The Use of Dowex-M43 Ion-exchange Resin in the Determination of Pt and Pd in Converter Matte by ICP-OES

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ABSTRACT

The method of choice for the separation of platinum group metals (PGMs) from base metals and easily ionizable elements (EIEs) is usually ion-exchange. This paper describes an anion-exchange procedure using Dowex-M43 for the separation of EIEs in geological samples (converter matte) from PGMs and Au. Aqueous commercial standards were used to study the adsorption capacity of the Dowex-M43 resin for both Pd and Pt metals (0–1000 μg mL^{-1}). The concentrations of Pd and Pt were determined using inductively coupled plasma optical emission spectroscopy (ICP-OES). The results from the analysis of solutions prepared from commercial standards after ion-exchange treatment showed quantitative recoveries of both Pt (97%) and Pd (99%) from Dowex-M43 resin using 0.1 mol L^{-1} thiourea solution. Good agreement was observed between results obtained in this method and those obtained with the use of the conventional acid dissolution method for the determination of Pd and Pt in converter matte.

KEYWORDS

Anion-exchange, converter matte, ICP-OES, platinum group metals.

1. Introduction

Converter matte is an oxidation product containing PGMs and Au. It originates from crushed rocks that are milled and subjected to flotation and heat treatment. Although several dissolution procedures have been described for the digestion of geological samples containing PGMs and Au, prior to analysis by ICP-OES or ICP-MS, there are few procedures used for the preparation of samples from converter matte. Once in solution, a variety of calibration methods are used to determine the PGMs and Au. These include an internal standards method,[1] a simplified general standard addition method for slurry nebulization[2] and reduction with SnCl$_2$.[3]

Nickel sulphide fire assay is one of the common methods for digestion of some geological material, the problem with it is that it does not always lead to quantitative recoveries of PGMs and Au, and a large amount of flux (Na$_2$O$_2$, LiB$_4$OH$_4$) is often required.[4–7] Alkali fusion has been described by a number of authors,[8–11] but the limitations are that complicated sample preparation is required and the methods are not always applicable to geological samples. The zirconium crucible is known to be the best material for temperatures up to 550 °C, showing greater resistance to attachment by the fusion mixture than platinum, silver or porcelain.[12]

The other preferred method for the preparation of geological samples is an ion-exchange procedure, although it is costly and metal-chloro complexes can form ion pairs with anion-exchangers.[13–16] In this regard the capacity of resin to adsorb metals as well as their lack of adsorption (break-through) are important when studying the efficiency of ion-exchange resin.[17] An anion-exchange resin, Dowex-M43, which is a weak base made up of styrene-divinylbase (DBV) macroporous matrix, was investigated as a possible alternative to cation-exchange resins.[18] This paper describes the use of Dowex-M43 anion exchange resin for the preparation of samples from converter matte for the determination of Pt and Pd by ICP-OES.

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2. Experimental

2.1. Instrumentation

A simultaneous Spectro Ciros^{ccd} ICP-OES (Spectro Analytical Instruments, Kleve, Germany) equipped with a Fassel-type fixed quartz torch and connected to 1.6 mm i.d. injector tube was used for all analytical measurements. A cross-flow nebulizer and an impact bead chamber (Perkin-Elmer, Wellesley, USA) were used for introducing the sample solution. Aqueous samples were continuously injected into the ICP with a peristaltic pump *via* 0.38 mm i.d. PTFE tubing. Fully automated instrument control and data acquisition were achieved by Smart Analyzer Vision software version 1.20, as supplied by Spectro Analytical Instruments. High purity Ar (Afrox, Johannesburg, RSA) was used as coolant, nebulizer and auxiliary gas in all determinations. Operating conditions for the instrument are presented in Table 1. The ICP-OES was calibrated using fresh standard solutions of PGMs in the concentration range of 0.1 to 50 μg mL^{-1}.

2.2. Wavelength Selection

The most sensitive emission lines chosen for PGMs are presented in Table 2. Detection limits (LOD) were determined as three times the standard deviation (3σ, $n = 6$) of a 0.1 mol L^{-1} HCl blank.

2.3. Materials and Reagents

Standard solutions were prepared using aliquots of single ele-

Table 1 Operating conditions for ICP-OES Spectro Ciros^{ccd}.

Operating parameters	Setting
Plasma power/W	1400
Coolant flow rate/L min^{-1}	12.5
Nebulizer flow rate/L min^{-1}	1.2
Auxilary flow/L min^{-1}	1.0
Pump speed/mL min^{-1}	2.0

Table 2 Detection limits for Pt and Pd by ICP-OES.

Element	Wavelength/nm	LOD/μg mL^{-1}
Pt (II)	214.423	0.112
Pd (I)	360.955	0.104

ment 1000 μg mL^{-1} solutions. PGMs and Au standard solutions were prepared using ultrapure chemical grades (Technolab A/S, Kolbotn, Norway). Working standard solutions containing 0.3 mol L^{-1} HCl (SMM Instruments, Vorna Valley, RSA) were freshly prepared by diluting appropriate aliquots of stock standards with high purity de-ionized water. Thiourea solutions (0.01–3.0 mol L^{-1}) were prepared by dissolving an appropriate mass of thiourea (Merck, Darmstadt, Germany) in dilute HCl. Zirconium crucibles were cleaned by soaking in hot HCl (10 mol L^{-1}), then rinsed with deionized water after one cycle of fusion. All other chemicals used were analytical reagent grade. Dowex-M43 anion-exchange resin was prepared by soaking in 0.3 mol L^{-1} HCl for 1 min before loading into a glass column (1 cm diameter × 10 cm long).

2.4. Sample Preparation

Alkali fusion was performed by weighing a mass of 1.0 ± 0.0001 g converter matte in a 35 mL zirconium crucible, and 5.0 g sodium peroxide (Promark Chemicals, Johannesburg, RSA) was added. The crucible was heated gently to evaporate the moisture by slowly passing it into and out of the top of a bunsen burner, then placing it in the full heat of the flame while slowly swirling the melted material contained in the crucible. Heating was continued for 3 to 4 min, and the resulting material was cooled to room temperature for 3 min before dissolution.

During sample dissolution, the cooled crucible was transferred into a 250 mL PTFE beaker. A volume of 10 mL deionized water was added slowly to the fused matte, and the sample was covered with a watch glass to avoid sputtering. After the reaction was complete, 30 mL of 6.0 mol L^{-1} HCl solution was slowly added to the sample solution, allowing the reaction to cease between additions. The contents in the crucible were transferred into the PTFE beaker and rinsed with 20 mL of 6.0 mol L^{-1} HCl. The watch glass was rinsed with 10 mL of deionized water. The resultant solution was accurately transferred into a 100 mL volumetric flask and diluted to the mark with deionized water.

2.5. Anion-exchange Separation

Dowex-M43 anion-exchange resin (Dow Chemical Company, Chloorkop, RSA) was wetted with 30 mL of 0.1 mol L^{-1} HCl and loaded onto a glass column. After draining the wetting solution in the column, a solution containing Pd and Pt was added into the column loaded with Dowex-M43 resin, and allowed to stand for 1 min. At the end of the adsorption time, an appropriate volume of thiourea solution prepared in HCl was used to elute the Pt and Pd from the column. The resultant solution was collected in 10 to 100 mL volumetric flasks and diluted to volume with 0.1 to 6.0 mol L^{-1} HCl. The concentrations of Pt and Pd were determined by using ICP-OES. Break-through of Pt and Pd on Dowex-M43 anion-exchange resin was determined by loading solutions of Pd and Pt standards onto columns containing different masses (0.5–3.0 g) of Dowex-M43 anion-exchange resin.

2.6. Regeneration of Resin

Standard samples of Pd were used to investigate the regeneration of Dowex-M43 resin. An aliquot of 1000 μg Pd standard solu-

tion was loaded onto a column loaded with 1.50 g Dowex-M43 resin. The effluent was collected in a 25 mL volumetric flask and diluted to the mark with 0.1 mol L^{-1} HCl. The adsorbed Pd was washed with 50 mL of 0.1 mol L^{-1} thiourea. The resin was further washed with 100 mL of 3.0 mol L^{-1} HCl before the second loading to recondition it for further use. A similar procedure was followed in the loading of the second, third and fourth aliquots of 1000 μg Pd solution onto the same resin as was used before.

3. Results and Discussion

3.1. Adsorption Capacity of Dowex-M43 Anion-exchange Resin for Pt and Pd

The ICP-OES analysis of standard solutions gave results that show high losses of Pd (19%) and Pt (35%) when a mass of 0.50 g Dowex-M43 resin was used to adsorb 1000 μg of these metals. An increase in mass of Dowex-M43 resin was required due to the high break-through of Pd and Pt, therefore an increase in resin mass to 1.0 g followed by the loading of 1000 μg of Pd and Pt was performed. Break-through recovery of <1% was achieved as a result of using 1.0 g Dowex-M43 resin, which indicates some improvement in the adsorption of the loaded metals. The further increase of the mass of resin by 0.5 g to 1.50 g resulted in break-through recovery of less than the detection limits of both Pt and Pd. These results indicate that a minimum mass of 1.50 g is required to adsorb up to 1000 μg masses of Pt and Pd.

The break-through study was performed by loading a solution with a mass of 1000 μg of Pd and Pt in the presence of 5000 μg Na on 1.50 g Dowex-M43 column to evaluate the adsorption efficiency of the resin for Pd and Pt. Total recovery of 100% Na was observed, whereby 75% recovery was observed in the effluent. The remaining 25% was eluted with 10 mL of deionized water. Both break-through recoveries of Pd and Pt were below the limits of quantitation (LOQ). Washing of Na with deionized water is therefore necessary to further reduce the amount of Na on the column before eluting Pd and Pt. In addition to the break-though study for Pd and Pt, the concentration of HCl for the preparation of Pd and Pt, and the eluent conditions were also optimized to improve the adsorption capacity of Dowex-M43 resin for these metals.

3.2. Optimization of HCl Concentration for the Preparation of Pd and Pt Solutions

The preparation of Pd and Pt standard solutions was optimized to assess the effect of increase in HCl concentration. Solutions containing 100 μg Pd and Pt prepared in concentrations ranging from 0.1 to 6.0 mol L^{-1} HCl were added onto a column loaded with a mass of 1.50 g Dowex-M43 resin followed by their determination using ICP-OES. Adsorption of Pd and Pt on Dowex-M43 decreased with an increase in the concentration of HCl for the preparation of these metals. These results are in agreement with the findings of Grant *et al.*,[18] that the adsorption capacity for base anion-exchangers decreases with increasing concentration of HCl, due to increasing competition between Cl$^-$ and metal complex anions.

3.3. Elution Profiles

Thiourea is considered to be one of the best eluents of PGMs from strong base anion-exchange resins.[14] The resultant complex has low affinity for strong base anion-exchange resin. The reactions of thiourea with Pt and Pd are presented in the equations below:[19]
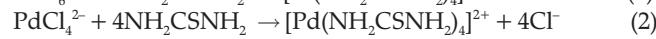
$$PtCl_6^{2-} + 4NH_2CSNH_2 \rightarrow [Pt(NH_2CSNH_2)_4]^{4+} + 6Cl^- \qquad (1)$$

$$PdCl_4^{2-} + 4NH_2CSNH_2 \rightarrow [Pd(NH_2CSNH_2)_4]^{2+} + 4Cl^- \qquad (2)$$

Table 3 Recovery of Pd and Pt with 10 mL of 0.1 mol L^{-1} thiourea in dilute HCl.

HCl concentration/mol L^{-1}	Recovery/%	
	Pd	Pt
0.1	90.7	89.3
1.0	32.9	54.7
3.0	33.1	45.2

Table 4 Recovery for Pt and Pd standard solutions in the presence of major matrix elements.

Element	Recovery/%	
	Input mass 500 μg	Input mass 50 μg
Pt	94.3	96.6
Pd	99.2	98.9

Jarvis *et al.*[16] used a concentration of 0.3 mol L^{-1} thiourea prepared in 0.1 mol L^{-1} HCl to elute PGMs from Dowex 1-X8. Recoveries of 90.7% and 89.3% for Pd and Pt, respectively (Table 3), were observed in this study when 10 mL of 0.1 mol L^{-1} thiourea prepared in 0.1 mol L^{-1} HCl was used to elute 1000 μg of these metals adsorbed onto a column of 1.50 g Dowex-M43 resin. The concentration of HCl for the preparation of thiourea was also optimized to improve the recovery of Pd and Pt from Dowex-M43 resin. The use of higher concentrations of HCl (1.0 and 3.0 mol L^{-1}) to prepare thiourea did not give better recoveries for either Pd or Pt compared with the use of 0.1 mol L^{-1} thiourea solution. Kovacheva *et al.*[19] also used 0.1 mol L^{-1} thiourea to elute Pt and Pd from Dowex 1-X10 anion-exchange resin.

The volume of thiourea solution required to elute the PGMs and Au depends on the rate of formation of thiourea complex.[20] The optimization of the thiourea volume required to elute Pd from Dowex-M43 resin was therefore necessary. A total volume of 40 and 45 mL thiourea was found to be sufficient for quantitative recovery of Pd (99%) and Pt (95%), respectively, from a column loaded with 1.50 g Dowex-M43 resin.

3.4. Determination of Pd and Pt in the Presence of other PGMs and Major Matrix Interference Elements found in Converter Matte

The optimized conditions for adsorption and desorption of Pd and Pt from a mass of 1.50 g Dowex-M43 resin were used to determine these metals in the solution spiked with 500 μg of other PGMs (Ru, Rh, Ir and Os) and the same mass of interference base elements (Na, Cu, Ni, Zr and Fe) found in fused converter matte samples. Masses of 50 μg and 500 μg were loaded separately onto 1.50 g Dowex-M43 resin. Recoveries of Pd and Pt of more than 90% were observed for both masses used (Table 4). The mean of three independent determinations for each concentration showed that Dowex-M43 anion-exchange resin has high adsorption capacity for Pd (II) and Pt (IV), even in the presence of major interfering base metals.

3.5. Analysis of Converter Matte Geological Sample

The certified reference material (SARM-7) contains very low concentrations of PGMs, and the elution method using Dowex-M43 requires dilution of the sample, therefore it could not be used as a control. Further adjustments to the method developed (when using aqueous standard solutions) were made to suit the presence of high concentrations for some elements present in converter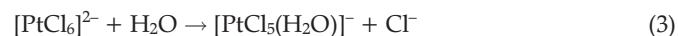 matte samples. A mass of 2.0 g Dowex-M43 resin was used and 75 mL and 90 mL of 0.1 mol L^{-1} thiourea solution were required for the quantitative elution of Pt and Pd, respectively. An additional step was required to wash Na and base metals remaining on the surface of the resin and a volume of 20 mL deionized water was used for this purpose.

Quantitative recovery of Pd was observed from the analysis of eluate solutions resulting from washing with thiourea (Table 5). Pt was present in both the effluent and eluate solutions obtained from treatment of converter matte sample with Dowex-M43 resin. A recovery of 40% of total Pt concentration was observed in the effluent solution. This differs from findings made earlier when aqueous standard solutions were used, where a very low amount (0.5%) of Pt was not adsorbed by Dowex-M43 resin. The total concentration of Pt found during ICP-OES analysis was therefore calculated from the amount found in the effluent containing the base metals added to the amount found in the eluate that resulted from washing with thiourea.

The poor adsorption of Pt may be attributed to the formation of hydroxy-chloro platinum complexes during oxidative fusion with sodium peroxide. Hydroxy-chloro complexes that are obtained when chloro-platinum (IV) is treated with sodium hydroxide[21] can be explained by the following equation:[11]

$$[PtCl_6]^{2-} + H_2O \rightarrow [PtCl_5(H_2O)]^- + Cl^- \quad (3)$$

Support for this hypothesis was found when pure Pt was subjected to fusion and the solution passed through the column. The element was again found in both effluent and eluate solutions.

The selectivity of the anion-exchange resin is much higher towards the chloro- than the hydroxy-complexes. The total found concentration of Pt gave comparable results with the acid dissolution method, presented in Table 5, even though some Pt was found in the solution with matrix interfering elements. Lower concentrations of Pt and Pd were obtained from the analysis of converter matte sample before treatment with Dowex-M43 resin (Table 5). These low results are due to signal suppression caused by the presence of high amounts of EIEs in the sample. This supports the use of ion-exchange resin to pre-concentrate and separate the EIEs and base metals from PGMs prior to their determination by ICP-OES.

The ion-exchange results obtained in this experiment were validated by comparing with the conventional acid dissolution method performed in an independent laboratory. The results obtained with the ion-exchange method are in agreement with those from the conventional acid dissolution method. The precision for the ion-exchange method is better than those for other methods (Table 5).

Table 5 Recoveries of Pd and Pt in converter matte after ion-exchange treatment.

Element	Conventional method/μg g^{-1}	No resin treatment[a]/μg g^{-1}	This work (ion-exchange)/μg g^{-1}	Correlation coefficient, R^2
Pd	1250 ± 75	1110 ± 90	1219 ± 15	0.99993
Pt	2775 ± 160	2470 ± 120	2720 ± 40	0.99987

[a]No resin treatment: fused samples were analyzed before ion-exchange treatment.

Table 6 Recovery of major matrix interference elements present in fused converter matte.

Element	Fused sample[a] /μg g^{-1}	Thio-eluent[b] /μg g^{-1}	H$_2$O-eluent[c] /μg g^{-1}
Na	79 958	815	66 634
Cu	43 485	396	48 643
Ni	73 410	227	73 409
Zr	9 447	140	10 725
Fe	6 952	791	1039

[a]Fused sample: converter matte sample without using Dowex-M43 resin.
[b]Effluent: sample solution not adsorbed by the resin.
[c] Eluent: 20 mL deionized H$_2$O then 90 mL thiourea (0.1 mol L^{-1}).

3.6. Adsorption Capacity of Dowex-M43 Resin for Major Matrix Interference Metals

Some amounts of matrix interference elements in the fused converter matte sample were found in the effluent when Dowex-M43 resin was used. The matrix elements still present in the column were eluted with 20 mL deionized water before eluting Pd and Pt with thiourea. The matrix interference elements present in the eluent with thiourea were within the acceptable levels to be analysed by ICP-OES (Table 6). The presence of matrix interference elements in the effluent did not affect the results obtained for ICP-OES determination of Pt. The fused converter matte samples had a very high concentration of Zr, due to the use of the Zr crucible for the fusion of converter matte samples. The Zr concentration was reduced to low levels after treatment of fused converter matte with Dowex-M43 resin (Table 6).

3.7. Regeneration of the Resin

High break-through recoveries were observed for Pd in the second and third loading cycles during the process of regenerating the Dowex-M43 resin (Table 7). This was also found by Jarvis *et al.*[16] The non-reusability of Dowex resin, however, is not a serious limitation due to its lower cost compared with other analytical grade resins such as AG-1X8.

4. Conclusion

Dowex-M43 anion-exchange resin quantitatively adsorbed chloro-complexes of Pd (II) and Pt (IV) when aqueous commercial standards were used. A common elution agent, thiourea, was effectively used in the elution of Pt (IV) and Pd (II) chloro-complexes. Quantitative recoveries of Pd were observed in the converter matte sample. Low adsorption of Pt was attributed to the formation of hydroxy-chloro complexes of Pt(IV). The developed method could also be applicable in the separation of PGMs from base metals in geological samples which can be prepared by using acid digestion techniques.

Table 7 Recovery of Pd during Dowex-M43 resin regeneration.

Sample	Pd break-through recovery/%
1	0.300
2	32.4
3	29.9

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