^{-1} for Na, 4–5 g l^{-1} for Ca, 10–12 g l^{-1} for Fe, 2–3 g l^{-1} for Ni and 2–3 g l^{-1} for Cu. Thus the determination of Pd and Pt was found to be possible under high concentrations of the main components of ores and alloys (Table 2).

The accuracy of the FIA-FAAS method proposed was proved by the determination of Pd and Pt in standard reference materials of ores and alloys (Table 3). Good agreement of the results obtained with the certified values was demonstrated. RSD of the determination is 0.03–0.08 and detection limits are 5 μg l^{-1} (propane–butane–air flame) and 3 μg l^{-1} (acetylene–air flame) for Pd and Pt for 1 min of preconcentration.

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