Retention Behavior of Transition Metal ions with Some Complexing Agents on Cation Exchanger

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Prediction of retention times in transition metal-mandelate and transition metal-tartrate complex systems were studied on the cation exchanger. Plots of k' vs [mandelate] and k' vs [tartrate] were obtained under the condition of a constant competing cation concentration. The equation to predict the retention time of transition metal ion was derived from the ion exchange equilibria. Individual capacity factors (k_1', k_2') and stability constants (K_1, K_2) of the complexes were calculated from the non-linear least square method. Good resolution of the transition metals was predicted by the stepwise equation in the gradient method. The values of retention times from the calculation and the experiment agreed well each other.

Introduction

Ion Chromatography has been rapidly developed since H. Small[1] et al. introduced a suppressor column to reduce conductivity of the eluent to separate and quantify the inorganic species.
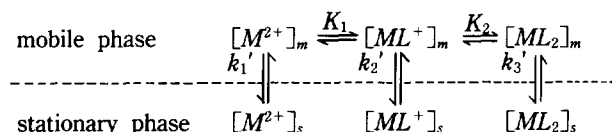
Complexing agent can be used to separate transition metals or lanthanides in ion chromatography because it can control the retention time of the cations and enhance the resolution by the difference in stability constants for each complex.

Recently, some workers have reported the equations to predict the retention times of transition metals or lanthanides[2-5]. In this research, the equations to predict their retention time were derived with the stability constants of the transition metal-mandelate and the transition metal-tartrate complexes. For the optimum separation condition in the cation exchange column isocratic, gradient and stepwise elution were performed.

Theory

Various chemical species are produced by complexation between metal cations and ligand anions in the column. These interact with functional groups in the stationary phase and counter ions in the mobile phase. The retention of metal ions can be predicted from the thermodynamic data of metal-ligand, metal-ion exchanger and competing cation-ion exchanger.

In case of transition metal ion and mandelate system, two chemical species of ML^+ and ML_2 are formed in the eluent, and their relation scheme is presented as follows.

mobile phase　$[M^{2+}]_m \overset{K_1}{\rightleftharpoons} [ML^+]_m \overset{K_2}{\rightleftharpoons} [ML_2]_m$
　　　　　　　　$k_1' \updownarrow$　　　$k_2' \updownarrow$　　　$k_3' \updownarrow$
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stationary phase　$[M^{2+}]_s$　　$[ML^+]_s$　　$[ML_2]_s$

where, M and L represent metal cation and ligand anion, m and s represent mobile phase and stationary phase, respectively. The equation for the relationship between capacity factor (k') and the concentration of the complexing agent

(L^-) was derived from chemical equilibria in the system.[4,6] Eq. (1) is obtained from the possible consideration of all chemical species between transition metal ion and mandelate ligand.

$$k' = \frac{k_1'[M^{2+}]_m + k_2'K_1[M^{2+}]_m[L^-]_m + k_3'K_1K_2[M^{2+}]_m[L^-]^2_m}{[M^{2+}]_m + K_1[M^{2+}]_m[L^-]_m + K_1K_2[M^{2+}]_m[L^-]^2_m} \quad (1)$$

As ML_2 is electrically neutral, the interaction of ML_2 with the species to the stationary phase is neglected. Thus, the third term in the nominator is ignored and the Eq. (2) is given as follow.

$$k' = \frac{k_1' + k_2'K_1[L^-]_m}{1 + K_1[L^-]_m + K_1K_2[L^-]^2_m} \quad (2)$$

where,

k': capacity factor
k_i': individual capacity factor of ML_{i-1} complex
K_i: stability constant
$[L^-]$: concentration of free ligand (M)

Assuming that M^{2+} forms complexes of ML^+ and ML_2, the relationship between retention of metal ion and the ligand concentration is obtained as a non-linear equation including capacity factors, concentration of ligand and stability constant. The constant values of k_1', k_2', K_1 and K_2 are calculated from the non-linear curve fitting with the Eq. (2). The capacity factor(k') can be obtained from these constants at any concentration of the ligand. In case that tartrate (L^{2-}) and transition metal ion (M^{2+}) form ML and ML_2^{2-} complexes, the Eq. of (3) and (4) for the retention are obtained by the same method as in the mandelate-transition metal complexes.

$$k' = \frac{k_1' + k_2'K_1[L^{2-}]_m + k_3'K_1K_2[L^{2-}]^2_m}{1 + K_1[L^{2-}]_m + K_1K_2[L^{2-}]^2_m} \quad (3)$$

$$k' = \frac{k_1'}{1 + K_1[L^{2-}]_m + K_1K_2[L^{2-}]^2_m} \quad (4)$$

Experimental

Apparatus and reagents. Ion chromatograph system consisted of Dionex 4500i series with G-2 and G-3 mixer, and injection valve fitted with a 50 µl sample loop, UV/VIS detector (Waters Associates M481), and a syringe pump (ISCO, LC-5000). HPIC-CS5(Dionex) and HPIC-CG5 were used as a separating column and protecting column, respectively. Column temperature was maintained at 25°C with water jacket. The flow rates of mobile phase and color-forming reagent(PAR) were controlled at 1.0 ml/min and 0.5 ml/min, respectively.

Mandelic acid (Aldrich Co.) and tartaric acid (Kanto Co.) of extra pure reagent grade were used as complexing agents. $NaClO_4$ (Aldrich Co.) was used to adjust Na^+ concentration. 4-(2-pyridylazo)-resorcinol(PAR) (Aldrich Co.) was used as a color-forming reagent. Demineralized water treated with Milli-Q system was used all through the experiment.

Procedure. Solutions for transition metal ion (Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and Mn^{2+}) were prepared by dilution of stock solutions (Junsei Co.) to a final concentration of 5 ppm with water. Solutions of mandelic and tartaric acid were made to be 0.4 M each. These two ligand solutions were titrated with sodium hydroxide to make the Na^+ concentration of 0.2 M, and $NaClO_4$ was added to adjust the concentration of competing cation up to 0.2 M in the eluent. PAR was prepared to be 4×10^{-4} M in mixture of 3 M NH_4OH and 1 M CH_3COOH (pH 9.6).

The retention time of transition metal ions was measured at various concentration of mandelic acid and $NaClO_4$ solution. For the transition metal-tartrate system, the same procedure was performed.

The capacity factors (k') were calculated with the measured retention time.

The retention time of transition metal ions was predicted with the capacity factors calculated in the isocratic elution. In addition, the retention time of the ions was also predicted for the optimum separation condition in stepwise and gradient elution. The calculated values were compared with those from experimental data.

Results and Discussion

Generally, Arsenazo I, Arsenazo III and PAR have been used as color-forming reagents for the detection of metal ions. In this work, PAR is taken because it gives a good reaction with transition metal.

Retention times of Cu^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+} and Mn^{2-} were measured from 0 M to 0.2 M of mandelate for the separation behavior of transition metal ions. Capacity factors of these metal ions were plotted in Figure 1. As shown in Figure 1, the retention times of the ions were nearly the same at the condition of 0.2 M $NaClO_4$ without mandelate ligand. Under this condition, these ions were not separated because hydration energies of these ions were similar, and exchange behaviors of hydrated cations were also similar in column[2]. The higher the concentration of mandelate, the shorter the retention time, and better resolution of these metals ions was achieved up to 0.1 M mandelate. However, the resolution was decreased over 0.1 M of mandelate.

The capacity factors (k_1', k_2') and stability constants (K_1,
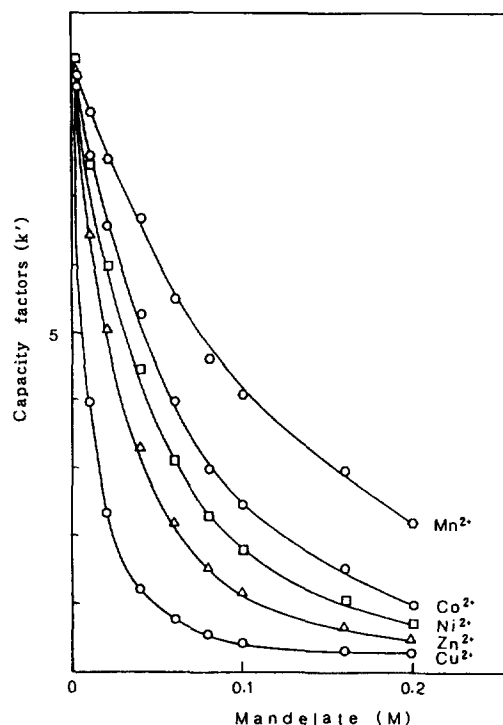
Figure 1. capacity factors of transition metal-mandelate complexes as a function of mandelate concentration.

Table 1. Individual capacity factors and stability constants of transition metal-mandelate complexes

Metal ions	k_1'	k_2'	log K_1	log K_2	STD
Cu^{2+}	7.28	0.50	2.01 (2.85[a])	1.31 (2.56[a])	0.157
Zn^{2+}	7.81	0.26	1.40 (1.51[b])	1.27 (1.07[b])	0.136
Ni^{2+}	8.55	0.58	1.33 (1.41[c])	1.13 (0.85[c])	0.155
Co^{2+}	8.41	1.28	1.20 (1.22[d])	1.10 (0.52[d])	0.203
Mn^{2+}	8.48	1.41	1.00	0.78	0.206

Pushing ion: 0.2 M Na^+, Cu^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}: 5 ppm respectively, temperature: 25°C, ( ): value from literature[10], [a]30 °C, 0.1 M $NaClO_4$ (gl.), [b]20°C, 2.0 M $NaClO_4$ (pot.), [c]25°C, 2.0 M $NaClO_4$ (pot.), [d]20°C, 2.0 M $NaClO_4$ (pot.), gl.: glass electrode, pot.: potentiometer.

$$STD = \{ [\sum_{i=1}^{n} (Y_{exp} - Y_{cal})^2] / (n-L) \}^{1/2}$$

n: number of data pairs, L: number of coefficients, Y_{exp}: experimental data, Y_{cal}: Calculated data.

K_2) of individual complexes were calculated by Eq. (2). These values were obtained by non-linear least square method (Table 1). The experimental values were also given in Table 1. Capacity factor of $ML^+(k_2')$ obtained from an Eq. (2) was smaller than k_1'. Capacity factors (k') of metal ions could be obtained at any ligand concentration based on the individual capacity factors and stability constants calculated. Capacity factors (k') in stepwise or gradient elution could be also predicted using the equations[5,7].

Consequently, the optimum condition for the separation was obtained for five transition metal ions using the stepwise equation[5,7]. All cations were separated over 2.5 in resolution.

Table 2. Comparison of retention time, resolution and peak width between experiment and calculation in stepwise gradient elution using mandelate

Metal ions	t_g (min.)		R_g	$W_{g1/2}$ (min.)	
	Exptl.	Calc.	Calc.	Exptl.	Calc.
Cu^{2+}	1.95	1.95	4.20	0.10	0.10
Zn^{2+}	2.63	2.68	3.53	0.12	0.11
Ni^{2+}	3.38	3.45	3.85	0.17	0.14
Co^{2+}	4.18	4.28	5.33	0.14	0.11
Mn^{2+}	5.53	5.64		0.19	0.19

Pushing ion: 0.2 M Na^+, Cu^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}: 5 ppm respectively, t_g: retention time in gradient elution, R_g: resolution in gradient elution, $W_{g1/2}$: FWHM in gradient elution, gradient condition.: 0-0.1 min 0.12 M mandelate, 0.1-8 min 0.2 M mandelate.
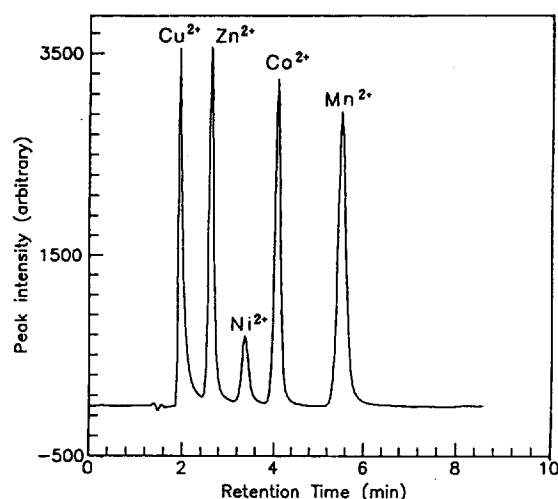
Figure 2. Separation of transition metal ions in stepwise gradient elution using mandelate.
column: HPIC-CS5 of Dionex, eluent: 0-0.1 min 0.12 M Mandelate, 0.1-8 min 0.2 M Mandelate in 0.2 M Na^+, flow rate: 1 ml/min, injection: 50 μl of Cu^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+} 5 ppm respectively, detection: PAR, 509 nm, UV-VIS spectrophotometer.

The resolution between Cu^{2+} and Zn^{2+} was still poor under this condition. Therefore, the stepwise elution technique using two steps of isocratic elutions was carried out in order to get the resolution over 2.5 in the concentration of mandelate less than 0.2 M and also minimize the unnecessarily long retention times of Co^{2+} and Mn^{2+}. The capacity factors of metal ions were obtained by Eq. (2) as a function of mandelate concentration, and then the optimum resolution (2.5) was predicted by substituting these values into the stepwise equations[5,7] and by calculating retention times and peakwidths. Calculated and experimental values of retention times and peakwidths were presented in Table 2. The chromatogram was also presented in Figure 2. As shown in Figure 2, all five metal ions were individually separated in 6 minutes.

Tartaric acid produces H_2L, HL^- and L^{2-} species in solution as a bidentate ligand. The concentration of L^{2-} was
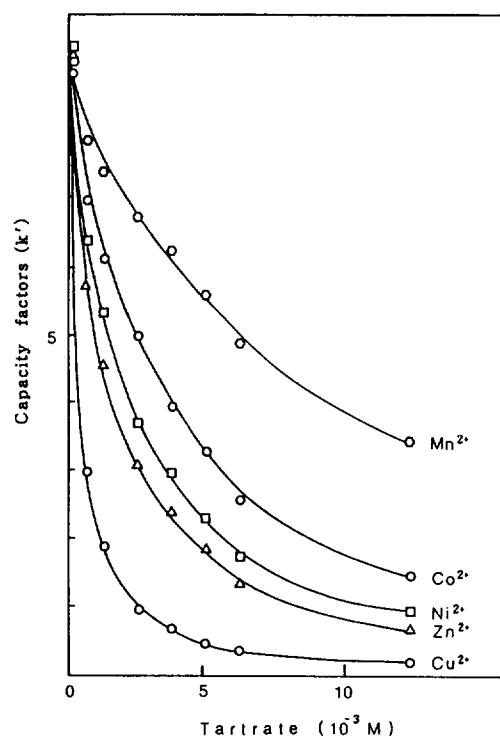
Figure 3. Capacity factors of transition metal-tartrate complexes as a function of tartrate concentration.

Table 3. Individual capacity factors and stability constants of transition metal-tartrate complexes

Metal ions	k_1'	log K_1	log K_2	STD
Cu^{2+}	8.59	3.39 (3.1[a])	2.13 (1.8[a])	0.091
Zn^{2+}	8.45	2.81 (3.31[b])	1.59 (1.85[b])	0.118
Ni^{2+}	8.86	2.71 (3.01[c])	1.52 (2.03[c])	0.110
Co^{2+}	8.54	2.48 (3.02[d])	1.42 (0.19[d])	0.078
Mn^{2+}	8.55	2.05 (1.44[e])	0.50	0.086

Pushing ion: 0.2 M Na^+, Cu^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}: 5 ppm respectively, temperature: 25°C, ( ): value from literature[8,10], [a]20°C, ix.[8] [b]25°C, dis.[8] [c]20°C, 0.1 M $NaClO_4$ (dis.)[10], [d]25°C, ix.[8] [e]32°C, 0.1 M $NaClO_4$ (gl.)[8] ix.: ion exchange, dis.: distribution, gl.: glass electrode.

calculated with $\log\beta_1 = 3.94$ and $\log\beta_2 = 6.82^8$. The fractions of distribution of H_2L, HL^- and L^{2-} were 0.528, 0.440 and 0.032, respectively under the condition of 0.4 M tartaric acid containing 0.2 M of Na^+. Accordingly, 12.78×10^{-3} M of tartrate(L^{2-}) concentration is produced in 0.4 M of tartaric acid. Figure 3 showed the capacity factors (k') of transition metal ions measured from 0 M to 12.78×10^{-3} M of tartrate. The trend of capacity factors in tartrate was similar to that in mandelate except the wider peak intervals between Cu^{2+} and Zn^{2+}, and between Co^{2+} and Mn^{2+} in tartrate. The separation factor of Co^{2+} and Mn^{2+} was enhanced in increasing the ligand concentration, and the resolution of Cu^{2+} and Zn^{2+} was good in range from 2×10^{-3} M to 4×10^{-3} M of tartrate. For the prediction of retention times of transition metal ions in tartaric acid, Eq. (4) was used to obtain k_1', K_1 and K_2 by non-linear least square method. These values showed a

Retention Behavior of Transition Metal Ions

Bull. Korean Chem. Soc., Vol. 14, No. 6, 1993 695

Table 4. Slope of log k' vs log α_M in transition metal-complexes

Metal ions	Slope	γ
Cu^{2+}	0.878	0.994
Zn^{2+}	0.997	0.999
Ni^{2+}	0.965	0.999
Co^{2+}	0.962	0.999
Mn^{2+}	0.976	0.997

γ: correlation coefficient.

Table 5. Comparison of retention time, resolution and peak width between experiment and calculation in gradient elution using tartrate

Metal ions	t_g (min.)		R_g	$W_{g1/2}$ (min.)	
	Exptl.	Calc.	Calc.	Exptl.	Calc.
Cu^{2+}	2.18	2.14	9.76	0.10	0.09
Zn^{2+}	4.28	4.25	2.46	0.18	0.16
Ni^{2+}	4.98	5.00	3.74	0.23	0.19
Co^{2+}	6.08	6.22	6.08	0.17	0.19
Mn^{2+}	8.35	8.56		0.24	0.26

Pushing ion: 0.2 M Na^+, Cu^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}: 5 ppm respectively, t_g: retention time in gradient elution, R_g: resolution in gradient elution, $W_{g1/2}$: FWHM in gradient elution, gradient condition: 0-1.1 min 4.73×10^{-3} M Tartrate, 1.1-3.8 min $4.73 \times 10^{-3} - 12.78 \times 10^{-3}$ M Tartrate, 3.8-12 min 12.78×10^{-3} M tartrate.

good agreement with the reported values (Table 3).

Eq. (4) was rearranged to verify the values of K_1 and K_2 obtained. Taking a logarithm of each term in Eq. (4), it gives

$$\log\, k' = \log\, k_1' + \log \frac{1}{1 + K_1[L^{2-}]_m + K_1K_2[L^{2-}]^2_m} \quad (5)$$

The second term in the Eq. (5) is expressed as a α_M[9].

$$\alpha_M = \frac{1}{1 + K_1[L^{2-}]_m + K_1K_2[L^{2-}]^2_m} \quad (6)$$

where, α_M is the fraction of the free metal ion against the total metal ion in solution. Substituting α_M into Eq. (5) gives

$$\log\, k' = \log\, \alpha_M + \log\, k_1' \quad (7)$$

The Eq. (7) is the same as the Eq. (8) derived from cation exchange modelling.[9]

$$\log\, k' = \log\, \alpha_M - (x/y)\, \log\, [E_m^{y+}] + \text{constant} \quad (8)$$

where, x is the charge of metal ion, E_m^{y+} is the competing ion. The ratio of log k'/log α_M was measured for various α_M in the Eq. (7) after α_M was calculated by substituting the values of K_1, K_2 and ligand concentration into Eq. (6). As shown in Table 4 the slopes (log k'/log α_M) of each metal ions were very close to 1 with the correlation coefficient from 0.994 to 0.999 having a good linearities. Therefore, the values of K_1 and K_2 obtained in tartrate system were proved
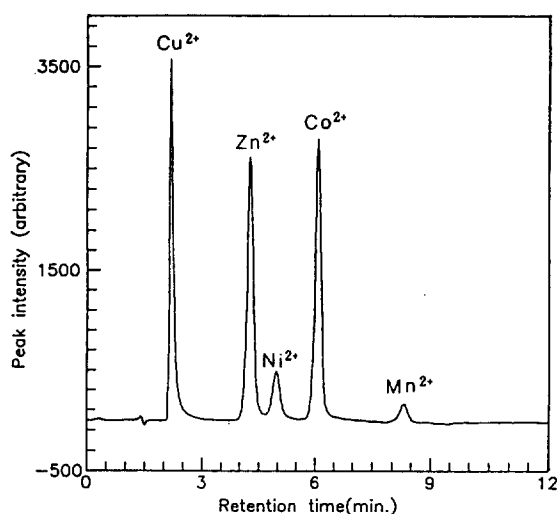
Figure 4. Separation of transition metal ions in stepwise gradient elution using tartrate.
column: HPIC-CS5 of Dionex, eluent: 0-1.1 min 4.73×10^{-3} M tartrate 1.1-3.8 min 4.73-12.78×10^{-3} M tartrate 3.8-12 min 12.78×10^{-3} M tartrate in 0.2 M Na^+, flow rate: 1 ml/min, injection: 50 μl of Cu^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+} 5 ppm respectively, detection: PAR, 509 nm, UV-VIS spectrophotometer.

to be acceptable. The optimum separation condition (Table 5) was obtained to have the resolution over 2.5 using the stepwise equations[5,7] with the use of k', K_1 and K_2 measured. As shown in Table 5 the experimental values were compared with the calculated ones to give a good agreement in regard to retention time, resolution and efficiency. The chromatogram of transition metal ions separated under the condition in Table 5 was shown in Figure 4. As shown in Figure 2 and Figure 4, mandelate ligand was found to be more effective than tartrate in retention time and its resolution for the separation of transition metals.

In the future, mixed ligand system will be studied for the prediction of retention time and for the optimum condition in the separation of transition metal ions.

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Determination of Trace Impurities in Gold by Isotope Dilution Inductively Coupled Plasma Mass Spectrometry

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Gold bonding wire of 0.076 mm in diameter used in semiconductor industry, is dissoved in aqua regia. The solution is then evaporated to near dryness several times with a few drops of HCl added to prepare the final sample solution in 5% HCl. The gold matrix is separated from trace impurities by controlled potential deposition. The whole electrolysis has been carried out inside a clean bench. An optimum potential is found to be +0.25 V to give more than 99.9% Au matrix removal with better than 90 analytes remaining in the electrolyte solution. Isotope dilution calibration is employed to get the best accuracy and precision. Analytical results are presented with determination limits of the analytical method.

Introduction

Inductively Coupled Plasma-Mass Spectrometry(ICP-MS) is being widely applied to the various application areas of trace element and isotope ratio determinations.[1] In contrast to the many application areas such as geological, environmental and clinical fields, only a few papers have been published on metallurgical applications.[2-5] Recently, the demand of high-purity metals is increasing especially in electronics industry. Since ICP-MS offers isotope dilution capability as well as extremely low detection limits, the determination of ultra trace impurities in pure metals can be also one of the important applications areas of ICP-MS.

Gold bonding wire is an important material in the production of the integrated circuits, where a high level of quality control is required. Trace impurities of transition metals such as Fe, Ni, and Cr adversely affect voltage threshold and etching uniformity. Trace impurities of radioactive elements increase the susceptibility to alpha-particle induced damage (soft errors). Reduction of the soft errors requires gold wires of high purity with respect to the radioactive elements such as U and Th, and thus the impurities of U and Th in the gold bonding wire are required to be below 1 ng/g.

Although part-per-trillion (ppt) levels of trace impurities in solution can be detected by ICP-MS, the matrix separation is almost always required for accurate and precise determination of ultra-trace impurities in pure metals. Of the many separation methods available at the present time, the controlled potential deposition[6,7] has a few advantage such as

simplicity and freedom from contamination. In this report, a new analytical method is introduced to determine trace impurities in gold wire of 0.076 mm in diameter. The gold matrix is removed from the sample solution by the controlled potential deposition prior to the isotope dilution analysis by ICP-MS.

Experimental

Reagents. The analytical-reagent grade mineral acids were purified using sub-boiling, quartz-distillator. All laboratory wares were washed with deionized water obtained from a Milli-Q system (Millipore, Bedford, MA, USA). The enriched stable isotopes were purchased from US Services (Summit, NJ, USA).

Instrumentation. The ICP-MS system used in this work was a laboratory-built unit and its schematic diagram was given in the previous work.[8] The typical ICP-MS operating conditions are listed in Table 1. Figure 1 shows the electrolysis cell configuration for the controlled potential electrodeposition. The cathode is made of platinum and is in a form of gauze cylinder 3 cm in diameter and 6 cm in length. The anode is made of platinum and is in a form of rod 4 mm in diameter. The saturated calomel electrode (SCE) is used as a reference electrode. A laboratory built potentiostat was used to control the applied potential and the electrolysis was performed inside a clean bench.

Sample Preparation. 0.5 g of gold wire is weighed into a 100 m*l* teflon beaker. Then 4 m*l* of aqua regia is added to dissolve the gold wire. The beaker is placed on a hot