

Silica gel chemically modified with ionic liquid – efficient sorbent for Au, Ir, Pd and Pt

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The efficiency of sorption of noble metals on the sorbent synthesized *via* chemical modification of silica gel with ionic liquid containing methylimidazolium group was studied. The surface of the sorbent is positively charged, and results obtained indicate quantitative retention of negatively charged chlorido complexes of noble metals. Experiments carried out defined an optimal HCl concentration range (0.05-0.1 M HCl) for quantitative retention of Au, Ir, Pd and Pt using 30 min sorption time. Complete elution of sorbed elements was achieved with 0.5 M of thiourea in 0.5 M HCl. In addition, high selectivity of the sorbent was found toward the sorption of base metals (Fe, Cu, Mn, Ni, Zn) usually coexisting with noble metals in industrial and environmental samples. Analytical procedure was developed and validated for the determination of Au, Ir, Pd and Pt in soils and geological samples.

Keywords: ionic liquids, noble metals, sorption, soils, geological samples

INTRODUCTION

Noble metals (Au, Ru, Rh, Pd, Os, Ir, Pt) are widely used in various industrial fields due to their properties such as electrical resistance, inertness to chemical attacks, hardness, excellent catalytic activity, which requires their reliable determination in environmental samples, raw materials, as well as in final products. Atomic spectrometric and mass spectrometric methods allow measurement of noble metals at low concentration levels, however the practical application of these methods in real samples is restricted by strong matrix interferences [1]. That is why separation and enrichment steps are generally included in most of the analytical procedures used for noble metals determination in environmental and industrial samples.

Solid phase extraction (SPE) is a preferable separation procedure because of its simplicity, reduced amounts of organic solvents used, high preconcentration factors and clean extracts. The properties of the incorporated sorbent are the most important factor for the high effectiveness of the developed SPE procedure. Various sorbents have been proposed for the SPE of noble metals [2–8]. Polymeric sorbents with high selectivity toward precious metals include functional groups such as thiourea [9], thiazole [10], dithiocarbamate [11], cysteine [12], ethylenediamine [13], 8-aminoquinoline [14], etc. Ionic liquids have been also used for SPE of noble metals in connection with

their ability to exchange negatively charged ions, e.g., for Au [15-19], Pd [20], Pt [21] and Pt(IV), Pt(II), and Pd(II) [22] in which imidazolium derivatives are bound to a polymer matrix.

In this paper, we use silica gel, an inert support chemically modified with 1-methylimidazolium groups (SiG-MIA) as a sorbent for SPE of noble metals. Extraction efficiency of the sorbent toward Au, Ir, Pd, Pt was studied in batch mode and optimal hydrochloric acid concentrations, contact time, and sorbent amount were defined. The results obtained indicate quantitative sorption of the chlorido complexes of Au, Ir, Pd, Pt from 0.05 M HCl with high selectivity even in the presence of base transition metals (Fe, Cu, Mn, Zn, Ni). The elution of the retained metals was achieved with 0.5 M thiourea in 0.5 M HCl. Based on the properties of the SiG-MIA sorbent an analytical procedure was developed for noble metals determination in soils, ore samples and copper concentrate. The accuracy and repeatability of the developed analytical procedures was confirmed by the analysis of certified reference materials.

EXPERIMENTAL

Apparatus

The concentrations of noble metals were measured on an inductively coupled plasma optical emission spectrometer (ICP-OES, Jobin Yvon

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Ultima 2) equipped with Meinhard glass concentric nebulizer and glass cyclonic chamber at optimal instrumental parameters (sheath gas 0.2 L/min, sample uptake 1 ml/min, plasma gas 12 L/min). All measurements were carried out at least in triplicate. The most sensitive wavelengths were used: Au 242.795 nm; Ir 224.268 nm; Pd 340.458 nm; Pt 214.423 nm.

Elemental analysis was performed using Euro EA CHNS-O elemental analyzer (EuroVector, Italy). An EBA 20 centrifuge (DJB Labcare Ltd., Newport Pagnell, England) was used to separate the silica particles from the solution containing noble metals in batch experiments.

Reagents and materials

All used reagents and solvents were of analytical-reagent grade. The stock standard solutions for Au, Ir, Pd and Pt were Sigma–Aldrich (Germany) in 5% HCl. The stock standard solutions for Cd, Cu, Co, Fe, Ni, Pb and Zn (1000 mg/L) were Titrisol, Merck (Darmstadt, Germany) in 2% HNO₃. Working aqueous standard solutions were daily prepared by appropriate dilution with doubly distilled water. The elution solutions were prepared from nitric acid, hydrochloric acid, L-cysteine and thiourea (Merck, Darmstadt, Germany). All acids used in sorption, elution and digestion procedures are Suprapur, Merck, Germany.

Certified reference material OREAS 45d, Ferruginous soil; certified reference material OREAS 13d, gabbro (prepared from ores of platinum group elements (PGEs), copper, nickel and gold dispersed in a gabbro matrix), certified reference material OREAS 505d (porphyry Cu-Au certified reference material prepared from a blend of ores, barren granodiorite and minor additions of copper and molybdenum concentrates).

Reagents used to prepare the SiG-MIA sorbent were silica gel 60 (Merck, Darmstadt, Germany), 1-

methylimidazole (MIA), 3-(chloropropyl)-trimethoxysilane (TMSP) (Sigma–Aldrich, Munich, Germany) and methanol (Labscan, Dublin, Ireland).

Procedures

• *Sorbent synthesis.* A three-step synthesis procedure was used:

First step: The silica gel (SiG) surface was activated by refluxing (10 g SiG with 80 mL 6 M HCl for 8 h). After cooling, the activated silica gel (aSiG) was filtered and washed with deionized water until a neutral reaction and dried under vacuum at a temperature of 60°C for 8 h.

Second step: Synthesis of 1-(trimethoxysilyl propyl)-3-methylimidazolium chloride ([TMSP-MIA]Cl) was carried out according to the procedure described by Valkenberg *et al.* with some modifications [12]. A mixture of 1-methylimidazole (2.84 g, 34.5 mmol) and 3-(chloropropyl)-trimethoxysilane (6.86 g, 34.5 mmol) was refluxed under nitrogen for 48 h at 70°C. The obtained product was a yellow-colored viscous liquid which was purified by extraction with diethyl ether (twice).

Third step: The chemical grafting of ([TMSP-MIA]Cl) onto aSiG was performed by autocondensation and co-condensation of the silanol groups and methoxy groups of the TMSP-MIA chloride. For this purpose, 1.7 g of [TMSP-MIA]Cl was dissolved in 20 mL of methanol and 1 g of aSiG was dispersed in this solution. The resulting suspension was stirred continuously for 1 day at room temperature. After completion of the reaction, the solid phase was separated by centrifugation and washed three times with methanol to remove the unreacted [TMSP-MIA]Cl, and then the resulting material (SiG-MIA) was dried under vacuum at 60°C for 8 h. Schematically, the synthesis of the sorbent is presented in Figure 1.

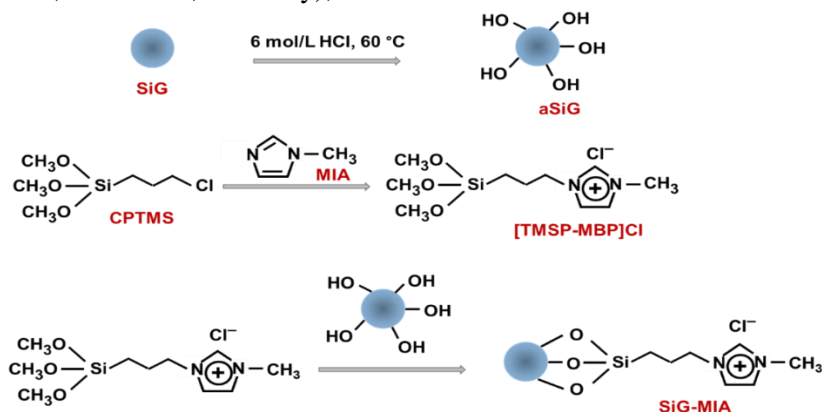


Fig. 1. Schematic representation of the synthesis of SiG-MIA.

- **Batch sorption procedure** The sorption efficiency of SiG-MIA toward chlorido complexes of Au, Ir, Pd and Pt was studied in a batch mode. The influence of HCl concentration on the degree of sorption of the analytes was investigated in the range 0.001 – 3 M. Aqueous solutions of HCl solution with desired concentration were mixed with 2 µg/ml of Au, Ir, Pd and Pt and 100 mg of SiG-MIA and shaken for 30 min. Samples were centrifuged (5800 rpm) for 10 min, supernatants were removed and concentrations of analytes were measured by ICP-OES. Degrees of sorption were calculated as follows:

$$D_S(\%) = \frac{A_i - A_{\text{eff}}}{A_i} \times 100, \quad (1)$$

where A_{eff} (µg) is the amount of the analyte in the supernatant solution and A_i (µg) is the initial amount of Au, Ir, Pd and Pt added.

- **Desorption studies.** Several mixtures of HCl acid and thiourea at different concentration levels were tested as potential eluents. All experiments were done after loading the sorbent with 2 µg of Au, Ir, Pd and Pt at optimal conditions, followed by treatment with 5.0 mL of each eluent for 30 min on an electrical shaker. Degree of elution (D_E , %) was defined as follows:

$$D_E(\%) = \frac{A_{\text{el}}}{A_i - A_{\text{eff}}} \times 100, \quad (2)$$

where A_{el} (µg) is the amount of Au, Ir, Pd and Pt in the eluate.

A. Selectivity studies. Model solutions containing 1000 µg/L of Fe, Cu, Mn, Zn, Ni were prepared in 0.05 M HCl, spiked with 100 µg/L of Au, Ir, Pd and Pt and mixed with 100 mg of SiG-MIA. The solutions were shaken for 30 min and centrifuged at 5000 rpm. The supernatant was removed and all elements were measured by ICP-OES. The SiG-MIA particles were washed with distilled water and shaken with 5 mL of 0.5 M thiourea in 0.5 M HCl for 30 min. After centrifugation the elements Au, Ir, Pd and Pt were measured in the eluate by ICP-OES. The degrees of sorption and elution were calculated using equations 1 and 2, respectively.

B. Procedure for Pd, Pt u Rh determination in soils after aqua regia digestion. A sample of approximately 2000 mg of soil sample was weighed in a PTFE beaker covered with a glass watch. A mixture of 21 ml conc. HCl and 7 ml conc. HNO₃ was added and samples were left to stay overnight. The sample solution was digested for about 3 h in the PTFE beaker covered with a glass watch. Then the watch glass was removed, 20 ml of HF were added and digestion continued until near dryness. The residue was dissolved in 5 mL of 0.5 M HCl on the

hot plate, the solution was transferred to a 25 mL volumetric flask and diluted up to the mark with doubly distilled water. A sample of 20 mL was filtered and transferred to a centrifuge tube. About 100 mg of the SiG-MIA sorbent was added and the sample was shaken for 30 min. After centrifugation, supernatant was removed, sorbent was washed with doubly distilled water and elution was carried out with 5 mL of 0.5 M thiourea in 0.5 M HCl. After centrifugation Au, Ir, Pd and Pt were measured in the supernatant by ICP-OES at optimal instrumental parameters.

C. Procedure for Au determination in ore and copper concentrate. A sample of copper concentrate of approximately 1000 mg was weighed in a PTFE beaker, a mixture of 12 mL of conc. HCl and 4 mL of conc. HNO₃ was added and the sample was left to stay overnight. The sample solution was digested for about 6 h in the PTFE beaker covered with a watch glass. Then the watch glass was removed and digestion continued until near dryness. The residue was dissolved in 5 mL of 0.5 M HCl, transferred to a 25 mL volumetric flask and diluted up to the mark with doubly distilled water. Two parallel samples of 10 mL were filtered and transferred to centrifuge tubes. About 100 mg of SiG-MIA sorbent was added and both samples were shaken for 30 min. After centrifugation, the supernatant was removed, sorbent was washed with doubly distilled water and elution was carried out with 5 mL of 0.5 M thiourea in 1 M HCl. After centrifugation Au, Pd, and Pt were measured in the supernatant by ICP-OES at optimal instrumental parameters.

RESULTS AND DISCUSSION

Sorbent synthesis

The successful synthesis of the sorbent was demonstrated by comparing the infrared spectra of the starting material (aSiG) and the final product (SiG-MIA). The bands at 473, 802 and 1097 cm⁻¹ observed in the spectra of both investigated materials are related to the Si–O–Si group in the silica gel. The broad band in the interval 3200–3600 cm⁻¹, present in both spectra, is due to the vibrations of the silanol –OH groups. The spectrum of SiG-MIA shows bands at 2854, 2926 and 2971 cm⁻¹ which prove the occurrence of C–H vibrations due to the presence of –CH₂ groups in the propyl residue in [TMSP-MIA]Cl. The bands at 1571 cm⁻¹ and 1653 cm⁻¹ are due to the C=C and C=N groups in the imidazole ring, respectively. This is evidence that SiG-MIA contains methylimidazole groups. The success of the synthesis procedure was also evaluated by elemental analysis of the prepared SiG-MIA.

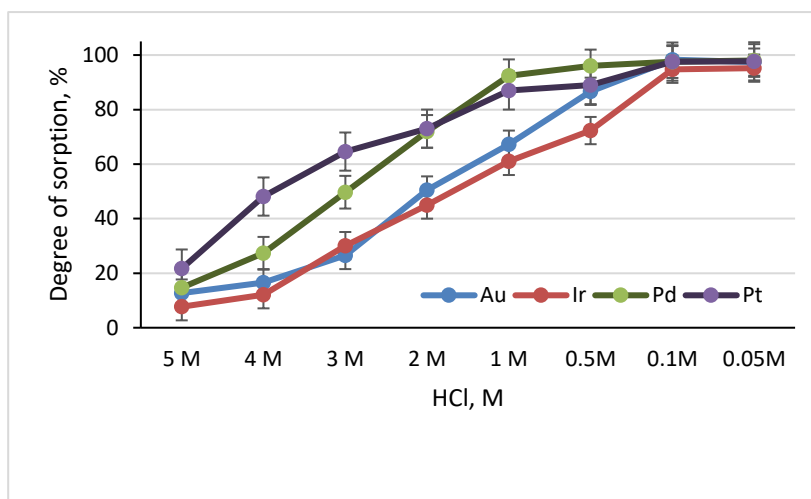


Fig. 2. The effect of HCl concentration on the degree of sorption of Au, Ir, Pd and Pt with SiG-MIA (three parallel experiments).

The results (7.27 wt. % C and 1.84 wt. % N) proved that the 1-(trimethoxysilylpropyl)-3-methylimidazolium fragment was successfully bound to the silica gel surface. The content of 1-methylimidazole groups was calculated to be 0.76 mmol per gram of sorbent.

Optimization studies of the extraction efficiency

- *Sorption efficiency.* The sorbent SiG-MIA might be accepted as a strongly basic anion exchanger due to the positively charged 1-methylimidazolium functional groups on its surface. This suggests the adsorption of the anionic chlorido-complex species of the studied noble metals which will depend on the HCl concentration.



The effect of HCl concentration on the degree of sorption of Au, Ir, Pd and Pt on MIA-PG was investigated in a wide range of HCl concentrations from 0.05 to 3.0 M and the results are presented in Figure 2. The main conclusions that can be drawn from these results are as follows:

- in all cases the degree of sorption of the corresponding analyte increases with decreasing hydrochloric acid concentration;
- quantitative sorption is achieved at HCl concentration: for Au at 0.05 – 0.1 M HCl; for Ir at 0.05 – 0.1 M HCl; for Pd at 0.05 – 0.5 M HCl; for Pt at 0.01 M – 0.05 M HCl.

The first conclusion might be explained by the fact that there is competition between chloride anions and anions of chlorido complexes of metals for a positively charged binding site on the sorbent surface. At high concentrations of hydrochloric acid the interaction with the chloride anions predominates, while at low concentrations the interaction with the anions of the chlorido complexes

of the metals prevails. Results obtained undoubtedly showed that at the optimal 0.05 M HCl, the proposed SiG-MIA sorbent ensures quantitative sorption for Au, Ir, Pd, and Pt. Experiments were performed to optimize the amount of SiG-MIA particles for the highest degree of sorption. Results showed that for the studied range 50–150 mg sorbent, the sorption was quantitative with at least 100 mg of SiG-MIA sorbent.

- *Sorption kinetics.* The sorption kinetics is an important characteristic of sorbents for its practical application. The sorption kinetics of Au, Ir, Pd and Pt was determined in a batch mode at the selected optimal concentration of hydrochloric acid of 0.05 M HCl for a sorption time ranging from 5 to 60 min. The results indicate a relatively fast sorption process. All studied analytes Au, Ir, Pd and Pt were quantitatively retained on the sorbent surface in 30 min, so this time was used in further experiments.

- *Desorption step.* The SiG-MIA sorbent, as a strong basic anion exchanger, is highly efficient for the retention of negatively charged chlorido complexes of Au, Ir, Pd and Pt from acidic media, but this also means relatively difficult desorption in the presence of any acid used as an elution reagent. As seen from the data presented in Table 1, the degree of elution is very low even if 3M HCl is used (higher HCl concentration affects the stability of functional groups on the surface of the sorbent). This means that the competitive complex formation using a chelating agent would be more effective in such case since the elution will be due to the decomposition of the chlorido complexes of Au, Ir, Pd and Pt and the formation of new more stable chelate complexes with the chelating agent used. The ligands thiourea and L-cysteine are well-known for their ability to form stable complexes with Au, Ir, Pd and Pt due to the presence of both amine and

sulfur groups. Experiments were carried out with mixtures of thiourea and L-cysteine in HCl in various concentrations, showing quantitative desorption of Au, Ir, Pd and Pt in 30 min. with 0.5 M thiourea in 0.5 M HCl (see Table 1).

Table 1. Degree of elution (D_E , %) for Au, Ir, Pd and Pt from SiG-MIA using different eluents.

Eluent	Degree of elution, %			
	Au	Ir	Pd	Pt
3 M HCl	32±5	12±3	22±5	18±5
0.2 M TU + 0.2 M HCl	85±6	81±5	88±5	86±5
0.5 M TU + 0.5 M HCl	98±2	96±3	97±3	95±3
0.5 M TU + 1 M HCl	99±2	98±2	98±2	96±2
0.2 M Cys + 0.2 M HCl	80±5	75±5	77±5	74±5
0.5 M Cys + 0.5 M HCl	90±4	80±4	81±4	83±5
0.5 M Cys + 1 M HCl	92±4	82±4	85±4	84±5

Desorption kinetics. To determine the desorption kinetics of the chlorido complexes of Au, Ir, Pd and Pt from the surface of SiG-MIA, experiments were performed in a static mode using the elution mixture 0.5 M thiourea in 0.5 M HCl with desorption times ranging from 10 to 60 min. It was found that complete elution is achieved for all studied analytes with 2-5 ml of 0.5 M thiourea in 0.5 M HCl for 30 min.

Selectivity studies (Solid phase extraction of a mixture of base transition and noble metal). Matrix interferences are the most serious problem for the determination of Au, Ir, Pd and Pt in complicated samples such as soils and geological samples. That is why the selectivity of the sorbent is of utmost importance. The selectivity of SiG-MIA was studied following the procedure described in paragraph A. Results obtained are presented in Table 2 and undoubtedly showed that even in the presence of high levels of coexisting base metals the recovery of Pd, Pt, Ir, and Au ions is more than 95% at the optimal HCl concentration of 0.05 M.

These results are expectable because Fe, Cu, Zn, Mn, Ni, Cd and Pb exist in sample solution as positively charged ions and are repelled by the

positively charged methylimidazole group on the surface of the sorbent. This makes SiG-MIA a highly suitable and promising sorbent for the quantification of noble metals in complicated matrices, ensuring interference-free measurement by ICP-OES.

Table 2. Selectivity studies – degree of sorption D_s (%) (mean±SD) of Au, Ir, Pd and Pt in the presence of 500 mg/L of base metals (three parallel experiments).

Element	Degree of sorption, D_s [%]
Au	98±2
Ir	96±2
Pd	97±1
Pt	98±2
Fe	<3
Cu	<1
Zn	<3
Mn	<1
Ni	<4
Cd	<4
Pb	<3

Determination of Pd and Pt in soils. The sorbent SiG-MIA was used in an analytical procedure based on solid phase extraction for the determination of Pd, Pt, Ir, and Au in soil samples. The soil sample was digested on a hot plate with a mix of HCl+HNO₃+HF for about 4 h. The dry residue obtained after soil digestion was dissolved in 5 mL of 0.5 M HCl, transferred to a 25 mL volumetric flask and diluted up to the mark, ensuring final optimal HCl concentration for the subsequent separation of Pd and Pt. Two parallel samples were used for the determination of Pd and Pt following the procedure described in paragraph B. The developed analytical procedure was applied to the CRM OREAS 45d, results obtained are presented in Table 3. Recoveries achieved for both elements, calculated based on the certified values were above 95%. Relative standard deviations varied between 6 and 11%. Calculated limit of quantification (10 σ criterion) based on the purity of acids used is 15 ppb for all analytes. The developed procedure is suitable for the analysis of soil samples.

Table 3. Recoveries achieved for studied elements and results for certified values (presented as in the certificate), (three parallel samples).

Sample	Element	Recovery, (%)	Certified values	Results
			Mean, ppb (sd)	Developed procedure Mean, ppb (sd)
CRM OREAS 45d (soil)	Au	96±2	23 (2)	22 (2)
	4	98±2	34.6 (2.3)	34 (3)
	Pt	101±2	48.5 (3.1)	49 (4)
CRM OREAS 13b	Au	98±2	211 (13)	208 (16)
	Pd	101±3	131 (9)	132 (12)
	Pt	97±2	197 (13)	191 (15)
CRM OREAS 505d	Au	99±2	552 (23)	549 (29)

Determination of Au, Pd, Pt in polymetallic ore and copper concentrate. Several copper mines are situated in Bulgaria and determination of Au, Pd and Pt in copper ore and copper concentrate is an important analytical task. The high selectivity of the SiG-MIA sorbent permits the development of an analytical procedure for Au, Pd, and Pt determination in copper concentrate. In this case *aqua regia* is conventionally used for sample digestion although the sample is only partially dissolved (experimental results confirmed complete dissolution of Au, Pd, and Pt). Analytical procedure described in paragraph C was applied to the CRMs OREAS 13b and OREAS 505d. The data, presented in Table 3, demonstrate a very good agreement between obtained results and certified values, thus confirming the validity of the developed procedure. Relative standard deviations varied between 7-12%. Calculated limit of quantification (10 σ criterion) based on the purity of acids used is 30 ppb for all analytes. The procedure is simple and easy to apply, suitable for laboratory practice in mining and industrial laboratories.

Model experiments showed that the extraction efficiency of the sorbent statistically dropped down after at least 20 sorption/desorption cycles. In addition, the sorption efficiency of the sorbents prepared by different batches is almost identical, confirming the repeatability of synthesis procedure.

CONCLUSION

In the present study, a new sorbent was synthesized based on the grafting of 1-(trimethoxysilylpropyl)-3-methylimidazolium chloride onto the surface of submicron silicon spheres, which was characterized by elemental analysis and IR spectroscopy. The sorbent showed high selectivity: in 0.05 M HCl the retention of Au, Ir, Pd and Pt is quantitative, while the sorption of base transition metals is negligible. The sorbed noble metals are effectively eluted with 0.5 M thiourea in 0.5 M HCl. Based on these results, the sorbent was incorporated in analytical procedures developed for the determination of Au, Pd and Pt in soils, polymetallic ore and copper concentrate. The validity and versatility of the proposed analytical procedure was confirmed by the analysis of suitable certified reference materials.

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