

Rapid and continuous ion chromatographic determination of trace heavy metal impurities in noble metals

Youbang Liu* and Qi Wang

Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou, Gansu (China)

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ABSTRACT

A rapid and continuous ion chromatographic method for the determination of trace heavy metal impurities in noble metals was developed. Some real samples were analysed and satisfactory results were obtained. In this method, a ternary complex eluent (sodium tartrate, sodium citrate and sodium chloride) was used to separate six heavy metal ions and the composition of the eluent was optimized by the simplex method. An on-line pre-enrichment column was used to remove the noble metal matrix in the form of chloro complex anions and to enrich trace heavy metal impurities in the form of cations in a single operation. The retained heavy metal ions were then separated on an analytical column and detected with a coulometric detector. The enrichment conditions were investigated and optimized.

INTRODUCTION

It is important to determine trace heavy metal impurities in products and intermediates of noble metals for quality control during in-plant manufacturing processes. Beamish and Van Loon [1,2] established and reviewed a series of cation-exchange methods for the separation of the noble metals platinum, palladium, rhodium, iridium and ruthenium from associated milligram amounts of the base heavy metals copper, iron, nickel, lead and zinc using the cation exchangers KU-2 and Dowex 50. The material to be analysed was treated with *aqua regia*, evaporated with hydrochloric acid and dissolved in hydrochloric acid (pH 1.0–1.5). The solution was passed through 2 g of the cation exchanger in a 200 mm × 15 mm I.D. column at 50–60 drops/min. In this procedure, the base heavy metals

were retained on the cation exchanger in the form of cations while the noble metals were drained out of the column in the form of chloro complex anions. The noble metals were recovered quantitatively.

Later, Chang [3] developed another cation-exchange method for the separation of trace amounts of copper and nickel from the base noble metals platinum and palladium based on the same principle as the earlier work, using the cation exchanger Dowex 50. The samples of platinum and palladium metals and their solutions of intermediate or final products during in-plant processing were treated with a similar procedure and dissolved in hydrochloric acid (pH 1.0–1.5). The solution with a concentration of 20–50 mg/ml of noble metals was passed through a 30–50 mm × 5 mm I.D. cation-exchange column at 50–60 drops/min. The copper and nickel impurities were retained on the cation exchanger in the form of cations while the base noble metals were drained out of the column in the form of chloro complex anions. The retained

* Corresponding author. Present address: Department of Chemistry, University of Missouri–Rolla, Rolla, MO 65401, USA.

copper and nickel ions were eluted with 1.0–2.0 M hydrochloric acid and the eluate was analysed by atomic absorption spectrometry (AAS). One element was determined in each operation hence this was not a rapid method. As other heavy metals such as lead, zinc, cobalt and cadmium could also be associated with noble metals, their presence would make the AAS method very tedious and time consuming. Further, if these heavy metals interfered with each other in the AAS measurement, they would also need to be separated. To solve this kind of problem, ion chromatography obviously has advantages.

The ion exchange chromatographic separation of six heavy metal ions, Cu^{2+} , Zn^{2+} , Ni^{2+} , Pb^{2+} , Co^{2+} and Cd^{2+} , on YSG- SO_3Na cation exchanger with a binary complex eluent (sodium tartrate–sodium chloride) has been reported [4,5]. In both studies, the elution order was in the order given. For better results, baseline separations between adjacent ion pair of Cu^{2+} and Zn^{2+} , Pb^{2+} and Co^{2+} , and Co^{2+} and Cd^{2+} were obtained, but between Zn^{2+} and Ni^{2+} and between Ni^{2+} and Pb^{2+} there was only 60–70% separation. Co^{2+} was eluted at about 30 min and Cd^{2+} at about 45 min. This condition was clearly not suitable for quantitative analysis. Earlier, Takata and Muto [6] reported an ion chromatographic separation of seven heavy metal ions, Hg^{2+} , Cu^{2+} , Zn^{2+} , Ni^{2+} , Pb^{2+} , Cd^{2+} and Co^{2+} , on Hitachi 2611 cation exchanger with a binary complex eluent (sodium tartrate–sodium chloride) within about 38 min. The resolutions between each adjacent ion pairs were acceptable for quantitative analysis. However, unfortunately, this kind of stationary phase was not available to us.

The objective of this work was to develop an ion chromatographic procedure for the determination of trace heavy metal impurities in base noble metals and to use this procedure to support the quality control in noble metal in-plant manufacturing. First, a ternary complex eluent (sodium tartrate–sodium citrate–sodium chloride) was used to separate the six heavy metal ions. The composition of the ternary eluent was optimized by the simplex method. As a result, the elution order was changed to Cu^{2+} , Ni^{2+} , Zn^{2+} , Pb^{2+} , Co^{2+} and Cd^{2+} . Nickel that eluted

between zinc and lead in earlier work [4,5] now eluted before zinc, and the last ion, cadmium, eluted at about 20 min. The resolutions between each adjacent ion pair were larger than 1.17. This result was even better than that in ref. 6. Second, an on-line pre-enrichment column was used to remove the noble metal matrix from heavy metals and to enrich trace heavy metal impurities in a single operation based on the same principle as in earlier work [1–3]. The enriched heavy metals were separated on an analytical column and detected with a coulometric detector after the eluent flow pattern was switched. A few real samples were analysed and satisfactory results were obtained.

EXPERIMENTAL

Apparatus

This work was performed on a Model SY 202 high-performance ion-exchange chromatograph (Sichuan Analytical Instrument Factory, Chongqing, China) [7]. An on-line pre-enrichment column and related equipment were installed. A schematic diagram of the chromatographic system is shown in Fig. 1.

Column

The analytical column was a glass column (100 mm \times 8 mm I.D.) jacketed by a Plexiglas tube. The enrichment column was specially designed in the laboratory and consisted of a Plexiglas tube (20 mm \times 5 mm I.D.) with both ends sealed with Teflon screws.

Column resin

The resin packed in the analytical column was a polystyrene-based strongly acidic cation exchanger, YSG- SO_3Na (15–20 μm), obtained from the Tianjin Second Reagent Factory (Tianjin, China). The same resin but of particle size 25–30 μm was used for the enrichment column. The resins were washed with 2 M hydrochloric acid, water, 2 M sodium hydroxide solution and water before use.

Mobile phase

The mobile phase was prepared by dissolving certain amounts of sodium tartrate, sodium

citrate and sodium chloride in distilled, ion-exchanged water and then adjusting the pH to 4.1 with 2 M nitric acid.

Detector

The detector in this work was a flow coulometric detector [7]. Carbon cloth was used for both working and auxiliary electrodes. The detection potential was -0.75 V for all heavy metal ions vs. 0.1 M $\text{Fe}(\text{CN})_6^{3-}$ – 0.1 M $\text{Fe}(\text{CN})_6^{4-}$ – 0.4 M NH_3 solution.

Electrolyte for working electrode reaction

The secondary coulometric method was used to detect the eluted heavy metal ions. The principle is as follows:



Instead of direct reduction, the eluted ion M^{2+} replaced Cu^{2+} in CuDTPA (DTPA = diethylenetriaminepentaacetate) and then the Cu^{2+} was reduced on the working electrode. The composition of the electrolyte for the working electrode reaction was 0.01 M DTPA– 0.01 M copper (II) sulphate– 0.1 M ammonium nitrate– 1.0 M ammonia solution.

Electrolyte for auxiliary electrode reaction

The electrolyte for the auxiliary electrode reaction was 0.1 M potassium hexacyanoferrate(III)– 0.1 M potassium hexacyanoferrate(II)– 0.4 M ammonia solution.

Standard solutions of heavy metal ions

Individual 0.5 M stock standard solutions of the heavy metal ions were prepared by dissolving 0.25 mol of the nitrates in hydrochloric acid (pH 1.5) in a 500-ml volumetric flask and diluting to volume with the same acid. The concentrations was accurately determined by titration with EDTA. Working standard solutions were prepared by diluting the stock standard solutions to the required concentrations (single or mixed)

with hydrochloric (pH 1.5) acid in a volumetric flask before use.

Purified noble metal solutions

The calculated amounts of PtCl_4 , PdCl_2 and IrCl_4 were dissolved in 6 M hydrochloric acid and the solutions were evaporated to dryness on a boiling water-bath. Then residues were dissolved in hydrochloric acid (pH 1.5) to give concentrations of 30.0 mg/ml of noble metals. The solutions were passed through a conventional cation-exchange column (100 mm \times 15 mm I.D.) packed with YSG– SO_3Na resin (30 – 40 μm) to isolate any associated heavy metal impurities. These solutions were used for mixing with standard heavy metal solutions for investigating the effects of the base noble metals on the enrichment efficiency of the heavy metals.

Real samples of noble metals

Three platinum and one palladium metal solution samples and one iridium intermediate solution sample prepared during in-plant manufacturing were obtained from the central laboratory of the Northwestern Nonferrous Metal Company of China. These samples had already been pre-treated and dissolved in 1.0 M hydrochloric acid at concentrations of 100.0 mg/ml for platinum and palladium and 50.0 mg/ml for iridium, and contained labelled concentrations of copper and nickel impurities based on pure noble metals. They were evaporated to dryness on a boiling water-bath and the residues were dissolved in hydrochloric acid (pH 1.5) with the original noble metal concentration and pH of the solutions was adjusted with sodium hydroxide to exactly 1.5 before use. A volume of 10 ml of each noble metal sample solution was pumped through the enrichment column and the residue was washed three times with a total of 10 ml ($4 + 3 + 3$ ml) of hydrochloric acid (pH 1.5) (the enrichment procedure is discussed in detail later).

Enrichment procedure

A schematic diagram of the chromatographic system is presented in Fig. 1. The enrichment column (4) was connected on the position normally used for the sample loop of the first six

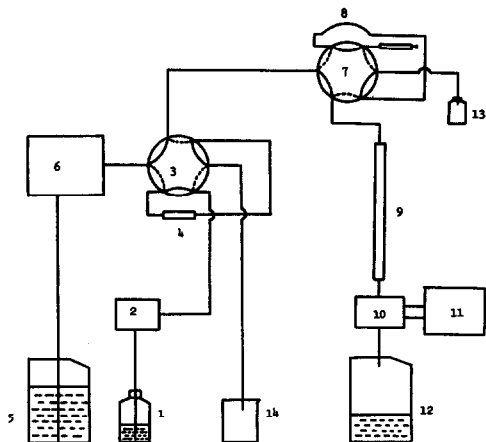


Fig. 1. Schematic diagram of the chromatographic system. 1 = Solution to be enriched; 2 = enrichment pump; 3 = first six-port valve; 4 = enrichment column; 5 = eluent; 6 = elution pump; 7 = second six-port valve; 8 = sample loop (10 μ l); 9 = analytical column; 10 = detector; 11 = recorder; 12 and 13 = waste solution; 14 = collected noble metal solution.

port valve (3). The eluent was led by means of the elution pump (6) to the first six port valve, where it could flow in either of two directions, one via the six-port valve (solid line) directly to the second six-port valve (7) and then the analytical column (9), and the other via the enrichment column (dotted line). When the enrichment operation was carried out, the first valve was set at the position such that the eluent did not pass through the enrichment column. Volumes of 10–100 ml of noble metal solution with heavy metal impurities in hydrochloric acid (pH 1.5) were pumped through the enrichment column continuously by the enrichment pump (2). In this procedure, the trace heavy metal impurities were retained on the enrichment column in the form of cations while the base noble metals were drained out of the column in the form of chloro complex anions. The residue was washed with a total of 10 ml (4 + 3 + 3 ml) hydrochloric acid (pH 1.5). Then 15 ml of 0.1 M sodium nitrate solution were pumped through the column to convert the ion exchanger from the H^+ to the Na^+ form. The reason for this additional ion-exchange conversion will be discussed later. When the enrichment was finished, the eluent flow pattern was switched from the solid line to the dotted line and the eluent was

passed through the enrichment column so that the retained heavy metal ions were eluted into the analytical column to be separated and determined.

This procedure maintained all the merits of the traditional method but was more convenient, rapid and effective because of the on-line pre-enrichment column and the high-performance ion chromatographic system.

Evaluation of enrichment efficiency

A 10- μ l volume of a mixed standard solution of the six heavy metal ions with a concentration of $5.00 \cdot 10^{-2}$ M of each ion was injected directly into the analytical column by the second six-port valve (10- μ l sample loop) and the eluted peak area for each heavy metal ion, $A_{i(\text{inject})}$, was measured. The same amount of the heavy metal ions, $5.00 \cdot 10^{-7}$ mol absolute amount, diluted in 10–100 ml hydrochloric acid (pH 1.5), was enriched by the enrichment procedure and the eluted peak area for each heavy metal ion, $A_{i(\text{enrich})}$, was measured. The enrichment efficiency (EE) of the heavy metal ions was given by:

$$EE = [A_{i(\text{enrich})}/A_{i(\text{inject})}] \cdot 100\%$$

Because the base noble metals did not interfere (see *Interference from associated noble metals*), they were not added to the solutions during the investigation of the enrichment efficiency.

Optimization procedure

A 10- μ l volume of mixed standard solution of the six heavy metal ions with a concentration of $5.00 \cdot 10^{-2}$ M of each ion was injected by the second six-port valve (10- μ l sample loop) and separated in the analytical column using a certain composition of the ternary eluent (sodium tartrate–sodium citrate–sodium chloride). The separation results were evaluated by the chromatographic optimization function (COF) [8], which will be discussed later. The new composition of the ternary eluent was calculated by the simplex method [9,10], which will also be discussed later. This procedure was repeated until satisfactory separation conditions were obtained.

Chemicals

All chemicals were of analytical-reagent grade from the Tianjin Second Reagent Factory (Tianjin, China) and the Shanghai Chemical Reagent Factory (Shanghai, China) and were used as received.

RESULTS AND DISCUSSIONS

Optimization of separation conditions

The equation for chromatographic resolution (R_s) is

$$R_s = \frac{1}{4} \cdot \frac{(\alpha - 1)}{\alpha} \cdot n^{1/2} \cdot \frac{k'}{k' + 1} \quad (3)$$

An increase in the separation factor, α , will result in an improvement in R_s . In ion-exchange chromatography, $\alpha = K_2/K_1$, where K_1 and K_2 are the partition coefficients of the first and second eluted ions, respectively on ion exchanger.

When n kinds of complex anions are present in solution, the partition coefficient on ion exchanger for any eluted ion is

$$\log K = \log K_x + Z \log Q - Z \log[M] - \log\left(\sum \alpha_{M(L_i)} - n + 1\right) \quad (4)$$

where K_x is the equilibrium constant of ion exchange, Z is the electric charge of the ion, Q is the exchange capacity of the resin, $[M]$ is the concentration of the ion and $\alpha_{M(L_i)}$ is the side-effect coefficient of the metal ion coordinated by the i th complex anion (in this paper, it could be sodium tartrate, sodium citrate or sodium chloride). $\alpha_{M(L_i)}$ is given by the following equation:

$$\alpha_{M(L_i)} = 1 + \beta_{i1}[L_i] + \beta_{i2}[L_i]^2 + \cdots + \beta_{in}[L_i]^n \quad (5)$$

where β_{ij} is the overall formation constant of the coordination complex between metal ion and the i th complex anion.

According to eqns. 4 and 5, a larger value of the separation factor α may be obtained by choosing different complex anions and/or changing their concentrations if the increments of $\alpha_{M(L_i)}$ and then K are different for the various heavy metal ions. By evaluating the β_{ij} of various

complex agents with the six heavy ions, we realized that the application of a ternary eluent composed of sodium tartrate, sodium citrate and sodium chloride would improve the separation of the six heavy metals because citrate anion has a relatively higher overall formation constant with Ni^{2+} . This was verified by experiments.

In order to obtain the optimum composition of the eluent, instead of the conventional single-factor method, the simplex method [8,9] was used and a satisfactory eluent composition was reached after ten experiments. During optimization, the chromatographic optimization function (COF) [7] was used as an objective function to evaluate the result of the optimization after each experiment. COF was given by

$$COF = \sum A_i \ln (R_i/R_{id}) - B(t_M - t_L) \quad (6)$$

where R_i is the measured resolution between any adjacent peaks on the chromatogram and R_{id} is the required resolution in a certain application. If $R_i \leq R_{id}$, the measured value is used; if $R_i > R_{id}$, let $R_i = R_{id}$. t_M is the retention time of the last-eluted peak on chromatogram and t_L is an acceptable analytical time in a certain application. If $t_M \geq t_L$, the measured value is used; if $t_M < t_L$, let $t_M = t_L$. A_i and B are weight factors. In this work, $R_{id} = 1.25$, $t_M = 20$ min, $A_i = 1$ and $B = 0.05$ were selected.

Among the different simplex methods, the modified simplex method (MSM) [8,9] was used in this work. The results of MSM are given in Table I. From Table I, the composition of the eluent in No. 10, i.e., 0.100 M sodium tartrate– $1.55 \cdot 10^{-2}$ M sodium citrate–0.150 M sodium chloride (pH 4.1), was considered to be the optimum. The chromatogram obtained with this optimum eluent is shown in Fig. 2.

Investigation of enrichment conditions

Flow-rate. The experimental results showed that the enrichment efficiency of various heavy metal ions decrease slightly with increase in flow-rate (Table II). This indicated that the ion-exchange equilibrium needed time to be completed. Although a higher enrichment efficiency could be obtained at low flow-rates, a longer enrichment time was required. When the flow-

TABLE I
RESULTS OF MODIFIED SIMPLEX METHOD

No.	Na tartrate (M)	Na citrate (10^{-2} M)	NaCl (M)	Type of point ^a	No. of apex	Resolution ^b					$t_{R \max}$ (min:s) ^c	COF
						R_1	R_2	R_3	R_4	R_5		
1	0.100	1.40	0.150	Apex	1, 2, 3, 4	3.84	1.02	1.67	1.34	2.01	21:27	-0.276
2	0.110	1.40	0.150	Apex	1, 2, 3, 4	3.71	0.79	1.57	1.55	1.95	18:32	-0.459
3	0.100	1.60	0.150	Apex	1, 2, 3, 4	3.50	1.17	1.65	1.05	2.05	21:23	-0.310
4	0.100	1.40	0.160	Apex	1, 2, 3, 4	3.72	0.95	1.53	1.27	1.68	20:22	-0.293
	0.100	1.47	0.153	c.g.	1, 2, 3, 4							
5	0.090	1.55	0.155	Reflect	1, 3, 4, 5	3.71	1.45	1.69	0.8	2.19	23:57	-0.644
6	0.105	1.45	0.150	Shrink	1, 3, 4, 6	3.56	0.99	1.55	1.29	2.05	20:08	-0.240
	0.102	1.48	0.150	c.g.	1, 3, 4, 6							
7	0.105	1.55	0.140	Reflect	1, 3, 6, 7	3.62	1.10	1.68	1.25	2.51	20:33	-0.155
8	0.105	1.60	0.135	Amplify	1, 3, 6, 8	3.55	1.15	1.33	0.95	2.22	21:27	-0.430
	0.103	1.47	0.147	c.g.	1, 3, 6, 7							
9	0.105	1.35	0.150	Reflect	1, 6, 7, 9	3.87	0.91	1.63	1.49	1.95	20:17	-0.332
10	0.100	1.55	0.150	Shrink	1, 6, 7, 10	3.58	1.17	1.60	1.23	2.42	20:42	-0.117

^a c.g. is the centre of gravity of the simplex. The reflection coefficient $\alpha = 1$, the shrink coefficient $\beta = 0.5$ and the amplifying coefficient $\gamma = 1.5$ were used in this work.

^b R_1, R_2, R_3, R_4 and R_5 are the resolutions between Cu^{2+} and Ni^{2+} , Ni^{2+} and Zn^{2+} , Zn^{2+} and Pb^{2+} , Pb^{2+} and Co^{2+} , and Co^{2+} and Cd^{2+} , respectively.

^c $t_{R \max}$ is the retention time of Cd^{2+} , the last-eluted ion.

rate was below 3.0 ml/min, the *EE* of all ions were more than 98.0%, without much sacrifice with regard to experimental error. Therefore, 3.0 ml/min was adopted in real enrichment operations.

Concentration of heavy metal ions. The six

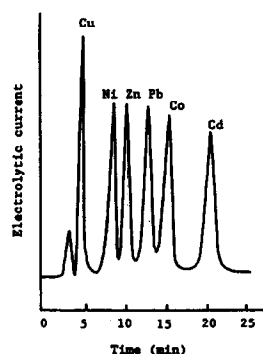


Fig. 2. Chromatogram of the six heavy metal ions. Sample size, $5.00 \cdot 10^{-7}$ mol of each heavy metal ion; resin, YSG- SO_3Na cation-exchange resin, 15–20 μm ; column 100 mm \times 8 mm I.D.; room temperature; eluent 0.100 M sodium tartrate– $1.55 \cdot 10^{-2}$ M sodium citrate–0.150 M sodium chloride (pH 4.1); flow-rate, 1.0 ml/min; electrolyte, 0.01 M CuDTPA –0.1 M NH_4NO_3 –1.0 M NH_3 solution; detection potential -0.75 V vs. $\text{Fe}(\text{CN})_6^{3-}$ – $\text{Fe}(\text{CN})_6^{4-}$.

heavy metal ions ($5.00 \cdot 10^{-7}$ mol) in 10-, 50- and 100-ml volumes were enriched and the influence of the concentration of the heavy metal ions on *EE* is shown in Table III. It can be seen that the concentration had no significant effect on the enrichment efficiency.

Acidity of enrichment solution. The experimental results showed that *EE* for all the heavy metal ions was larger than 97.0% if the pH of the metal ion solution to be enriched was between 1.0 and 7.0 in hydrochloric acid medium. However, *EE* decreased rapidly when the pH was lower than 1.0 (Table IV). The reason was thought to be that part of the heavy metal ions also formed chloro complex anions at high acidity and could not be retained on the enrichment column. As noble metals could form chloro complex anions completely and *EE* for all the heavy metal ions was larger than 98.0% in hydrochloric acid of pH 1.5, we chose pH 1.5 as the acidity of the enrichment solution (hydrochloric acid medium).

Amount of sodium nitrate. When investigating the effects of acidity, we observed that *EE* for Cu^{2+} was as high as 140% at pH 3.0 and even

TABLE II
EFFECT OF ENRICHMENT FLOW-RATE ON ENRICHMENT EFFICIENCY

10 ml of $5.00 \cdot 10^{-5}$ M of the mixed heavy metal ions in hydrochloric acid (pH 1.5) were used.

Flow-rate (ml/min)	Enrichment efficiency (%)					
	Cu ²⁺	Ni ²⁺	Zn ²⁺	Pb ²⁺	Co ²⁺	Cd ²⁺
1.0	101.0	99.6	100.4	99.2	99.5	99.8
2.0	99.6	99.2	99.3	98.6	99.1	98.2
3.0	98.5	98.3	98.4	98.3	98.5	98.0
4.0	97.6	97.3	97.2	97.3	97.5	96.8
5.0	95.8	96.0	95.3	95.5	95.7	94.4

TABLE III
EFFECT OF CONCENTRATION OF HEAVY METALS ON ENRICHMENT EFFICIENCY

The flow-rate was 3.0 ml/min, the pH of the solution was 1.5 in hydrochloric acid and the amount of each heavy metal ion was $5 \cdot 10^{-7}$ mol.

Volume (ml)	Enrichment efficiency (%)					
	Cu ²⁺	Ni ²⁺	Zn ²⁺	Pb ²⁺	Co ²⁺	Cd ²⁺
10	99.7	98.9	100.1	98.7	99.1	99.0
50	99.2	99.4	99.6	99.2	98.8	98.5
100	98.6	98.5	98.8	98.2	98.5	98.7

higher at pH < 3.0. The signal at the elution position of Cu²⁺ was so large that the determination of the other ions was seriously affected. We suggest that the reason might be as follows.

As mentioned under Experimental, the sec-

ondary coulometric detection method was used in this work. Instead of direct reduction, the eluted ion M²⁺ replaced Cu²⁺ in CuDTPA and then the Cu²⁺ was reduced on the working electrode. When the acidic heavy metal solution

TABLE IV
EFFECT OF ACIDITY ON ENRICHMENT EFFICIENCY

A 10-ml volume of $5.00 \cdot 10^{-5}$ M of the mixed heavy metal ions was enriched at a flow-rate of 3.0 ml/min.

pH	Enrichment efficiency (%)					
	Cu ²⁺	Ni ²⁺	Zn ²⁺	Pb ²⁺	Co ²⁺	Cd ²⁺
7.0	99.4	100.0	100.6	99.4	99.2	99.4
3.0	99.7	99.6	101.2	98.8	100.4	98.6
1.5	99.5	100.8	100.3	98.5	99.4	98.5
1.0	98.9	98.2	98.6	97.2	98.9	97.3
0.0	22.1	49.7	44.6	9.6	37.7	6.5

was introduced into the enrichment column, a large amount of H^+ was retained on the exchanger so that the resin was converted from the Na^+ to the H^+ form. When the eluent flow pattern was switched after completion of enrichment, the retained H^+ entered the eluent in the analytical step and caused the mobile phase to be sectionally acidified. When the acidified section of the eluent reached the detector, H^+ combined with DTPA and a large amount of Cu^{2+} was released from $CuDTPA$. These extra Cu^{2+} ions were electrolysed and the above-mentioned phenomenon appeared.

In order to solve this problem, $NaNO_3$ solution was pumped through the enrichment column after enrichment to convert the exchanger back from the H^+ into the Na^+ form. After this treatment, the detector worked normally. However, the optimum amount of $NaNO_3$ should be considered. If the amount of $NaNO_3$ was insufficient, the conversion of the enrichment column was incomplete. On the other hand, too much $NaNO_3$ would lead to the risk of the enriched heavy metal ions being partially eluted from the enrichment column, mainly because of Na^+ replacing the enriched heavy metal ions. Throughout the experiments, a suitable amount was found to be 15 ml of 0.1 M $NaNO_3$ solution. *EE* for all the heavy metal ions was larger than 98% under this condition (Table V).

Interference from associated noble metals

A solution containing absolute amounts of 30.0 mg of noble metals (platinum, palladium

and iridium) and $5.00 \cdot 10^{-7}$ mol of each heavy metal ion in 10 ml of hydrochloric acid (pH 1.5) was used to investigate the effects of associated noble metals on the enrichment efficiency of trace heavy metals. *EE* for all the heavy metal ions was larger than 98%. Hence base noble metals would not affect the enrichment under the experimental conditions used.

Interference from other ions

The coulometric detector is a selective detector. Under the experimental conditions it did not respond to Li^+ , Na^+ , K^+ , Fe^{3+} , Fe^{2+} , Al^{3+} and Sn^{4+} , and the retention times of Mn^{2+} , Ca^{2+} and Mg^{2+} were 38, 45 and 56 min respectively. The six heavy metal ions of interest were not interfered with by any of these common ions.

Analysis of real samples

Mixed standard solutions containing various amounts of copper, nickel and lead in 10 ml of hydrochloric acid were passed through the enrichment column to obtain a calibration graph. The single peak area on the chromatogram was used in quantitative analysis. The calibration graphs were obtained by plotting the peak area of a certain heavy metal ion against the absolute mass of the ion in 10.0 ml of solution. As base noble metals did not interfere with *EE* for the trace heavy metals, they were not added to the solution used to obtain the calibration graph. Three heavy metals, copper, nickel and lead, were measured because they were the only

TABLE V

THE EFFECT OF CONCENTRATION OF $NaNO_3$ ON ENRICHMENT EFFICIENCY

A 15-ml volume of $NaNO_3$ solution was used.

$NaNO_3$ (M)	Enrichment efficiency (%)					
	Cu^{2+}	Ni^{2+}	Zn^{2+}	Pb^{2+}	Co^{2+}	Cd^{2+}
0.05	114.8	101.2	100.4	99.2	100.0	98.8
0.10	100.1	99.7	100.7	98.3	99.2	99.6
0.15	95.6	96.4	94.7	94.3	95.4	96.1
0.20	82.4	85.2	83.6	84.3	83.2	80.8
0.30	72.9	76.3	75.1	70.5	73.8	71.4

impurities in the available real samples. The calibration graphs can be expressed as follows, where y is peak area and x is amount (μg):

$$\text{Cu}^{2+}: y = 0.70 + 11.70x \quad (r = 0.9999) \quad (7)$$

$$\text{Ni}^{2+}: y = -1.05 + 19.70x \quad (r = 0.9998) \quad (8)$$

$$\text{Pb}^{2+}: y = 1.30 + 6.84x \quad (r = 0.9998) \quad (9)$$

Several real noble metal samples were analysed by the developed method. The results are given in Table VI. The palladium and platinum samples were pure noble metals. No lead was indicated for the platinum samples but it was

detected by this method. Because the amounts of the platinum samples were limited, only two measurements were made. A certain amount of lead was added to the palladium sample owing to the absence of lead impurity in this sample. The iridium sample was an intermediate prepared during in-plant production. All three heavy metals were added as they did not exist in the original sample. From Table VI, the relative standard deviations were less than 3.5%, the recoveries of the added heavy metal impurities were higher than 97% and the relative error of the determination was less than $\pm 6.0\%$. As this error range is acceptable in trace analysis, the results are considered satisfactory.

TABLE VI

RESULTS OF THE DETERMINATION OF HEAVY METAL IMPURITIES IN REAL NOBLE METAL SAMPLES

HM = Heavy metal elements determined in the noble metal samples, Standard value = labelled heavy metal impurity concentration in the noble metal samples. AD = Added standard heavy metal ions which were absent in the noble metal samples supplied. \bar{X} = Mean. R.S.D. = relative standard deviation (σ_{n-1}/\bar{X}). RE = relative Error. Recovery of the added heavy metal ions in the noble metal samples \bar{X}/AD . All concentrations of the heavy metals in this table were based on the form of pure noble metals in the real samples.

Sample	HM	Standard value ($10^{-3}\%$)	AD ($10^{-3}\%$)	Found ($10^{-3}\%$)	\bar{X} ($10^{-3}\%$)	R.S.D. (%)	RE (%)	Recovery (%)
Pd	Cu	1.25	–	1.24, 1.22, 1.30, 1.22, 1.22, 1.18, 1.44	1.22	3.3	–2.4	–
	Ni	1.23	–	1.28, 1.24, 1.30, 1.26, 1.25, 1.20, 1.20	1.25	3.0	1.6	–
	Pb	–	1.50	1.45, 1.49, 1.53, 1.52, 1.47, 1.53, 1.43	1.47	2.8	–2.0	98
Pt (1)	Cu	1.50	–	1.51, 1.58	1.55	–	3.3	–
	Ni	1.00	–	1.03, 1.08	1.06	–	6.0	–
	Pb	–	–	2.27, 2.33	2.30	–	–	–
Pt (2)	Cu	2.10	–	2.09, 2.05	2.07	–	–1.4	–
	Ni	0.20	–	0.21, 0.20	0.21	–	5.0	–
	Pb	–	–	1.78, 1.81	1.80	–	–	–
Pt (3)	Cu	1.80	–	1.87, 1.81	1.84	–	2.2	–
	Ni	0.55	–	0.60, 0.56	0.58	–	5.5	–
	Pb	–	–	2.11, 2.05	2.08	–	–	–
Ir	Cu	0.00	2.00	1.88, 1.94, 1.96, 2.02, 1.96	1.96	2.6	–2.0	98
	Ni	0.00	2.00	1.90, 1.96, 2.02, 2.04, 1.96	1.98	2.8	–1.0	99
	Pb	–	3.00	2.82, 2.90, 2.98, 3.00, 2.92	2.92	2.4	–2.7	97

CONCLUSIONS

A sensitive, rapid and continuous ion chromatographic method was developed for the determination of trace heavy metal impurities in noble metals, in which a three-component eluent was used to improve the chromatographic resolution and the simplex method was used to optimize the composition of the eluent. An on-line pre-enrichment column was used to remove the noble metal matrix and to enrich trace heavy metal impurities in a single operation. The resolution between each adjacent pair of the six heavy metal ions was larger than 1.17 and the enrichment efficiency of the ions was above 98% under the experimental conditions. The method was applied to real samples and the results were satisfactory.

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