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Determination of Noble Metals After Separation and Preconcentration with Silica-Bonded Complexing Ligands

Thomas Schilling[1], Peter Schramel[1,*], Bernhard Michalke[1], and Günter Knapp[2]

[1] GSF Research Center for Environment and Health, Institute of Ecological Chemistry, Neuherberg, D-85758 Oberschleißheim, Federal Republic of Germany

[2] Institute of Analytical Chemistry, Micro- and Radiochemistry, Technical University Graz, A-8010 Graz, Austria

Abstract. Noble metals are preconcentrated and separated from the matrix elements by adsorption on proper complexing ligands immobilized on silica gel and subsequent elution. Preconcentration factors of 5–10 were achieved. The reliability of the method was proved by analysis of a spiked soil material and a CRM with ICP-AES and ICP-MS. Ag, Au, Pd and Pt showed a good recovery in the spiked material. The indicative value for gold in the CRM (145 BCR) could be confirmed.

Key words: noble metals, palladium, platinum, gold, silver, separation, complexing agents, preconcentration, ICP-AES, ICP-MS.

The determination of noble metals in medical and environmental samples requires preconcentration of the analyte elements [1–3]. Further separation is necessary from the matrix-elements and partially from other noble metals [4]. The separation of different noble metals in aqueous solutions, using the modified silica gels (Fig. 1), is described in [5].

Based on [5], in this study, complexing ligands immobilized on silica were investigated with regard to their selective sorption of noble metals in real samples, i.e. in synthetic matrix containing solutions and spiked soil material. There, matrix elements were adsorbed only in a low degree to the modified silica, thus the investigated noble metals were separated and preconcentrated for the analysis without published interferences [6]. Finally, gold was analysed in a sludge material with indicatively reported content (CRM 145 BCR; sewage sludge) because of the lack of a reference material with certified contents of noble metals in environmental-equivalent concentrations and matrices. It is demonstrated that the modified silica gels are suitable for the trace-matrix separation in noble metal analysis.

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[*] To whom correspondence should be addressed

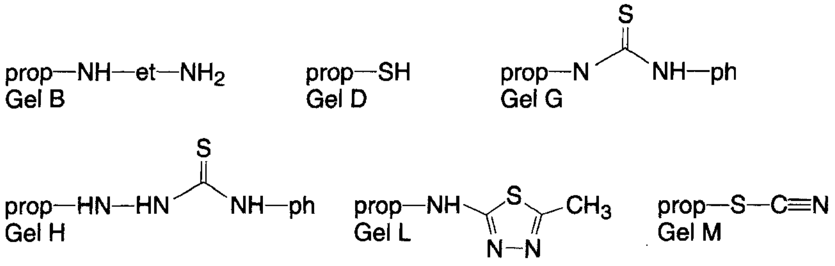

Fig. 1. Formulae of the silica-immobilized ligands

Experimental

Apparatus

The pH-values were adjusted with the gas phase-neutralizer GPN (Knapp Logistik, Austria). For the metal determinations a sequential ICP-OES JY 38P (Instruments SA, France) and an ICP-MS ELAN 5000 (Perkin Elmer Sciex, Canada) were used. The noble metals were preconcentrated using the TRACECON-System (Knapp Logistik, Austria).

Reagents

By Aldrich (Germany): ammonium acetate (99% +, gold-label), DL-penicillamine, AAS-standard-solution of $AgNO_3$, Pd_{metal} and H_2PtCl_6 [5]; by Johnson Matthey (Germany): AAS-standard-solution of $AuCl_3$ [5]; by Merck (Germany): thiourea, hydrochloric acid (suprapure and p.a. -quality), aqueous ammonia (p.a. -quality), nitric acid (p.a. -quality), H_2O suprapure (Milli-Q, Millipore, Germany).

Samples

Metal extraction: Aqua regia extraction following DIN 38414.

Removing of NO_x: The filtered aqua regia solution is evaporated to minimizing the ligand-oxidation by NO_x. The residue is taken up in 49 ml H_2O and 1 ml HCl. The solution is buffered by adding of 50 mg ammonium acetate. The different pH-values were adjusted by a gas phase-neutralizer as described in [5].

Table 1. pH values for the adsorption of the noble metals from the sample on the modified silica and for the elution of the noble metals [5]

	pH_{sample}	pH_{eluent}
Gel B	1,5	1,0
Gel D	1,5	1,0
Gel G	1,5	7,0
Gel H	2,5	1,0
Gel L	2,5	1,0
Gel M	1,5	1,0

Table 2. Content of matrix metals in the eluates (100% = 2 mg/l; 5% means metal-contents in the order of 5% or below)

	Al	Ba	Ca	K	Mg	Sr
B: SCN:	5	5	5	65	7	5
Thh:	5	5	25	40	10	5
DTO:	5	5	90	30	30	5
D: Thh:	7	10	40	35	10	5
DMPS:	5	5	50	10	5	5
G: Thh:	5	5	30	60	5	5
DMPS:	5	5	20	20	5	5
Pen:	5	5	20	45	5	5
H: Thh:	5	5	10	33	5	5
DTO:	6	5	90	10	22	5
Pen:	5	5	10	5	5	5
L: Thh:	5	5	5	25	5	5
Pen:	6	5	10	22	5	5
M: NaSCN:	7	9	50	40	5	5
Thh:	5	5	5	5	5	5
DMPS:	5	5	25	52	5	5

	Cd	Co	Cu	Fe	Mn	Mo	Ni	Ti	V	Zn
B: SCN:	5	5	5	5	5	15	5	60	10	5
Thh:	5	5	5	5	5	15	5	50	10	5
DTO:	5	5	5	10	5	12	5	60	10	5
D: Thh:	5	5	75	5	5	7	5	7	5	5
DMPS:	5	5	30	5	5	5	5	5	5	5
G: Thh:	5	5	5	5	5	5	5	5	5	5
DMPS:	5	5	15	5	5	5	5	5	5	5
Pen:	15	5	10	5	5	5	15	5	5	5
H: Thh:	5	5	30	20	5	90	5	75	75	5
DTO:	5	5	5	14	5	90	5	90	90	6
Pen:	5	5	5	33	5	10	5	5	5	5
L: Thh:	5	5	5	7	5	90	5	75	80	5
Pen:	5	5	6	6	5	75	5	80	75	5
M: SCN:	5	5	5	5	5	6	5	8	5	5
Thh:	5	5	5	6	5	7	5	10	5	5
DMPS:	5	5	5	5	5	5	5	5	5	5

Spike of the light sandy soil material: Before the aqua regia treatment 1 ml of a solution containing 5 ml/l of each noble metal (prepared by mixing of AAS-standard solutions – containing 1000 mg/l of each noble metal – and diluting with 2% HNO_3) was added to 1 g of the soil material (adding of the spike to the aqua regia solution after the treatment gave the same recovery). The homogeneity of the spiking procedure is obvious because of the use of the complete spiked sample for analysis. Table 4 presents the mean values of these experiments.

Column Preparation

The silica was functionalized with the ligands as described in [5]. A small column (30 × 3 mm ID) was filled with about 0.2 g of the respective gel and different sample volumes (5, 10 and 50 ml) were pumped through the column (1.5 ml/min) as described in [5]. Subsequently, 5 ml of eluents were pumped in reverse direction (all eluents were used in 4 ‰ w/v solutions) and collected in a quartz vessel. The metal content of the eluate was determined by ICP-OES and ICP-MS. Table 1 shows the optimized pH values of the samples and the eluents in combination with the different gels [5].

Results and Discussion

Synthetic solutions containing 2 mg/l of different matrix elements and 100 µg/l of the noble metals were prepared to estimate the capability of separation of the noble metals from the other elements. As shown in Table 2, in most of the cases the matrix element were reduced down to 5% or below, only a few gels hold back matrix metals in higher contents. The (partial) sorption of matrix metals seem to follow the HSAB concept (hard and soft acids and bases [5]) as well as the sorption of analyte elements (i.e., gels with hard ligands as thiosemicarbazide absorb hard cations as iron or molybdenum). Especially the matrix metals with the highest potential of possible interferences (Fe, Cu, V, Mn, Al and Ni [6]) are decreased to a content lower than 5% compared to the original solution. In this synthetic solutions Ag, Au, Pd and Pt could be preconcentrated about a factor of 10 with different gels and eluents (Table 3). Because of sufficient preconcentration of the noble metals with the modified silica gels and the large decrease of the matrix elements in a next step a real sample (CRM 142 BCR) was spiked with gold, silver, palladium and platinum to investigate the recovery in aqua regia extracts because of the possibility of adsorption of the noble metals on the silicate residue. As shown in Table 4, quantitative

Table 3. Successful combinations of modified gel and eluent for the preconcentration of noble metals from matrix-containing solutions (until a preconcentration factor of 10, if nothing other noted)

Ag:	B/Thh	D/Thh	G/Pen (fakt. 4 possible)		H/Thh	
Au:	D/Thh	H/Thh	H/Pen	M/Thh	M/DMPS	
Pd:	B/Thh	H/Thh	H/DTO (fakt. 4 possible)		L/Thh	M/DMPS
Pt:	B/Thh	H/Thh	L/Thh	L/Pen (fakt. 5 possible)		

Table 4. Recovery (%) of noble metal spikes in a soil sample (CRM 142 BCR) ($AgNO_3$, $AuCl_3$, $PdCl_2$, H_2PtCl_6)

	B/Thh	D/Thh	G/Pen	H/Thh	L/Thh	M/Thh
Ag	105	114	85	110	90	<50
Au	<50	101	102	92	<50	92
Pd	<50	82	92	93	<50	87
Pt	80	<50	<50	91	<50	<50

Table 5. Determination of gold in a CRM (145 BCR) with indicated values (Au: 3.35 ± 0.2 mg/kg)

	ICP-OES (all $n = 4$)	ICP-MS (all $n = 3$)
Direct measurement	3,68 ± 0.20	4,35 ± 0.24
Gel D/thiourea without preconcentration	3,61 ± 0.18	2,90 ± 0.21
Gel D/thiourea 5-fold preconcentration	3,20 ± 0.15	2,90 ± 0.17
Gel D/thiourea 10-fold preconcentration	3,09 ± 0.21	3,41 ± 0.17

recovery could be observed with various combinations of immobilized ligands and eluents. In spite of this in some cases the content of iron was too high, so the reduction of iron by about 60–90% was not sufficient to suppress all interferences. So it can be reported that only some of the silica gels tested with synthetic solutions are suitable for the use with real samples containing a high level of iron. Six combinations of a suitable gel with thiourea or penicillamine as eluents are applicable to separate the investigated noble metals quantitatively from the matrix elements with a recovery of more than 80%.

Finally, a CRM with indicatively reported gold values was investigated (BCR 145). Table 5 shows the good agreement between the indicative values and the detected gold concentration after matrix separation and preconcentration with the immobilized thiole and subsequent elution with thiourea. The direct analysis of gold with ICP-MS without any separation procedure seems to be interfered by a high matrix-content. Using the modified silica and a proper eluent these interferences are avoided and a good agreement between the results of the indicated value and the results of our analysis was obtained.

Conclusion

This paper describes the applicability of some new complexing agents for the matrix-separation and preconcentration of noble metals. Pt, Pd, Au and Ag are separated from the matrix metals in synthetic solutions and preconcentrated by the use of a suitable modified gel with the proper eluent under the described conditions. There, the matrix metals were decreased down to a content lower than 5%. Further the presented method demonstrates its suitability for the analytical practice by a good recovery of the spiked noble metals in soil material.

Likewise the good agreement between the indicated values for gold in a certified reference material (CRM 142 BCR) and the found content of gold after matrix separation and (partially) preconcentration shows the applicability of this method for the analysis of noble metals in real samples. Finally, it should be mentioned that commercially available CRM's with certified contents of different noble metals in environmental-equivalent matrices have to be developed to support further investigations.

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