Microchim Acta 150, 159–165 (2005)
DOI 10.1007/s00604-005-0343-6

Microchimica Acta
Printed in Austria

Original Paper

On the Applicability of Duolite GT-73 to Column Preconcentration of Gold and Palladium Prior to Determination by Inductively Coupled Plasma Atomic Emission Spectrometry

Pawel Pohl* and **Bartlomiej Prusisz**

Wroclaw University of Technology, Institute of Inorganic Chemistry and Metallurgy of Rare Elements,
Wybrzeze Wyspianskiego 27, 50-370 Wroclaw, Poland

Received November 29, 2004; accepted February 8, 2005; published online May 9, 2005

Abstract. The preconcentration of Au and Pd on Duolite GT-73 chelating resin with the thiol functional group was investigated prior to determination of these noble metals by means of inductively coupled plasma atomic emission spectrometry. It was found that Au^{III} and Pd^{II} were retained on the resin along with other concomitant metals (Al, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb and Zn) from different HCl-containing media. A two-step elution procedure was developed for the release of the noble metals. First $4.0\,\mathrm{mol\,L^{-1}}$ HNO_3 solution was used to elute the base metals. The recovery of Au and Pd was performed afterwards using $0.50\,\mathrm{mol\,L^{-1}}$ solution of $(NH_2)_2CS$. Retrieval of Au and Pd retained on Duolite GT-73 was also carried out by decomposition of the resin in the open vessel system using H_2SO_4 with H_2O_2. The detection limits of Au and Pd evaluated for the devised protocol, with a preconcentration factor of 50, were $0.085\,\mathrm{\mu g\,L^{-1}}$ and $0.28\,\mathrm{\mu g\,L^{-1}}$, respectively. The proposed method was applied to the determination of Au and Pd in spiked electrolytic bath samples.

Key words: Preconcentration; Duolite GT-73; gold; palladium; inductively coupled plasma atomic emission spectrometry.

The separation and the preconcentration of gold and platinum group elements (PGE) has long been a problem of particular interest to the metallurgical industry and in geo-chemical exploration, because these metals play an important part in a variety of industrial processes and products [1]. The significance of developing accurate and dependable analytic procedures for noble metal analysis is related to their increasing presence in the environment and to a growing interest in the elucidation of their role in living organisms and their impact on human health [1, 2]. However, direct determination of traces of noble metals in complex geological, metallurgical or environmental samples by means of atomic spectrometry methods usually poses numerous difficulties due to the low sensitivity and selectivity of the instrumentation applied. Typically, prior to analysis, advanced analytical schemes of sample treatment are required, comprising initial separation of the analytes from other concomitant sample constituents and/or subsequent enrichment of the noble metals.

Aside from nickel sulfide fire assay and solvent extraction [1], ion exchange and adsorption [4–10] are the most extensively used methods for preconcentration and separation of Au and PGE. It is well-known that in the procedures of enrichment and

---

* Author for correspondence. E-mail: pawel.pohl@pwr.wroc.pl

isolation of the precious metals, the resin of choice should have a much stronger affinity for the selected metals than for the base metals in order to allow not only their successful preconcentration but also their separation. This requirement can be fulfilled by ion exchange of the chlorocomplexes of the noble metals using commercially available strong anion exchangers with quaternary amine groups, e.g. Dowex 1 [4–6], or weak anion exchange resins with tertiary amine groups, e.g. Amberlite IRA-35 [7]. In addition, commercial macroreticular polystyrene-divinylbenzene co-polymers (e.g. Amberlite XAD-16 [8, 9]) or nanometer-size titanium dioxide [10] have been employed for that purpose mainly due to the high resistance of these materials to chemicals and their special adsorption properties. Beside conventional ion-exchangers and adsorbents, a series of novel poly-epoxy macroporous chelating resins has also been synthesized [11, 12], using the benefits provided by different functional groups containing N, O and S electron donor atoms. These atoms, according to the theory of hard and soft acids and bases, may act as hard, intermediate or soft bases, respectively, and for that reason interact with the precious metals as soft acids [13].

The resins with thiol functional groups have been of particular interest concerning noble metal preconcentration purposes. Formerly, two of such commercially available resins, namely Spheron Thiol 1000 [14, 15] and Duolite GT-73 [16], were used for the enrichment of Au and Pd; however, the latter was mainly used in industrial processes for removing heavy metals from wastewaters (e.g. Hg [17]) rather than for analytical applications. Unfortunately, serious drawbacks concerning the preconcentration and recovery approaches have been reported in the cited publications. The use of batch methods, for instance, was time-consuming during the enrichment and retrieval steps; strong binding of precious metals led to difficulties in eluting Au and Pd, which resulted in the recoveries being far from quantitative, i.e. 59% and 60% for Pd [14, 16], and 80% for Au [16].

The problem of time consumption and low effectiveness of batch protocols prompted us to investigate the sorption properties of Au and Pd on Duolite GT-73 resin employing the column-based procedure prior to measurement of these noble metals by inductively coupled plasma atomic emission spectrometry. The effect of the concentration of HCl and mixtures of HCl and HNO_3 as well as the presence of various base metals on the adsorption efficiency of Au and Pd was studied. Mineral acid solutions of different concentrations along with solutions of complexing agents were used to elute the retained noble metals and co-existing transition metals. Digestion of the resin was also examined as an approach to the recovery of the precious metals. With regard to this, various mineralization procedures using different mixtures of the reagents and masses of the resin were tested in order to find the appropriate method for complete decomposition of Duolite GT-73.

Experimental

Instrumentation

A sequential atomic emission spectrometer of inductively coupled argon plasma JY 38S (ISA Jobin Yvon, France), equipped with a cyclone spray chamber (ISA Jobin Yvon, France) and a concentric nebulizer TR 50-C1 (J.E. Meinhard, Associates INC California, USA) was used. The operating parameters for the ICP-AES apparatus were set as follows: supplied power: 1.0 kW; plasma gas flow rate: 13 L min^{-1}; auxiliary gas flow rate: 0.25 L min^{-1}; nebulizing gas flow rate: 0.30 L min^{-1}; pressure on nebuliser: 3.0 bar; observation height: 12 mm above the load coil; slit width (entrance/exit): 20 μm/50 μm; integration time per one point: 0.10 s; sample uptake flow rate: 1.0 mL min^{-1}; drain flow rate: 4.2 mL min^{-1}. The following analytic lines of Au and Pd were chosen for the investigation: Au 242.795 nm and Pd 340.458 nm. For the other noble metals and the base metals examined in this study, the following sensitive and interference-free ionic and atomic emission lines were measured: Ir 224.268 nm, Pt 214.423 nm, Rh 343.489 nm, Ru 240.272 nm, Al 396.152 nm, Ca 317.933 nm, Cd 228.802 nm, Co 228.616 nm, Cr 205.559 nm, Cu 324.754 nm, Fe 259.940 nm, Mg 285.213 nm, Mn 259.373 nm, Ni 221.647 nm, Pb 220.353 nm and Zn 202.548 nm.

A closed-vessel microwave digestion unit MLS-1200 MEGA (Milestone, Italy) with a microwave digestion rotor MDR-1000/6/100/110 and six 100 mL Teflon vessels was used for the digestion of the resin. The following program was run for the digestion procedure: 1st step – 250 W for 2 minutes, 2nd step – 0 W for 5 minutes, 3rd step – 250 W for 5 minutes, 4th step – 400 W for 5 minutes, 5th step – 0 W for 5 minutes, 6th step – 600 W for 5 minutes, and finally ventilation for 5 minutes.

Reagents and Materials

Macroporous ion exchange resin Duolite GT-73 (mesh size 16–50, total capacity of 1.4 eq L^{-1}) based on a cross-linked polystyrene matrix, was purchased from Supelco (USA). The functionality of the resin is provided by thiol (–SH) groups.

De-ionized water, obtained with the EASYpure^{TM} system, model D7033 (Barnstead, USA), was used throughout. Single-element stock standard solutions (1000 μg mL^{-1}) of Au^{III} and Pd^{II} and the other noble metals, i.e. Ir^{III}, Pt^{IV}, Rh^{III} and Ru^{III}, were from Fluka Chemie GmbH (Switzerland). A multi-element standard solution containing Al, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Pb and Zn was obtained from Merck (Germany). Working solutions of noble metals (0.1 or 1.0 μg mL^{-1}) were prepared by dilution of the appropriate stock solutions. For acidification of the solutions, HCl (Merck, Germany) and mixtures of HCl and HNO_3 (Merck, Germany) at volume ratios of 1:1 or 3:1 were applied. The concentrations of H^+ ions in the resulting solutions was equal to 0.010, 0.050 and 0.10 mol L^{-1}, corresponding to a pH of 2.0, 1.3 and 1.0, respectively.

Other reagents, i.e. H_2SO_4, H_2O_2, KSCN, KCN and $(NH_2)_2CS$, were of analytical grade and purchased from POCH (Poland).

Column Preparation

Glass columns (Supelco, USA) with an inner diameter of 1.0 cm, equipped with porous frits and Teflon stopcocks were used. The resin as received (portion of 1.25 g) was packed into the columns by pouring it as water slurry. The height of the resin beds was ca. 2.5 cm. The bottoms of the columns were connected to the peristaltic pumps (LabCraft, France) via Tygon tubes to control the flow rate of the aliquots of the effluents and the eluates coming from the columns. Before loading the solutions onto the columns, the resin beds were conditioned by flushing at a flow rate of 0.50 mL min^{-1} with 20 mL of 2.0 mol L^{-1} HCl solution followed by 50 mL of water.

General Procedure

Test solutions of Au and Pd (with or without the concomitant metal ions) of 100 mL were passed through the columns at a flow rate of 0.50 mL min^{-1}. The effluents from the columns were collected prior to determining the metal contents by ICP-AES and assessing the retention efficiencies (mean values of three independent replicates with confidence intervals for 90% confidence level).

The procedure of recovering the retained metals by plain elution was performed by rinsing the columns with 20 mL portions of the selected eluents at a flow rate of 0.50 mL min^{-1}. Each 20 mL fraction of the eluate was collected discarding the first 1 mL aliquot of the solution referred to the dead volume of the resin bed. The eluates were subjected to analysis of each metal by ICP-AES, and then the desorption efficiency of the elution procedure was calculated (mean values of three independent replicates with confidence intervals for 90% confidence level).

Another approach to recovering Au and Pd from the columns was the decomposition of the resin after the preconcentration/separation step. This was carried out by wet digestion in the open vessel system using concentrated H_2SO_4 and followed by addition of 30% (m v^{-1}) H_2O_2 solution. To this end, after loading the solutions containing the noble metals and the matrix elements, the columns were rinsed with 20 mL of 4.0 mol L^{-1} HNO_3 solution in order to release the base metals. Next, the resin beds were transferred from the columns into 150 mL borosilicate glass beakers, and 10 mL of concentrated H_2SO_4 was added. The beakers were covered with watch glasses and heated on a hot plate until no solid residues could be observed in the solutions and all signals of charring had disappeared (ca. 3–4 hours). Then the solutions were cooled, 5 mL of H_2O_2 was added, and the solutions were heated again for at least half an hour until they turned colorless. Finally, the resulting solutions were transferred to 25 mL calibrated flasks and analyzed for Au and Pd. The efficiency of the digestion recovery procedure was evaluated as the mean value of three independent replicates.

Determination of the Elements

Determination of the noble metals and the other metals investigated in all the effluents and eluates was carried out by the calibration curve method. To minimize potential matrix effects, the concentrations of acids and complexing agents in the standard solutions used for calibration were matched exactly with those in the solutions analyzed. In the case of solution measurements performed after decomposition of the resins, the standard addition method was applied to eliminate interference effects from complex matrices and differences in the viscosity of sample and standard solutions.

Results and Discussion

At the outset, in order to verify the resin's purity and to select a suitable preconditioning treatment for Duolite GT-73, several decomposition methods for digestion of the resin were examined. These included open vessel digestion procedures using HNO_3, a mixture of HNO_3 and H_2O_2, a mixture of H_2SO_4 and H_2O_2 and finally a mixture of H_2SO_4 and HNO_3, as well as digestions in a closed pressurized system facilitated by microwave energy using a mixture of HNO_3 and H_2O_2 alongside a mixture of HNO_3 and H_2SO_4.

Finding an efficient method of resin digestion was difficult due to the high resistivity of the styrene copolymerized with divinylbenzene matrix and the large particle size distribution of the resin beads (from 0.3 to 1.2 mm in diameter). The mineralization procedure in the open vessel system using H_2SO_4 (10 mL) and H_2O_2 (5 mL) appeared to be better for complete destruction of the resin (mass of 1.25 g) than the other methods studied. This was mainly because of the very high temperature of the boiling point of the eutectic mixture of sulfuric acid and water and the strong oxidation properties of the acid itself. The mixture of H_2SO_4 (10 mL) and HNO_3 (5.0 mL) was also beneficial to the decomposition of the polymeric matrix of the resin, but it was discarded due to high content of acids in the resulting solutions. Wet digestion methods using HNO_3 (10 mL) and the mixture of HNO_3 (5.0 mL) and H_2O_2 (5.0 mL) in the open vessel system were useless; no acid attack on the resin was observed even after several hours of heating.

In the case of wet digestion in the closed microwave system, the use of both microwave digestion procedures, i.e. with a mixture of HNO_3 (5.0 mL) and H_2O_2 (1.0 mL) as well as a mixture of HNO_3 (5.0 mL) and H_2SO_4 (1.0 mL), was efficient (the resin was completely digested). However, the only limitation was the mass of the organic matter with regard to safe performance of the decomposition procedure. It was found that the maximum portion of resin to be digested should not exceed 0.6 g if potentially dangerous reactions and high over-pressure was to be avoided.

Conditioning of the Resin

The element concentrations in Duolite GT-73 determined after wet digestion of the resin are listed in Table 1. The results obtained for different decomposition procedures are in very good agreement. It was found that the resin as received did not contain the metals of interest, i.e. Au, and Pd, or the other noble metals (Ir, Pt, Rh and Ru). Unfortunately, it had a very high degree of metal contamination, especially Fe, Ni, Al, Cr and Mn, which probably derived from the manufacturing process. Consequently, in order to condition the resin as received and to remove the impurities, the resin beds were flushed at a flow rate of 0.50 mL min^{-1} with 20 mL of 1.0, 2.0 and 4.0 mol L^{-1} HCl solutions, respectively. The effluents from the columns were collected as 20 mL fractions and subjected to analysis. Then the quantities of the metals released from the resin were calculated. They are given in Table 2 for the preconditioning procedure performed using 1.0 and 2.0 mol L^{-1} solutions of HCl.

It can be seen that washing the resin with HCl solutions is a satisfactory means of conditioning since the initial contents of such metals as Fe, Mn and Ni had appreciably dropped. Since there was practically no difference between the effect of 2.0 and 4.0 mol L^{-1} HCl solutions on the metal release, the solution of lower concentration was used to condition Duolite GT-73 prior to all further column preparations.

After conditioning the column beds with 20 mL of 2.0 mol L^{-1} HCl solution, the remaining metals were determined by decomposition of the resin with a mixture of H_2SO_4 and H_2O_2 in the open vessel system (column C of Table 2). The results achieved were in agreement with the values obtained when subtracting the concentrations of the metals removed from the resin by washing it with HCl solution (column B of Table 2) from the values obtained with the fresh resin (column A of Table 1). Although the metal concentrations in the resin were still considerable, especially in the case of Al, Cr, Fe and Ni, they contributed only to the blanks obtained during the wet digestion recovery procedure and did not affect the measurements of Au and Pd.

Table 1. Metal contents[a] (in μg g^{-1}) in Duolite GT-73 obtained after decomposition of the resin in mixtures of: A, H_2SO_4 and H_2O_2; B, HNO_3 and H_2O_2; C, H_2SO_4 and HNO_3

Metal	A[b]	B[c]	C[c]
Al	7.25 ± 1.64	6.93 ± 0.87	7.04 ± 0.64
Cd	0.0757 ± 0.0140	nd	nd
Co	0.938 ± 0.021	0.877 ± 0.009	0.886 ± 0.095
Cr	14.7 ± 1.7	14.5 ± 1.1	14.2 ± 1.0
Cu	0.969 ± 0.054	1.03 ± 0.04	0.916 ± 0.026
Fe	256 ± 8	221 ± 3	252 ± 8
Mn	2.47 ± 0.08	2.17 ± 0.02	2.39 ± 0.03
Ni	39.5 ± 0.8	37.1 ± 1.2	38.9 ± 1.1
Pb	nd	nd	nd
Zn	0.257 ± 0.071	0.262 ± 0.078	0.258 ± 0.066

[a] Mean values for n = 3 ± confidence intervals for p = 0.10.
[b] Digestion in the open vessel system, mass of resin used 1.25 g.
[c] Digestion in the microwave pressurized closed system, mass of resin used 0.62 g, *nd* not detectable.

Table 2. Amounts of metals (in μg g^{-1}) released from Duolite GT-73 by conditioning the resin beds with A, 1.0; and B, 2.0 mol L^{-1} HCl solutions; and C, remaining in the resin after preconditioning

Metal	A	B	C[a]
Al	3.13 ± 0.09	3.74 ± 0.12	11.0 ± 1.2
Cd	nd	nd	nd
Co	0.602 ± 0.031	0.691 ± 0.102	0.244 ± 0.020
Cr	0.852 ± 0.016	0.899 ± 0.007	13.7 ± 0.7
Cu	0.379 ± 0.046	0.378 ± 0.041	0.549 ± 0.045
Fe	160 ± 3	163 ± 2	96.3 ± 3.4
Mn	1.59 ± 0.02	1.78 ± 0.23	0.671 ± 0.050
Ni	23.3 ± 0.3	23.9 ± 1.2	14.1 ± 1.3
Pb	nd	nd	nd
Zn	nd	nd	0.263 ± 0.031

[a] Digestion in the open vessel system using H_2SO_4 and H_2O_2 mixture, *nd* not detectable.

Adsorption of the Noble Metals

To investigate the adsorption of Au^{III} and Pd^{II} on Duolite GT-73 from different HCl-containing media, 100 mL solutions of noble metals with concentrations of 1.0 μg mL^{-1} and pH values of 1.0, 1.3 and 2.0, respectively, were loaded onto the columns. The effluents from the columns were collected, and the concentrations of the noble metals were measured by ICP-AES. The percentages of the retained metals were calculated as the ratios of their concentrations in the effluents to the concentrations in the initial solutions.

It was established that Au and Pd were quantitatively retained (from 98.9 ± 3.7 to 101 ± 4%) on Duolite GT-73 from all examined solutions, i.e. in the media of HCl and mixtures of HCl and HNO_3 at volume ratios of 1:1 or 3:1. Under these conditions, Au and Pd were probably present in the solutions in the form of $AuCl_4^{-}$ and $PdCl_4^{2-}$ complexes which are selectively sorbed by the anionic exchangers having functional groups with sulphur and nitrogen donor atoms [7].

Previously Duolite GT-73 was employed for the preconcentration of Au^{III} and Pd^{II} from the solutions acidified with HCl using the batch method [16]. The quoted contribution reported high retention of these two noble metals, however, obtained after 24 hours of mixing the resin with the sample solutions (100 mL). In this case column operation was used, and complete retention of Au and Pd chlorocomplexes from the 100 mL solutions was achieved after 3.3 hours.

In addition, the sorption properties of other noble metals (Ir, Pt, Rh and Ru) on Duolite GT-73 were also investigated. Unfortunately, it was found that Ir, Pt and Rh ions were not sorbed by the resin in the range of the examined solution pH. Ruthenium, under these conditions, was only partially retained.

Adsorption of the Noble Metals in the Presence of Base Metals

To check the retention efficiency for Au and Pd in the presence of various concomitant metals, solutions of noble metals ($0.10\,\mu g\,mL^{-1}$) containing Al, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Pb and Zn at concentrations corresponding to 20 and $200\,\mu g\,mL^{-1}$, respectively, were used. The solutions were acidified to pH 1.3 and 2.0 using HCl, a mixture of HCl and HNO_3 (1:1) or a mixture of HCl and HNO_3 (3:1). After passing the solutions through the columns packed with Duolite GT-73, the effluents were collected and the concentrations of metals were measured to assess the adsorption efficiency for Au and Pd as well as the base metals.

Table 3. Efficiencies (in %) of adsorption of noble and base metals from HCl media

Metal	pH 1.3	pH 2.0
Au	99.5 ± 0.7	101 ± 1
Pd	103 ± 2	99.9 ± 0.8
Al	96.6 ± 2.7	99.1 ± 1.0
Ca	97.2 ± 4.0	96.7 ± 3.7
Cd	99.8 ± 0.2	99.8 ± 0.2
Co	99.9 ± 0.2	100 ± 0.2
Cr	99.7 ± 0.7	99.9 ± 0.2
Cu	99.5 ± 0.3	99.7 ± 0.2
Fe	99.5 ± 0.2	99.8 ± 0.2
Mg	99.4 ± 0.8	99.4 ± 0.7
Mn	99.9 ± 0.2	99.9 ± 0.2
Ni	99.9 ± 0.2	99.9 ± 0.2
Pb	99.4 ± 1.7	99.6 ± 0.2
Zn	99.8 ± 0.7	99.9 ± 0.2

It was established that the studied matrix metals present in the solutions at levels of 200 and 2000 times higher than the concentration of Au and Pd had no effect on their retention on Duolite GT-73. The noble metals were adsorbed on the columns with an average efficiency of 100 ± 1% for Au and 101 ± 2% for Pd. It was also determined that under these conditions the examined base metals were retained on the resin as well. This is demonstrated for instance by the adsorption efficiencies evaluated for the solutions acidified with HCl (see Table 3).

Recovery of the Metals by Plain Elution

Previously, only batch desorption experiments for the retrieval of Cd and Cu [19] and Au, Pd and Cu [16] were performed on Duolite GT-73 using the solutions of HCl, H_2SO_4 and $(NH_2)_2CS$. However, the procedures in both cited contributions were relatively long (up to 24 hours) and, in addition, the results attained for the noble metals were rather unsuitable for analytical purposes, i.e. a recovery of 60% for Pd and 80% for Au was obtained using the solution of thiourea [16].

In the present study, with respect to the recovery of Au and Pd adsorbed from the solutions acidified with HCl and mixtures of HCl and HNO_3, the following eluents found so far to be appropriate for the release of these two noble metals from different ion exchangers [6–10, 16, 20, 21] were employed: solutions of HCl and HNO_3 at concentrations of 1.0, 2.0 and $4.0\,mol\,L^{-1}$, respectively, and the solutions of the complexing agents (KSCN, KCN and $(NH_2)_2CS$) at concentrations of $0.50\,mol\,L^{-1}$. After loading the solutions of Au and Pd ($0.10\,\mu g\,mL^{-1}$) and the base metals (at concentrations 200 and 2000 higher than the concentration of the precious metals), a 20 mL portion of each stripping solution was passed through the columns and the corresponding 20 mL fraction of the eluate was collected and then analyzed for noble and base metals prior to evaluation of their recoveries.

It was found that the solutions of HCl and HNO_3 were ineffective for desorption of Au and Pd. The recoveries evaluated for these metals were lower than 1%. As apparent from the data in Table 4 giving the desorption percentages for Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn, applying 20 mL acid solutions, especially $4.0\,mol\,L^{-1}$ HNO_3, was very suitable for the release of all the base metals (except for Cr) with an efficiency higher than 90%. This possibility was of

Table 4. Recoveries (in %) of noble and base metals using 20 mL portions of A, 2.0 mol L^{-1} HCl; B, 4.0 mol L^{-1} HCl; C, 2.0 mol L^{-1} HNO_3 and D, 4.0 mol L^{-1} HNO_3

Metal	A	B	C	D
Au	0.9 ± 0.3	0.5 ± 0.2	0.2 ± 0.1	0.2 ± 0.2
Pd	0.1 ± 0.1	0.4 ± 0.2	0.7 ± 0.3	0.2 ± 0.1
Al	64.6 ± 0.8	72.0 ± 3.4	92.5 ± 3.4	106 ± 3
Cd	96.9 ± 5.0	96.0 ± 9.8	99.4 ± 3.2	103 ± 5
Co	80.6 ± 4.7	89.1 ± 6.7	91.3 ± 3.7	98.3 ± 5.0
Cr	62.4 ± 4.0	73.1 ± 0.5	69.0 ± 1.7	74.7 ± 2.0
Cu	81.3 ± 3.5	80.3 ± 1.3	85.6 ± 3.4	92.1 ± 2.9
Fe	98.2 ± 6.9	104 ± 7	90.6 ± 5.9	94.7 ± 6.7
Mn	87.2 ± 1.5	91.8 ± 3.4	98.6 ± 1.7	105 ± 2
Ni	70.8 ± 5.7	80.8 ± 11	79.7 ± 4.9	90.3 ± 6.6
Pb	101 ± 8	102 ± 2	85.4 ± 6.7	97.3 ± 5.6
Zn	85.7 ± 3.4	94.3 ± 6.2	99.8 ± 1.5	107 ± 5

special interest since it enabled the separation of Au and Pd from the concomitant metals by release of these from the column later on using HNO_3 solution. The same observation for Duolite GT-73 had been reported in Refs. [16, 19], where Cu and Cd were completely desorbed by means of moderately concentrated HCl solutions, while the noble metals under these conditions remained unresolved.

The use of KCN solution, described formerly as being convenient for quantitative desorption of Pd [8], did not produce the desired effect for the recovery of the noble metals; only 1.8 ± 0.3% and 2.4 ± 0.7% of the initial contents of Au and Pd, respectively, were desorbed. The solution of KSCN was capable of complete desorption of Au (105 ± 4%) and reasonably good recovery for Pd (85.7 ± 5.1%). The solution of $(NH_2)_2CS$, able to form positively charged stable complexes of noble metals [21], was found to be the most effective solvent for quantitative stripping of Au and Pd from the resin. The recoveries obtained for both noble metals were in the range of 98.7% to 103%.

Consequently, a sequential elution procedure using 20 mL of 4.0 mol L^{-1} HNO_3 to release the concomitant metals followed by 20 mL of 0.50 mol L^{-1} solution of $(NH_2)_2CS$ to recover the preconcentrated Au and Pd was used for further experiments.

Recovery of the Noble Metals by Digestion of Resin

Recently, the destruction of graphite tubes by aggressive vapors evolving from the pyrolysis of eluates resulting from the elution of Pd and Pt from Dowex 1 × 10 by means of thiourea solutions was described [21] as occuring during the determination of these metals by graphite furnace atomic absorption spectrometry. Hence, the decomposition of the resin after the preconcentration/separation step was also proposed in the present study as an alternative approach to solvent elution for the recovery of Au and Pd from Duolite GT-73. This approach has been applied before in the determination of Au, Pd, Pt, Ir and Rh preconcentrated on Metalfix Chelamine [22]; since plain elution failed to release the noble metals, the resin was destroyed using a microwave-assisted heating procedure in the mixture of HCl, HNO_3 and H_2O_2.

Regarding the mass of the resin used for the column operations (1.25 g) and the complexity and resistivity of the polystyrene matrix, the method of digestion in the open vessel system with concentrated H_2SO_4 and 30% (m v^{-1}) H_2O_2 was employed here for destruction of the resin and release of the adsorbed Au and Pd from Duolite GT-73. Lately, this procedure has been successfully applied to the recovery of Hg [18].

To ascertain the efficiency of the digestion protocol, 100 mL solutions acidified with HCl to pH 2.0 and containing 0.10 µg mL^{-1} of Au and Pd and the base metals at concentrations of 20 µg mL^{-1} were loaded onto the columns at a flow rate of 0.50 mL min^{-1}. Next, 20 mL of 4.0 mol L^{-1} HNO_3 solution was passed through the column for desorption of the concomitant metals. After that, the resin beds were transferred from the columns into the beakers, and the digestion procedure was carried out. The resulting solutions (volume of 25 mL) were analyzed for Au and Pd by means of ICP-AES. The respective recoveries of noble metals (mean values of three replicates with confidence intervals for 90% certainty level) were found to be 99.8 ± 4.6% for Au and 100 ± 5% for Pd. It should be emphasized that smaller amounts of the resin (up to 0.6 g) taken for the column operation allowed the use of microwave-facilitated digestion in the closed pressurized system and led to a substantial reduction of the time needed for recovery of Au and Pd by resin decomposition.

Analytical Performance

The precision of the method expressed as relative standard deviation for three replicate measurements varied on average between 0.5% and 3%. The accuracy of the proposed two-step elution procedure was tested by analyzing electrolytic nickel, copper and zinc sulfates and chloride bath samples spiked with

Au and Pd. The amounts of the noble metals recovered were in very good agreement with those added to the samples; the relative errors found were within the range of 2% to 6%.

A preconcentration factor of up to 50 for Au and Pd was achieved by passing through Duolite GT-73 columns 1000 mL solutions containing 100 μg of the noble metals, the concomitant metals (a 200 times higher amount than for Au and Pd) and acidifying with HCl to a concentration of $0.010\,\mathrm{mol\,L^{-1}}$. After the preconcentration step, the columns were rinsed with 20 mL of $4.0\,\mathrm{mol\,L^{-1}}$ HNO_3 solution and then with 20 mL of $0.50\,\mathrm{mol\,L^{-1}}$ solution of $(NH_2)_2CS$. The respective recoveries for Au and Pd were found to be 99.4 ± 2.5% and 99.3 ± 3.4%.

The limits of detection for Au ($0.085\,\mu g\,L^{-1}$) and Pd ($0.28\,\mu g\,L^{-1}$) found with the enrichment factor achieved were improved by one order of magnitude compared to those established for direct measurements.

Conclusions

The present paper presents the unique capabilities of Duolite GT-73 for the preconcentration of Au and Pd and the separation of these noble metals from various base metals (Al, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb and Zn) from different HCl-containing media. Compared to previous studies describing the application of resins containing thiol functional groups, the column operation and the two-step elution protocol developed here enable the enrichment of Au and Pd prior to the interference-free determination of these metals by ICP-AES and other spectrometric methods in a simple and convenient way. In this scheme, matrix metals, adsorbed alongside with Au and Pd, were released from the resin and separated from the noble metals by elution with a moderately concentrated solution of HNO_3. Finally, the quantitative recovery of Au and Pd was carried out by elution with $(NH_2)_2CS$ solution. An alternative to the solvent elution approach for retrieval of the noble metals is decomposition of the resin with a mixture of H_2SO_4 and H_2O_2.

Acknowledgements. Pawel Pohl expresses his gratitude to the Foundation for Polish Science for the annual grant received in 2004.

References

[1] Qu YB (1996) Analyst 121: 139
[2] Balcerzak M (1997) Analyst 122: 67R
[3] de Godoi Pereira M, Arruda MAZ (2003) Microchim Acta 141: 115
[4] Brzezicka M, Baranowska I (2001) Spectrochim Acta Part B 56: 2513
[5] Meisel T, Moser J, Fellner N, Wegscheider W, Schoenberg R (2001) Analyst 126: 322
[6] Jarvis I, Totland MM, Jarvis KE (1997) Analyst 122: 19
[7] Matsubara I, Takeda Y, Ishida K (2000) Fresenius J Anal Chem 366: 213
[8] Tunçeli A, Türker AR (2000) Anal Sci 16: 81
[9] Tunçeli A, Türker AR (1997) Analyst 122: 239
[10] Qing Y, Hang Y, Wanjaul R, Jiang Z, Hu B (2003) Anal Sci 19: 1417
[11] Chang X-J, Gong B-L, Su Z-X, Yang D, Luo X-Y (1998) Fresenius J Anal Chem 360: 736
[12] Chang X, Su Z, Yang D, Gong B, Pu Q, Li S-K (1997) Anal Chim Acta 354: 143
[13] Kantipuly C, Katragadda S, Chow A, Gesser HD (1990) Talanta 37: 491
[14] Anticó E, Masana A, Salvadó V, Hidalgo M, Valiente M (1994) Ana Chim Acta 296: 325
[15] Polakovicová J, Medved J, Stresko V, Kubová J, Celková A (1996) Anal Chim Acta 320: 145
[16] Iglesias M, Anticó E, Salvadó V (1999) Anal Chim Acta 381: 61
[17] Chiarle S, Ratto M, Rovatti M (2000) Wat Res 34: 2971
[18] Pohl P, Prusisz B (2004) Anal Sci 20: 1367
[19] Saha B, Iglesias M, Cumming IW, Streat M (2000) Solvent Extr Ion Exch 18: 133
[20] Coedo AG, Dorado MT, Padilla I, Alguacil F (1997) Anal Chim Acta 340: 31
[21] Kovacheva P, Djingova R (2002) Anal Chim Acta 464: 7
[22] Chwastowska J, Skwara W, Sterlińska E, Pszonicki L (2004) Talanta 64: 224