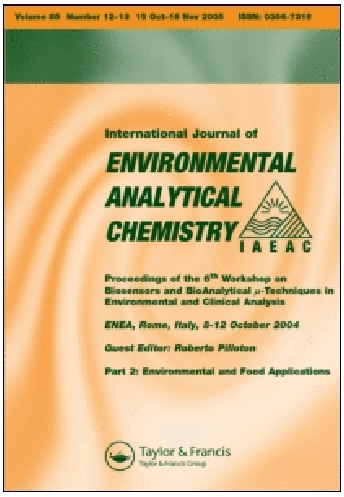

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MG-W CELL—ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY—DETERMINATION OF GOLD IN ENVIRONMENTAL SAMPLES

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An electrodeposition method of trace elements using a Mg-W cell is reported. This method does not need a power supply (electric source) like a potentiostat or a battery. Some elements electrodeposited on a W sheet were detected by electrothermal atomic absorption spectrometry (ETAAS) with a tungsten atomizer. The detection limits of Au, Sb, Te and Tl by Mg-W cell-ETAAS were 55, 48, 47 and 880 pg/mL, respectively. The severe interferences of Al, Ca, Cu, Fe, K, Na, Pb and Zn on Au-AAsignal, which were observed in AAS, were eliminated by use of the Mg-W cell. The Mg-W cell electrodeposition method was applied to the determination of Au in sea and surface water samples. The recovery of gold in spiked environmental samples was in the range of 91 to 104%.

Keywords: Preconcentration; electrodeposition; Mg-W cell; electrothermal atomic absorption spectrometry

INTRODUCTION

Preconcentration methods have frequently been applied to the analytical determination of ultra trace elements in complex matrix samples.[1] Adsorption, chromatography, coprecipitation, electrolytic deposition, evaporation, extraction,

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*Corresponding author. Fax: +81-59-231-9427. E-mail: na60235@cc.mie-u.ac.jp floatation, freezing, and ion exchange, are well known as preconcentration methods in analytical chemistry. Most of them are inconvenient and time-consuming, except the adsorption methods. Therefore, activated carbon, porous polymer, polyurethane foam, silica gel, glass beads and tungsten wire have been reported as adsorbents of trace elements.[2] Though metal ions are effectively collected with an electrolytic deposition method, it is bulky because of the use of a potentiostat or a battery. We developed a Mg-W cell and have reported a new simple preconcentration method by use of the cell.[3-5]

In the present work, detection limits of some elements by the Mg-W cell—ETAAS are presented. The elimination of chemical interferences by the Mg-W cell is studied for gold determination. The cell was applied to the determination of trace gold in sea and surface waters.

EXPERIMENTAL

Apparatus

The Mg-W cell developed for preconcentration of trace elements consists of a tungsten wire or sheet as a cathode, a magnesium sheet as an anode, and a beaker, which has been illustrated in a previous paper.[3]

The tungsten sheet was 2.5 × 2.5 mm, 99.95% purity, Rambar Co and the tungsten wire was 20 mm long and 0.5 mm in diameter, 99.95% purity, Rambar Co. The magnesium sheet was 8 × 8-20 mm, 0.10 mm thick, 99.9% purity, Nilaco Co. Both electrodes were connected with a copper wire having clips at both ends. The Mg-W unit was dipped into a sample solution (pH1 with nitric acid) for 120s as stirring. ETAAS consists of a monochromator (Nippon Jarrell-Ash 0.5m Ebert-type), an amplifier, a storage oscilloscope (Iwatsu MS-5021), and a microcomputer (Sord M223). The analytical lines for Au, Sb, Te and Tl were 242.8, 217.7, 214.3 and 276.8nm (hollow cathode lamp, Hamamatsu photonics Co), respectively. The atomizer was a tungsten tube (20 mm long and 2.0 mm id, made from a sheet, 0.05 mm thickness and 99.95% purity, Rambar Co) as shown in Figure 1. The atomizer has a slit (0.08 × 2.7 mm) at the mid-point of the tube to insert the W-sheet. The electric power for heating the atomizer was supplied with two transformers (Yamabishi volt-slider, S-130-30, Cap 3kVA). The atomizer is enclosed in a glass chamber, on which silica end-windows are sealed. The glass chamber is flushed with inert gas to protect the atomizer from oxidation by entrained air. Two pinhole apertures were placed in front of and in the rear of the atomizer, in order to collimate the light beam and eliminate the radiation from the atomizer surface.

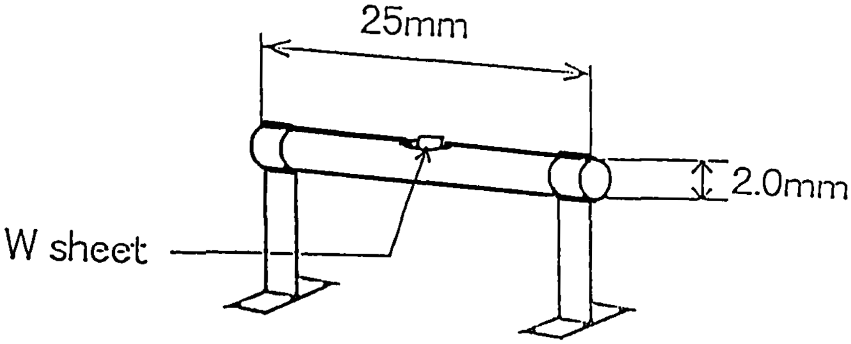

FIGURE 1 Tungsten atomizer including W-sheet.

Reagents

Standard stock solutions (1 mg/mL, 0.1M HNO_3 or HCl solution) of Au, Te, Tl, and Sb (spectroscopic purity) were obtained from Nacalai Tesque Inc, Kyoto, Japan and Wako Inc, Osaka, Japan. The solutions of matrix elements for the interference study were prepared as chlorides in 0.1-6 M hydrochloric acid. All other chemicals used here were of analytical grade or spectroscopic purity.

Procedures

Mg sheet, W sheet and W wire used as electrodes were defatted with acetone and then washed with 0.1 mol/L HCl prior to electrodeposition. The sample solution (3-10 mL) was put into a beaker and the pH was adjusted to 1-2 with HNO_3. The Mg-W electrode unit was dipped into the solution, and the solution was stirred for 60s. The W-sheet was removed, washed with demineralized water, and then perpendicularly inserted into a slit on the tungsten tube atomizer, as shown in Figure 1. The upper part of the W-sheet was exposed from the atomizer. The W wire was inserted from an opening of the end to the atomizer.

Au-AA signal was measured under the optimum experimental conditions reported previously;[6] purge gas Ar 480 mL/min and H_2 20 mL/min, pyrolysis temperature 410°C, and atomization temperature 2240°C. Hydrogen was added to protect the atomizer from oxidation by trace of oxygen in argon. In the case of Sb, Te and Tl, the W-sheet (wire) in the atomizer was dried at 90°C for 20s, pyrolyzed at 410°C for 10s and atomized at 2410°C for 3s in Ar (480 mL/min) and H_2 (20 mL/min) purge gas.

RESULTS AND DISCUSSION

A spontaneous redox reaction in galvanic cells was used to obtain electricity for the electrodeposition of metal ions in solutions. Redox half-reactions for Au, Sb, Te and Tl are as follows:

$$Au^{3+}\ (aq) + 3e^{-} \rightarrow Au(s)\ E^{0} = 1.498\ V$$

$$SbO^{-}\ (aq) + 2H^{+} + 3e^{-} \rightarrow Sb\ (s)\ E^{0} = 0.212\ V$$

$$Te^{4+}\ (aq) + 4e^{-} \rightarrow Te\ (s)\ E^{0} = 0.568\ V$$

$$Tl^{3+}\ (aq) + 3e^{-} \rightarrow Tl(s)\ E^{0} = 0.741\ V$$

A typical redox reaction (Au) in the Mg-W cell is as follows111:

$$\begin{array}{c} Au^{3+}\ (aq) + 3e- \rightarrow Au(s)\ E^{0} = 1.498\ V \\ \underline{Mg^{2+}\ (aq) + 2e- \rightarrow Mg(s)\ E^{0} = -2.372\ V} \\ \hline 2Au^{3+} + 3Mg \rightarrow 2Au + 3Mg^{2+}\ E^{0} = 3.870V \end{array}$$

$$K = \frac{[Au]^{2}[Mg^{2+}]^{3}}{[Au^{3+}]^{2}[Mg]^{3}} = \frac{[Mg^{2+}]^{3}}{[Au^{3+}]^{2}} = 3.63 \times 10^{393}$$

Since the K value is so large, the reaction proceeds spontaneously from left to right so that Mg-W cell would be available for the preconcentration of gold. K values calculated for other elements were also very large. It was found that those redox reactions proceed spontaneously from left to right. The Mg-W cell-ETAAS was evaluated with the determination of gold in surface and sea water.

Effects of pH and Immersing Time on the Electrodeposition of Gold

It has been reported that electrolytic deposition, sorption and adsorption of the metal ion were frequently affected by pH and immersing time.[1-2] Therefore, the effects of pH and immersing time on the electrodeposition of gold in a Mg-W cell were investigated. The effect of pH was examined for 120s of immersing time. The result is shown in Figure 2. Over pH 2, the amount of electrodeposition of gold dramatically decreased as pH increased. More than 1M HNO_3 gold did not deposit on the W sheet. Therefore, 1.48 was recommended as an optimum pH for the Au-deposition.

The effect of immersing time on gold electrodeposition was investigated Au-adsorption amounts gradually increased with time up to 30s and over 30s the curve was up sharply, as shown in Figure 3. The amount became constant >60s. Subsequently, an immersing time of 60s was recommended for the electrodeposition.

Effect of Electrodeposition on Interferences

In the determination of gold by ETAAS with a metal atomizer, chemical interferences by foreign elements were severe.[6] Therefore, the electrodeposition of gold on W-sheet in the presence of the interferences such as Al, Ca, Cu, Fe, K, Na, Pb and Zn (1000-1000000 folds) were investigated.

The peak height at gold AA signal was measured for the interference study. The results are summarized in Table I. Most coexisting elements did not interfere with gold absorbance. The reason probably comes from the standard potentials of these elements. The standard potentials of major coexisting ions are as follows:[7]

$$Cu^{2+}\,(aq) + 2e^- \rightarrow Cu\,(s)\ E^0 = 0.342V$$

$$Fe^{3+}\,(aq) + 3e^- \rightarrow Fe\,(s)\ E^0 = -0.037V$$

$$Pb^{2+}\,(aq) + 2e^- \rightarrow Pb\,(s)\ E^0 = -0.126V$$

$$Zn^{2+}\,(aq) + 2e^- \rightarrow Zn\,(s)\ E^0 = -0.762V$$

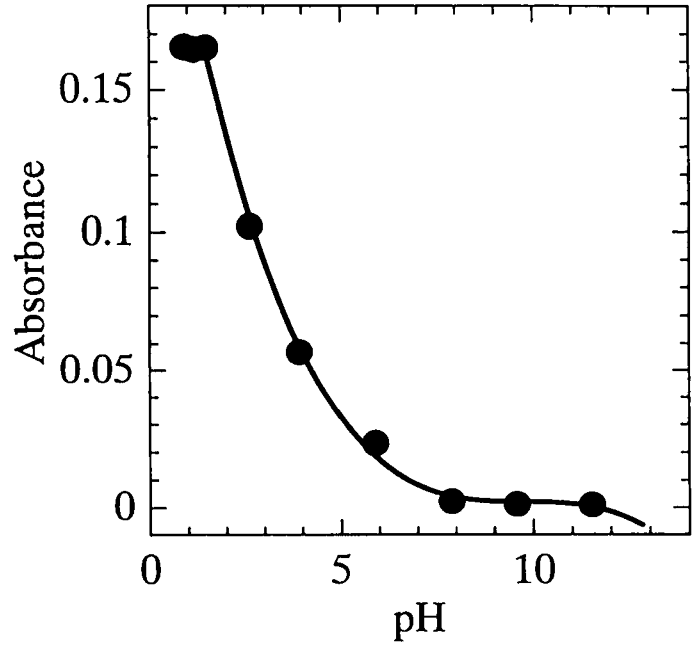

FIGURE 2 Effect of pH on the electrodepsiton of gold. Au 1 ng/mL, sample volume; 3 mL, Electrodeposition time; 60 s.

The potentials of alkaline and alkalinearth elements were lower than the potential of these elements. From these potentials it can be understood that, except for copper, gold is preferentially electrodeposited on the W sheet. Therefore, on this interference study it is reasonable that the coexisting metals investigated did not interfere with the gold signal.

Since this electrodeposition method served to eleminate severe interferences, it seems that the Mg-W cell electrodeposition method is useful to determine gold in environmental samples.

Detection Limit and Reproducibility

Detection limits (D.L.) of Au, Sb, Te and Tl by Mg-W cell/ETAAS were investigated at pH1-2 and immersing time 60s. The D.Ls. of Ag, Cu, Pd, Pt and Rh compared with D.Ls. obtained by GFAAS and ICP-MS, are summarized in

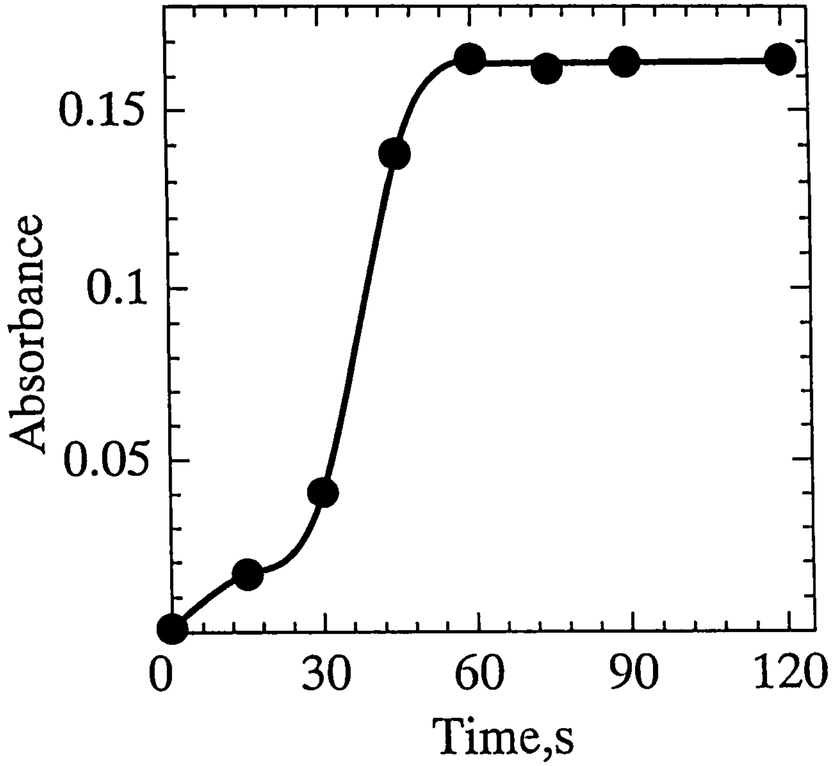

FIGURE 3 Effect of immersing time on the electrodeposition of gold. Au 1 ng/mL, sample volume; 3 mL, pH 1.48.

TABLE I Elimination of chemical interferences by Mg-W-ETAAS.

Matrix element	Peak height Abs.
Au (1 ng/mL)*	0.167 ± 0.019
Al (1 μg/mL)	0.171 ± 0.023
Ca (1 μg/mL)	0.168 ± 0.049
(10 μg/mL)	0.154 ± 0.015
(1 mg/mL)	0.173 ± 0.013
Cu (1 μg/mL)	0.176 ± 0.052
Fe (1 μg/mL)	0.183 ± 0.023
K (1 μg/mL)	0.181 ± 0.006
(10 μg/mL)	0.162 ± 0.016
(1 mg/mL)	0.170 ± 0.026
Na (1 μg/mL)	0.183 ± 0.037
(10 μg/mL)	0.162 ± 0.030
(1 mg/mL)	0.174 ± 0.009
Pb (1 μg/mL)	0.172 ± 0.022
Zn (1 μg/mL)	0.177 ± 0.008
(10 μg/mL)	0.150 ± 0.017

* Au alone n > 5

TABLE II Detection limits obtained by Mg-W cell preconcentration, compared with those by GFAAS and ICP-MS methods.

detection limit, ng/mL Element	pH	ImmersingTime(s)	This work, Mg-W ETAAS	GFAAS*	ICP-MS*
Ag	1.0	120	$0.021^{\#}$	0.005	0.03^{++}
Au	1.6	60	0.020	0.0004^{+}	0.0000002^{+++}
Cu	1.7	120	$0.0012^{\#}$	0.02	0.1
Pd	1.2	60	$0.37^{\#}$	1	0.06^{++}
Pt	1.2	180	$1000^{\#}$	0.2	0.03^{++}
Rh	1.0	120	$14^{\#}$	1	0.2
Sb	1.0	120	0.048	0.1	
Te	1.0	120	0.047	0.1	0.5
Tl	1.0	120	0.88	0.1	0.1

n > 10 measurements #. Ref.[3] *. Ref.[8] +. Ref.[9]++. Ref.[10] +++. Ref.[11]

Table II. The detection limits of Au, Sb, Te and Tl were 20, 48, 47 and 880 pg/mL (3S/N), respectively. The detection limit of Au obtained by Mg-W/ETAAS was worse than those with an ion exchange preconcentraion prior to GFAAS (0.4 pg/mL), a solvent extraction method prior to ICP-MS (0.2 pg/mL),[9] and flow injection ICP-MS/ion exchange preconcentration method by Falkner and Edmond (0.2 fg Au/mL).[11] For Tl, also, the detection limit was worse than those obtained by GFAAS and ICP-MS. However, the detection limits for Sb and Te were better than those of GFAAS and ICP-MS. GFAAS and ICP-MS methods combined with ion exchange preconcentration described above were complicated and time-consuming. At this point, Mg-W cell preconcentration method is simple and convenient.

The reproducibility for AAS signal of gold adsorbed on W sheet was investigated. The relative standard deviation for 100 ng Au/mL was 3.0% for 10 measurements.

Next we discussed a relation between the sensitivity by Mg-W cell method and physical values (boiling point and bond strength). The detection limits of Au, Ag, Cu, Pd, Sb, Te and Tl, were relatively good in these elements tested by the Mg-W cell method, but, for Pt and Rh the method was less sensitive. A reason for the worse detection limit for the Pt seems to be due to Pt-chlorocomplex anion formed as given below:

$$[PtCl_6]^{2-}(aq) + 2e^- \rightarrow [PtCl_4]^{2-}(aq) + 2Cl^- \quad E^0 = 0.68V$$

$$[PtCl_4]^{2-}(aq) + 2Cl^- \rightarrow Pt\ (s) + 4Cl^- \quad E^0 = 0.755V$$

A surface of W metal was covered with tungsten oxide in air.[12] It was reported that some metal elements adsorbed on a W sheet by ion-exchange.[13] Therefore, O^- on W sheet traps cations in aqueous solution. The bond strength of O-metal might be related to the detection limit of Ag, Au, Cu, Pd, Pt, Rh, Sb and Te. The bond strength of these element are 220.1, 221.8, 269.0, 380.7, 391.6, 405.0, 434.3, and 376.1 kJ/mol, respectively.[7] The bond energy of W-O is 672.0 kJ/mol. Relatively low bond strength elements tend to have better sensitivity except for Sb. The boiling points of Ag, Au, Cu, Pd, Sb, Te, and Tl are lower than 3000°C (Ag, 2212°C, Au: 2808°C, Cu: 2567°C, Pd: 2970°C, Pt: 3827°C, Rh: 3727°C, Sb: 1750°C, Te: 1390°C, Tl: 1457°C).[7] Thus, it seems that those detection limits were also related to the boiling point.

Determination of Gold

Environmental samples spiked with 1.0-1.5 ng Au/mL were analyzed by the Mg-W cell-ETAAS method under the optimum conditions. The calibration graph prepared with standard solutions of gold was linear up to 7.5 ng/mL. Table III shows analytical results obtained for river and sea waters, and rock. The recovery of gold-spiked in those samples was in the range of 91 to 104%. The relative standard deviation for the determination of gold in the environmental samples by the proposed method was in the range 0.6-8.0 %.

TABLE III Determination of gold in environmental and rock samples

Sample	Amount of gold, ng/g			
	added	Found	Recovery(%)	LiteratureValue
Sea water				
Machiya beach	-	0.262 ± 0.018		0.03-1000
	1.5	1.62 ± 0.01	91	
River water				
Anoh river	-	nd		
	1.0	1.04 ± 0.01	104	
Iwata river	-	0.137 ± 0.011		
Rock sample				
GSJ JB-1*	-	nd		
	1.5	1.48 ± 0.02	99	

n > 5 *NIES standard rock sample nd;not detected

CONCLUSIONS

The Mg-W cell preconcentration method developed is simple, rapid, and relatively interference free caused by coexisting elements. By the combination with ETAAS, the electrodeposition method is useful to the determination of trace element in complex matrix samples, just after only the Mg-W unit is dipped into sample solution for about 2 min.

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