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Application of Metalfix Chelamine prior to the determination of noble metals by the inductively coupled plasma atomic emission spectrometry

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Abstract

Metalfix Chelamine chelating resins of two different bead sizes (150–300 and 40–80 μm) were examined and compared regarding their application for sorption of Au, Ir, Pd, Pt, Rh and Ru ions from medium of HCl, HNO_3 and mixtures of HCl and HNO_3. The quantitative enrichment of Au, Ir, Pd and Pt was established for the resin of 150–300 μm particle size and for solutions acidified with HCl and HNO_3 (3:1) up to the concentration of $0.50\,\mathrm{mol\,l^{-1}}$. In the case of Rh and Ru, the uptake of these metals by the resin was lower than 50%. For the elution, solutions of different reagents, i.e. HCl, HNO_3, KCN, KI, KSCN and $(NH_2)_2CS$, were studied with respect to the complete release of the analytes retained by the resin. In addition, influence of various base metals, i.e. Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn, on the retention of the noble metals was investigated. Under the selected conditions for the retention and elution of Au, Ir, Pd and Pt, the analytical performance of the proposed pre-concentration procedure was evaluated and it was applied to the determination of these noble metals in anodic sludge sample.

Keywords: Metalfix Chelamine; Noble metals; Pre-concentration; Matrix separation; Inductively coupled plasma atomic emission spectrometry

1. Introduction

Despite a great progress in the analytical instrumentation, direct measurements of noble metals in geological, metallurgical or environmental samples are often not possible, mainly due to the very low concentration levels of these elements or interference effects coming from other constituents of the analysed samples [1]. Even in the case of very sensitive methods, the detection limits of gold and platinum group elements depend upon the reagent blanks, memory effects, matrix effects and mainly spectral interferences (e.g. for ETV-AAS) or isobaric interferences from different monoatomic and polyatomic oxide ions (for instance for ICP-MS) [1–6]. Thus, a chemical separation of noble metals is usually desirable in order to increase the analytical sensitivity of the spectrometric method used and to eliminate the interferences from the other elements. Typically, column procedures or batch protocols based on usage of different ion exchangers, chelating resins or adsorption media are applied for that purpose [1,2,5,6]. The main advantage of ion-exchange pre-concentration approach is a possibility of the determination of low analyte concentrations and separation of the analytes from matrix constituents hampered the detection of the noble metals.

Among a variety of commercial chelating resins introduced in the last decade for trace analysis purposes, Metalfix Chelamine, being tetraethylenepentamine polymer bound, merits a special notice. From a practical point of view, the resin is very attractive for the pre-concentration of traces of metals in the measurements carried out by the spectrometric methods. It possess a high exchange capacity and a high affinity for heavy metal cations as well as exposes no interference effects by the alkali and alkaline earth metals, which are not bound by the resin. Earlier published papers regarding analytical performance of Metalfix Chelamine [7–13] through its high selectivity toward the transition metal ions reports very

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encouraging results. So far, that chelating resin was used for the enrichment of various metals (Cd, Co, Cu, Hg, Mn, Ni, Pb, Zn and V) in samples of complex matrices in which determination of the species of interest would not be possible in a direct way due to very low concentrations of the metal ions and likely interference effects, i.e. sea water [7,8,12], fresh and saline water [10] and fir wood [9].

Carrying very specific tetraethylenepentamine functional groups containing donor nitrogen atoms, Metalfix Chelamine should also exhibit large ability for the selective retention of the noble metals. However, only in a couple of contributions [14–16], the resin has been applied for the enrichment of gold and platinum group elements using ICP-MS and F-AAS. Besides, the results presented in the cited publications, especially concerning the elution of the noble metals from the resin, are inconsistent. In the work by Coedo et al. [14], wherein Au, Ir, Pd, Pt and Rh were adsorbed by Metalfix Chelamine in the form of their chlorocomplexes on a mini-column, the recovery of the analytes was not feasible and a procedure of acid digestion of the resin was required in order to release the analytes into the solution. On the contrary, Iglesias et al. [15] observed in batch experiments that the desorption of Au, Pd and Pt was achieved without destruction of the resin, but shaking it with the solution of thiourea. However, the recoveries found for Au and Pt were far from being quantitative and suitable for the analytical purposes.

Lack of the consistent knowledge relating to the behaviour of noble metals on Metalfix Chelamine, has led us to cope with the resin for a complete understanding of its sorption and desorption properties and evaluation of its analytical application to the determination of gold and platinum group elements by the spectrometric methods. In the present work, the adsorption of noble metals, i.e. Au, Ir, Pd, Pt, Rh and Ru, from the solutions acidified with HCl, HNO_3 and mixtures of HCl and HNO_3 was studied using the resin of two different particle sizes. In order to find the most favourable conditions for the desorption of the noble metals retained by the resin, solutions of mineral acids and various complexing agents of different concentrations and volumes were used. The effect of several base metals on the uptake of the noble metals by the resin was examined as well. Under the selected conditions, the devised procedure was employed for the determination of Au, Ir, Pd and Pt in the anodic sludge sample.

2. Experimental

2.1. Apparatus

The instrument used in measurements was a JY 38S sequential inductively coupled plasma atomic emission spectrometer (ISA Jobin Yvon, France) equipped with a cyclone spray chamber (ISA Jobin Yvon, France) and a concentric nebuliser TR 50-C1 (J.E. Meinhard Associates Inc., California, USA). The operating parameters applied were as follows: incident power, 1.0 kW; outer argon flow rate, 13 l min^{-1}; intermediate argon flow rate, 0.20 l min^{-1}; aerosol carrier flow rate, 0.30 l min^{-1}; nebuliser pressure, 3.0 bar; sample uptake rate, 0.75 ml min^{-1}; waste draining rate, 4.2 ml min^{-1}; vertical observation height, 12 mm above the load coil, slit widths (entrance/exit) setting, 20 μm/50 μm; integration period, 0.1 s per one data point; and photomultiplier tension, 985 V. The most prominent and sensitive atomic and ionic emission lines of noble metals were chosen and measured for the investigation: Au(I), 242.795 nm; Ir(II), 224.268 nm; Pd(I), 340.458 nm; Pt(II), 214.423 nm; Rh(II), 233.477 nm; and Ru(II), 245.657 nm.

2.2. Materials and reagents

Metalfix Chelamine chelating resin of different particle size, i.e. 150–300 and 40–80 μm, was purchased from Fluka Chemie (Switzerland). The functionality of the resin is provided by immobilised tetraethylenepentamine (1,4,7,10,13-pentaazatridecane) ligands into an organic polymer. Liquid chromatography experiments were performed using Supelco glass columns (1.0 cm of internal diameter) ended with glass frits to support the resin and Teflon stopcocks. The flow rates of solvents percolated through the resin beds were controlled by peristaltic pumps (Gilson, France).

For the evaluation of the adsorption efficiency of noble metals on the resin from different acidic media, multi-element standard solutions of Au(III), Ir(III), Pd(II), Pt(IV), Rh(III) and Ru(III) of volume of 200 ml and concentration of 1.0 μg ml^{-1} were used. The solutions were prepared from 1000 μg ml^{-1} stock solutions of the respective metals (Fluka Chemie, Switzerland) and acidified with HCl (Merck, Germany), HNO_3 (Merck, Germany) or mixtures of HCl and HNO_3 at volume ratio of 1:1 or 3:1. The final concentration of acid was corresponding to 0.10, 0.20, 0.50, 1.0 and 2.0 mol l^{-1}, respectively. In the case of the HCl and HNO_3 mixtures, the required concentration referred to the amount of H^+ ions in the solution. For the examination of the influence of concomitant metals on sorption of noble metals on the resin, working standard solutions of volume of 200 ml containing precious metals investigated at concentration of 0.10 μg ml^{-1} as well as base metals from a CertiPUR® ICP multi-element standard solution (Merck, Germany) were prepared. The concentrations of base metals were equal to 2.0, 10 and 50 μg ml^{-1}, respectively. The amount of the analytes in all the solutions used at optimisation step was selected following previously published reports [17–20].

To elute precious metals retained on Metalfix Chelamine, solutions of acids (HCl and HNO_3) of different concentrations were prepared by dilution of the concentrated reagents. In addition, solutions of KCN, KSCN, KI and $(NH_2)_2CS$ were also made for that purpose by dissolution of the suitable amounts of solid analytical grade chemicals (POCH, Poland) in water.

Ultra-pure deionised water (18.3 MΩ) obtained from EASYpure™ D7033 deionisation system (Barnstead, USA) was used for the preparation of the solutions of samples and standards. All the chemical reagents used were of analytical grade or better.

2.3. Pre-concentration and elution procedure

To fill the columns with Metalfix Chelamine of 150–300 μm particle size, a slurry method was applied. Portion of the resin as received of mass of 2.5 g was soaked in water for a half an hour, and then the resulting suspension of the resin was poured into the column. For every experiment, new aliquot of the resin was taken. Conditioning treatment of the resin bed was performed by washing it with 10 ml of a 1.0 mol l^{-1} HCl solution and followed by rinsing with deionised water (approximately 100 ml).

For the enrichment of noble metals and separation of concomitant metals, synthetic and real sample solutions were loaded onto the columns at a flow rate of 2 ml min^{-1}. The effluents from the columns were collected and analysed by the ICP-AES. In order to evaluate the efficiency of the pre-concentration procedure, the concentrations of noble and base metals found were compared with the initial concentrations in the solution loaded on the columns.

The precious metals retained on the columns were recovered by plain elution. Consequently, the resin beds were flushed with 10 or 20 ml portions of a chosen eluent (solutions of HCl, HNO_3, KCN, KSCN, KI and $(NH_2)_2CS$) at a flow rate of 2 ml min^{-1}. The aliquots referring to the dead volumes of the resin beds were discarded and then 10 or 20 ml fractions of the eluate were collected prior to determination of the recovery.

To maintain the exact determination of the analyte concentrations in the solutions of effluents and eluates collected, the adjustment of matrix contents in all standard solutions was made.

2.4. Sample preparation and analysis

An anodic sludge from the electrolytic rafination of silver, achieved from copper ores in Polish Copper Mine and Smelter Company (KGHM S.A.), was analysed. A portion of 0.15 g of dried at 450 °C and powdered sludge sample was weighted into a quartz beaker. Then, 3.0 ml of concentrated HCl were added, followed by the addition of 1.0 ml of concentrated HNO_3. The beaker was covered with a watch glass and heated on a hot plate until the sample was dissolved. After cooling, the solution was filtered through a 0.45 μm Nylon 66 membrane (Supelco, USA) to separate the precipitate of silver chloride. The precipitate was washed with a 5 ml portion of a 0.10 mol l^{-1} HCl solution, then the filtrate and washings were merged and finally diluted to the volume of 100 ml. Afterwards, 2.0 ml of the resulting solution was taken into a 250 ml calibrated flask, followed by the addition of 3.0 ml of concentrated HCl and 1.0 ml of concentrated HNO_3, and finally brought up with water to the mark. Next, the solution was passed through the column packed with Metalfix Chelamine (150–300 μm particle size) at a flow rate of 2 ml min^{-1}. Noble metals retained on the resin were recovered using 10 ml of a 1.0 mol l^{-1} solution of KCN. The eluate collected was analysed and the amounts of noble metals (Au, Ir, Pd and Pt) in the sludge sample were determined. The results obtained were compared with those determined before in our laboratory by means of hydrometallurgical procedures based on gravimetric methods [21].

3. Results and discussion

3.1. Sorption of noble metals from different acidic media

Dissolution in HNO_3, HCl or aqua regia has been recognised to be one of the most suitable method for converting of gold and platinum group elements from hydrometallurgical and geological samples into their soluble complexes [2,5,6]. For that reason, in the present contribution sorption of Au, Ir, Pd, Pt, Rh and Ru ions by Metalfix Chelamine from different acidic media, i.e. solutions of HCl, HNO_3, mixture of HCl and HNO_3 (1:1) and mixture of HCl and HNO_3 (3:1), was investigated in details using resins of different particle size (150–300 and 40–80 μm). The concentration of acids used for acidification of samples of noble metals was varied from 0.10 to 2.0 mol l^{-1} and referred to the total content of H^+ ions in the solution.

3.1.1. Metalfix Chelamine 150–300 μm

Apparently from the literature, Metalfix Chelamine of 150–300 μm particle size was not used for the enrichment of noble metals so far. As can be seen from Fig. 1. depicting adsorption efficiencies of noble metals as mean values for three independent replicates, the selectivity of that Metalfix Chelamine for Au, Ir, Pd and Pt is very high. Gold and palladium were completely retained by the resin from different solutions containing HCl, in the whole range of acid concentration applied, except for the most concentrated solutions (2.0 mol l^{-1}). It is worth noticing that these precious metals were also quantitatively adsorbed by the resin from the solutions acidified only with HNO_3. In the case of Pt, the complete retention of that metal occurred from the solutions acidified with different media but only to the concentrations not higher than 0.50 mol l^{-1}. Uptake of Ir was quantitative for the solutions acidified only with HCl or mixture of HCl and HNO_3 (3:1). In the case of medium of HNO_3 or mixture of HCl and HNO_3 (1:1), the retention efficiency of that element was reasonably high, however, did not exceed 85%. The reproducibility of all the results achieved was very good; the calculated values of one standard deviation were typically in the range from 1 to 6%.

Although, the retention of Rh on Metalfix Chelamine from 0.1 to 2.0 mol l^{-1} HCl solutions was reported before [14] to be from 72 to 97%, respectively, here, the retention efficiency found for Rh was lower than 50% for all the studied acid media. The same was also observed for Ru. Such a sorption behaviour of Metalfix Chelamine toward

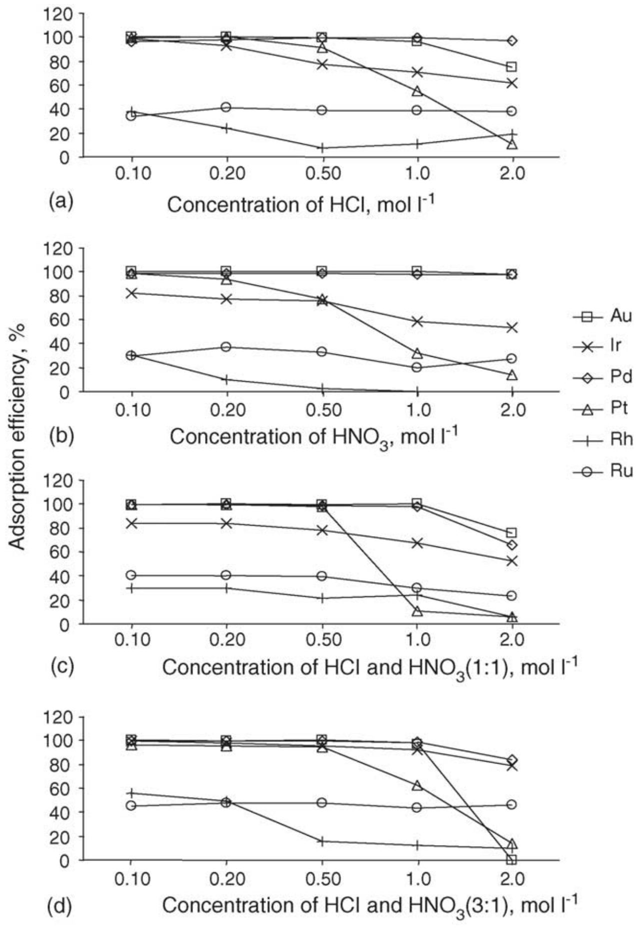

Fig. 1. Adsorption of Au, Ir, Pd, Pt, Rh and Ru from solutions of (a) HCl; (b) HNO_3; (c) HCl and HNO_3 (1:1); (d) HCl and HNO_3 (3:1) using Metalfix Chelamine of 150–300 μm particle size.

the noble metals investigated might be explained bearing in mind a role of nitrogen atoms of tetraethylenepentamine functional groups which facilitate binding of precious metals [15,22]. The nitrogen atoms of tetraethylenepentamine could fix the noble metals by an exchange of one of the chloride atoms in chlorocomplexes and linking the noble metal atoms through the coordination metal–nitrogen bonds or the protonated nitrogen atoms could form ion pairs by association with noble metal chloride complexes. The above two processes might occur simultaneously, but in acidic conditions the later one mechanism should be predominantly [15]. Formerly, it was also recognised [22] that the highly charged anhydrous chlorocomplexes of noble metals were more efficiently retained on the resin with functional groups containing nitrogen atoms than their corresponding aqua-complexes.

The values of stability constants of Rh(III) and Ru(III) chlorocomplexes are much lower in comparison to those corresponding to the complexes of Au(III), Ir(III), Pd(II) and Pt(IV) [23], and thus, in the case of Rh and Ru, formation of aqua-complexes was much probable. It could lead to weaker uptake of Rh and Ru by the resin under the studied conditions what resulted in poorer adsorption efficiencies of these two noble metals.

It was considered that the best conditions for the pre-concentration of Au, Ir, Pd and Pt on Metalfix Chelamine of 150–300 μm particle size were for the solutions moderately acidified with HCl and HNO_3 (3:1) mixtures. Under these conditions, the retention of Rh and Rh was low but reproducible.

3.1.2. *Metalfix Chelamine 40–80 μm*

Metalfix Chelamine of 40–80 μm particle size was used before for the pre-concentration of noble metals by Iglesias et al. [15] who reported sorption of Au(III), Pd(II) and Pt(IV) ions under a batch procedure from the solutions of $0.10\,\mathrm{mol\,l^{-1}}$ HCl. However, the efficiency of retention of these noble metals was 85, 70 and 100%, respectively, for Au, Pd and Pt. Later, the same laboratory group made use of the selectivity of the resin for Pd in an on-line determination of that element using mini-column system [16]. The same type of the resin was also applied earlier by Coedo et al. [14] for the separation of Au, Ir, Pd, Pt and Rh retained on the column from different base metals. In that contribution, the noble metals investigated were quantitatively adsorbed from the solutions containing HCl at concentrations higher than $0.50\,\mathrm{mol\,l^{-1}}$.

To verify the results achieved here with those described in the literature [14–16], sorption properties of 40–80 μm particle size Metalfix Chelamine toward gold and platinum group elements present in the medium of HCl were examined thoroughly. Unfortunately, the pre-conditioning procedure applied for the resin of 150–300 μm particle size, i.e. soaking in water, pouring into the column as a water slurry and then washing with a $1.0\,\mathrm{mol\,l^{-1}}$ solution of HCl, failed because the resin beds split up during the column operation due to a contracting of the resin beads. To resolve this dilemma, portions of the resin as received (mass of 2.5 g) were immersed in solutions of HCl of the same concentration as in the solutions loaded onto the columns. Next, the resin was packed into the columns by pouring as slurry. After that, solutions containing Au, Ir, Pd, Pt, Rh and Ru ions ($1.0\,\mathrm{\mu g\,ml^{-1}}$) and acidified with HCl to the concentration of 0.10, 0.20, 0.50, 1.0 and $2.0\,\mathrm{mol\,l^{-1}}$, respectively, were passed through the columns at a flow rate of $2\,\mathrm{ml\,min^{-1}}$. The content of the noble metals in the solutions leaving the columns was determined prior to the estimation of the retention efficiency (mean values for three independent replicates).

The results obtained in the present study for Metalfix Chelamine of 40–80 μm particle size confirmed the adsorption characteristics of the resin described previously [14], but only for Au, Ir, Pd and Pt. In the case of Rh, the retention efficiency found was about two times lower (range from 40 to 55%). The sorption efficiency evaluated for Ru was of the same magnitude as for Rh. For instance, for the solution of $0.20\,\mathrm{mol\,l^{-1}}$ HCl, the retention of Au, Ir, Pd, Pt, Rh and Ru on the resin was equal to 100 ± 3, 99 ± 2, 100 ± 1, 95 ± 4, 54 ± 4 and 47 ± 4%, respectively. Passing through the columns solutions of the studied precious metals and acidified with HCl to the concentration of 1.0 mol l^{-1}, the adsorption efficiencies found were as follows: 100 ± 1% for Au, 98 ± 2 for Ir, 97 ± 3% for Pd, 90 ± 3% for Pt, 52 ± 2% for Rh and 44 ± 4% for Ru.

3.2. Solvent elution

Elution experiments were conducted using 200 ml solutions of noble metals (1.0 μg ml^{-1}), acidified with HCl and HNO_3 (3:1) mixture to the concentration of 0.20 mol l^{-1}. After loading the solutions onto the columns packed with Metalfix Chelamine at a flow rate of 2 ml min^{-1}, solutions of different reagents capable of forming stable complexes with Au, Ir, Pd and Pt [24], i.e. HCl, KCN, KI, KSCN and $(NH_2)_2CS$, and HNO_3 in addition, were used for the recovery of noble metals from the resin. For that aim, 10 or 20 ml portions of the elution solutions were passed through the columns at a flow rate of 2 ml min^{-1}. The fractions of the eluate corresponding to the volumes of 10 and 20 ml, respectively, were collected and then analysed by the ICP-AES method to assess the desorption efficiencies for Au, Ir, Pd and Pt. The contents of Rh and Ru were not measured due to the partial uptake of these two noble metals by the resin.

The results (mean values for three replicates with standard deviations) achieved for Metalfix Chelamine of 150–300 μm particle size are given in Tables 1–3. As apparent from the recovery values obtained for different eluents used, the chlorocomplexes of the noble metals investigated (Au, Ir, Pd and Pt) had a very high affinity to Metalfix Chelamine, which bound them very strongly. Unfortunately, usage of solutions of such reagents as HCl, HNO_3, KI, KSCN and $(NH_2)_2CS$, recognised formerly to be beneficial for the off-line recovery of gold and platinum group elements from various adsorption and ion-exchange media [17–20,25], was ineffective for the simultaneous release of Au, Ir, Pd and Pt.

Reasonably good recoveries were obtained for thiourea solutions. Application of a 1.0 mol l^{-1} solution of that complexing agent led to the complete recovery of Pd and over 60% release of Au and Pt but it was useless for the release of Ir. Very similar results were reported before in Ref. [15] where in batch experiments Pd was completely eluted from Metalfix Chelamine while Au and especially Pt were recovered partially.

Table 2
Recoveries (in %) of Au, Ir, Pd and Pt from Metalfix Chelemine of 150–300 μm particle size obtained using KCN and KI stripping solutions ($n = 3$)

	Eluent			
	Au	Ir	Pd	Pt
KCN				
10 ml of 0.50 mol l^{-1}	103 ± 2	99 ± 3	101 ± 2	72 ± 2
20 ml of 0.50 mol l^{-1}	102 ± 2	99 ± 3	100 ± 3	83 ± 2
10 ml of 1.0 mol l^{-1}	100 ± 2	104 ± 4	102 ± 4	97 ± 3
20 ml of 1.0 mol l^{-1}	103 ± 4	102 ± 3	101 ± 3	101 ± 2
KI				
10 ml of 0.50 mol l^{-1}	11 ± 2	0.8 ± 0.3	ND	15 ± 2
20 ml of 0.50 mol l^{-1}	36 ± 3	0.9 ± 0.4	ND	29 ± 2
10 ml of 1.0 mol l^{-1}	21 ± 3	5.6 ± 0.5	ND	14 ± 2
20 ml of 1.0 mol l^{-1}	57 ± 3	11 ± 2	ND	27 ± 3

ND, not detected.
Error terms are 1 standard deviation.

Here, the best results were achieved for solutions of KCN, which appeared to be very suitable for the quantitative recovery of Au, Ir, Pd and Pt (see Table 2). Use of 10 ml of a 1.0 mol l^{-1} solution of KCN provided desorption of all the noble metals examined with the average efficiency equal to 101%. Such a concentration of KCN was found to be tolerable by the plasma without any disturbance what resulted in good precision of the intensity measurements. Previously, usage of 1.0 mol l^{-1} KCN solution was also described to be useful for the quantitative desorption of Pd from Amberlite XAD-16 prior to the determination by F-AAS [26].

In the case of Metalfix Chelamine of 40–80 μm particle size, the elution approach by means of column operation was unfeasible. The main problem associated with that resin was its swelling or contracting when stripping solutions were

Table 1
Recoveries (in %) of Au, Ir, Pd and Pt from Metalfix Chelemine of 150–300 μm particle size obtained using HCl and HNO_3 stripping solutions ($n = 3$)

	Eluent			
	Au	Ir	Pd	Pt
HCl				
10 ml of 4.0 mol l^{-1}	5.0 ± 0.3	3.5 ± 0.1	9.4 ± 0.5	34 ± 1
20 ml of 4.0 mol l^{-1}	6.1 ± 0.4	12 ± 1	52 ± 2	50 ± 3
10 ml of 6.0 mol l^{-1}	11 ± 1	2.4 ± 0.2	17 ± 2	32 ± 2
20 ml of 6.0 mol l^{-1}	12 ± 1	10 ± 1	60 ± 2	49 ± 2
HNO_3				
10 ml of 3.0 mol l^{-1}	ND	8.9 ± 0.8	0.9 ± 0.1	36 ± 1
20 ml of 3.0 mol l^{-1}	1.3 ± 0.2	20 ± 2	1.3 ± 0.3	48 ± 2
10 ml of 5.0 mol l^{-1}	68 ± 3	46 ± 3	1.7 ± 0.1	31 ± 2
20 ml of 5.0 mol l^{-1}	70 ± 3	73 ± 4	3 ± 1	43 ± 2

ND, not detected.
Error terms are 1 standard deviation.

Table 3
Recoveries (in %) of Au, Ir, Pd and Pt from Metalfix Chelemine of 150–300 μm particle size obtained using KSCN and $(NH_2)_2CS$ stripping solutions ($n = 3$)

	Eluent			
	Au	Ir	Pd	Pt
KSCN				
10 ml of 0.50 mol l^{-1}	ND	1.1 ± 0.2	ND	12 ± 1
20 ml of 0.50 mol l^{-1}	ND	5.5 ± 0.5	ND	24 ± 2
10 ml of 1.0 mol l^{-1}	ND	24 ± 1	ND	15 ± 1
20 ml of 1.0 mol l^{-1}	1.6 ± 0.3	52 ± 2	ND	32 ± 2
$(NH_2)_2CS$				
10 ml of 0.50 mol l^{-1}	17 ± 2	ND	95 ± 2	57 ± 2
20 ml of 0.50 mol l^{-1}	28 ± 2	ND	100 ± 2	68 ± 3
10 ml of 1.0 mol l^{-1}	61 ± 2	ND	102 ± 3	64 ± 2
20 ml of 1.0 mol l^{-1}	69 ± 3	ND	103 ± 3	73 ± 3

ND, not detected.
Error terms are 1 standard deviation.

passed through the columns for the release of Au, Ir, Pd and Pt. It resulted in break up of the resin beds and in these conditions performance of the elution procedure was impossible. Probably for that reason, to liberate noble metals from the resin, Coedo et al. [14] used the procedure of its decomposition instead of the elution approach. In the case of Ref. [16], where Pd(II) was adsorbed by Metalfix Chelamine of 40–80 μm particle size from the solutions of 0.1 mol l^{-1} HCl, to avoid differences in the osmotic pressures of the external and internal solutions on the column, a 0.5 mol l^{-1} solution of thiourea in 0.1 mol l^{-1} HCl was used for the elution of the analyte.

3.3. *Effect of co-existing metal ions*

In order to examine the effect of different co-existing metal ions on the process of sorption of Au, Ir, Pd and Pt, 200 ml solutions containing the noble metals (0.1 μg ml^{-1}) and various base metals (Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn) at the concentrations of 2, 10 and 50 μg ml^{-1} were loaded onto the columns packed with Metalfix Chelamine (150–300 μm) at a flow rate of 2 ml min^{-1}. The solutions were acidified with HCl and HNO_3 mixture (3:1) to the concentrations of 0.10, 0.20 and 0.50 mol l^{-1}. After that, the resin beds were flushed with 10 ml of a 1.0 mol l^{-1} solution of KCN. The effluents and the eluates were collected and the concentrations of Au, Ir, Pd and Pt as well as other metals were determined.

It was observed that the accompanying metals did not affect the retention of noble metals on the resin. Under the conditions examined, Au, Ir, Pd and Pt were retained on the columns with the efficiency being within the range from 95 to 106%. Furthermore, it was established that the base metal ions, i.e. Al(III), Cd(II), Co(II), Cr(III), Cu(II), Fe(III), Mn(II), Ni(II), Pb(II) and Zn(II), were not bound by the resin under the mentioned experimental conditions. The recoveries of the co-existing transition metals from the effluents collected were typically ranged from 98 ± 3 to 111 ± 4% ($n = 3$). With respect to that, it was possible to separate precious metals (Au, Ir, Pd and Pt) from various base metals from solutions acidified with aqua regia. Formerly, the possibility of separation of noble metals from different concomitant metals, e.g. Al, Cr, Cu, Fe, Ni, Mn, which were not adsorbed by Metalfix Chelamine at low pH adjusted with HCl was also reported [14,15].

Concluding, usage of Metalfix Chelamine in the pre-concentration procedure of Au, Ir, Pd and Pt presented here had such an advantage over the procedures using ion-exchangers [24,25] that it was not necessary to use sequential elution approach for the separation of interfering transition metals forming negatively charged chlorocomplexes and retaining on the column together with the noble metals.

3.4. *Evaluation of the procedure and analytical application*

The precision of the whole procedure, expressed as relative standard deviation, was of the order of 4% for all the noble metals examined. In comparison to direct measurements, the detection limits (3σ) attained with the pre-concentration protocol proposed were enhanced over a one order of magnitude and equalled to 0.5, 2, 0.8 and 1 ng ml^{-1}, respectively, for Au, Ir, Pd and Pt. The enrichment factor achieved for Au, Ir, Pd and Pt was equal to 20 and was significantly improved concerning those reported so far for Metalfix Chelamine of 40–80 μm particle size [14,15].

Table 4
Contents (in %) of Au, Ir, Pd and Pt in anodic sludge sample

Element	From Ref. [19]	This work[a]	R.S.D. (%)
Au	10.2	10.8 ± 0.4	4.2
Ir	–	2.29 ± 0.09	3.9
Pd	8.8	9.1 ± 0.4	4.1
Pt	5.3	5.0 ± 0.2	3.5

[a] Mean values for three individual analyses.

To assess the applicability of Metalfix Chelamine (150–300 μm particle size) column pre-concentration to the determination of noble metals in the solutions arising from the digestion of the metallurgical samples in aqua regia, the devised procedure was applied for measurements of Au, Ir, Pd and Pt in a set of solutions of a very high content of matrix base metals, i.e. up to 5% of Cd, Cu, Fe and Zn, and spiked with the noble metals to the concentrations in a range from 0.10 to 20 μg ml^{-1}. The recoveries of Au, Ir, Pd and Pt from the studied sample solutions were found to be from 95 to 103%.

Additionally, the sample of an anodic sludge from the electrolytic rafination of silver (Polish Copper Mine and Smelter Company, Lubin, Poland) was prepared according to the description given in Section 2.4 and analysed using the method proposed. The results obtained are presented in Table 4 and compared with those achieved earlier in our laboratory using gravimetric methods [21]. As can be seen, the previous and the present outcomes are in a very good accordance.

4. Conclusions

The present study demonstrates that Metalfix Chelamine in acid media has a high affinity for Au, Ir, Pd and Pt ions over various co-existing metal ions (Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn). The resin of 150–300 μm particle size is much more favourable for column operation than the resin of lower particle size. The later one resin is more prone to swelling or contracting by differences in pH and ionic strength of the external and internal solutions in the resin bed. Thus, the recovery of the noble metals retained from the resin of that particle size by solvent elution is problematical.

In contrast to the already reported contributions, the proposed procedure based on usage of Metalfix Chelamine of 150–300 μm particle size enables quantitative adsorption of Au, Ir, Pd and Pt from different acid solutions, especially a medium of aqua regia. The quantitative recovery of Au, Ir, Pd and Pt can be readily performed in a quick and convenient way by means of a KCN solution.

Reasonably high pre-concentration factor, good precision and reliability of the results as well as possibility of separation of noble metals from different concomitant transition metals, present usually in geological and metallurgical samples, make the described procedure attractive and suitable for the determination of noble metals by the inductively coupled plasma atomic emission spectrometry and other spectrometric methods.

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