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Preconcentration by coprecipitation of lead and selenium with Ni/pyrrolidine dithiocarbamate complex and their simultaneous determination by internal standard atomic absorption spectrometry with the solid sampling technique

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Abstract - In order to determine concentrations below µg/kg level of Pb and Se in water samples, the direct simultaneous determination of solid samples by graphite furnace-AAS using a miniature cup technique is applied to coprecipitation samples obtained by using a combination of ammonium pyrrolidine dithiocarbamate (APDC) and Ni as a carrier element. In the present work, the internal standard method was employed for AAS determination. In case of using the internal standard method weighing was not necessary. Examinations on the coprecipitation of Pb and Se with the Ni-APDC complex have been carried out. Detection limits for Pb (II) and Se (IV) are 30 ng and 70 ng/L, respectively, based on 100-mL sample volume. Precision (relative standard deviation of 10 determinations) of the determination of Pb and Se at concentration of 0.05 µg/L was 6.9 and 4.5 %, respetively.

INTRODUCTION

In recent years, many papers have been written on the determination of trace amounts of lead or selenium by such methods as hydride generation atomic absorption spectrometry [1-5], solid sampling techniques with atomic absorption spectrometry [6-8], and high-performance liquid chromatography with fluorescence detection [9].

Graphite furnace atomic absorption spectrometry (GF-AAS) is also one of the most sensitive methods for the determination of these elements[10], The instrumental sensitivity of GF-AAS is sometimes less than necessary for the level of the elements in tap water or secondary effluent water (discharge water from a sewage treatment plant), so that an appropriate preconcentration procedure must be applied. Usual preconcentration procedures for lead or selenium, such as solvent extraction [11], ion exchange [12], adsorption by C_{18}-bonded silicagel [13] and coprecipitation [14] normally offer concentration factors of 10-100, but these procedures are laborious and time-consuming.

On the other hand it is reported that it becomes possible to increase the analytical sensitivity 1000-fold when the direct determination of solid samples by GF-AAS using the miniature cup technique is applied to coprecipitation samples obtained by using a combination of an organic complex agent and a carrier metal ion which is ashed completely at the ashing step [15-17].

This method has been applied for the determination of lead and selenium in water samples.

The purpose of the present work was to study the conditions of coprecipitation of lead and selenium in tap water and secondary effluent water with Ni/pyrrolidine dithiocarbamate complex and their direct simultaneous determination of precipitates using the solid sampling technique with a miniature cup employing an internal standard method.

EXPERIMENTAL SECTION

Reagents

Acids and ammonium hydroxide were of the purest available reagent grade (ELSS and ELS, respectively, Kanto Chemical Co., Japan). Ultra-clean water was obtained from a Milli-Q purification system (Millipore Co., U.S.A.). In all analytical procedures, Milli-Q water (MQ-water) was used.

Ammonium pyrrolidine dithiocarbamate (APDC) (Wako Pure Chemical Co., Japan) was dissolved in pure water and a 2 % (w/v) solution was prepared. The solution of nickel (10 mg/mL) as a carrier metal ion, which was prepared by dissolving the pure metal (99.99 %) in nitric acid, evaporated to dryness and then dissolved in 1M-hydrochloric acid, was used. The reason why nickel as the carrier metal was used is that nickel is suitable for the determination of selenium by GF-AAS because of the stabilization of selenium at the ashing step.

Stock standard solutions (Wako Pure Chemical Co., Japan) for atomic absorption (1,000 μg of metal per milliliter of $0.1M-HNO_3$) were used.

Apparatus

An Hitachi (Japan) simultaneous multi-element Zeeman atomic absorption spectrometer, Model Z-9000, equipped with a cup-type graphite furnace, and an Hitachi AA data processor to measure the peak area and peak height, and also for recording absorption profiles, was used.

A Mettler (Switzerland) microbance, Model M3, readability of which is 1 μg, was used. The maximum weight for this balance is 2.9 g.

A home-made miniature cup (mini-cup: o.d.,4.8 mm; i.d.,,4 mm; depth,2.5 mm) was used in conjunction with the cup-type Hitachi furnace to overcome problems such as weighing small amounts of powdered samples. This system enables the introduction of the sample into the furnace without any loss of material and removal of the residue [8]. One mini-cup could be used for at least 150 firings.

Home-made forceps with tantalum tips were used for the insertion and removal of the mini-cup from the graphite furnace. The tips were bent outward to facilitate removal of the mini-cup.

Coprecipitation procedure

An aliquot of sample solution (100-300 mL) containing around 0.1 %w/v HNO_3 was placed in a borosilicate glass conical beaker (300-500 mL), into which 4.00 mg of nickel and 2 mL of APDC (2.0 %) solution were added. This solution was adjusted to pH 9 by adding concentrated aqueous ammonia solution (about 17 % w/v NH_4), and allowed to age for 1h at room temperature. It was then filtered by a glass filter (No.4G:5-10 μm, Shibata Co., Japan), and then dried at 110 °C for 1 h in a drying oven. When the internal standard method was not employed, the glass filter was weighed accurately before the filtration, and then dried at 110 °C for 1 h in a drying oven. The glass filter containing the coprecipitate was again weighed accurately. The difference in weight showed the net weight of the coprecipitate. This coprecipitate was submitted for the AAS determination.

AAS determination

A mini-cup (ca.45 mg) was weighed by use of the microbalance. The coprecipitation powder sample weighing from 0.1 to 1.5 mg in this case was placed in the mini-cup.

The mini-cup loaded with the coprecipitation sample was again weighed. The difference in weight showed the net weight of the coprecipitate [8]. In case of using the internal standard method weighing was not necessary.

The mini-cup was then inserted into the furnace using the forceps. Then, the coprecipitation powder sample was determined according to the instrumental conditions in Tables 1 and 2.

RESULTS AND DISCUSSION

Optimization of instrumental conditions

The relations between the absorbances of lead, selenium and the internal standard elements and the ashing temperature are shown in Fig.1. The absorbances of these elements remained constant between 500 and 800°C, therefore an ashing temperature of 600°C was selected.

Table 1. Instrumental conditions

		Cu	In	Se	Pb
Spectral line	(nm)	222.6	410.5	196.0	283.3
Lamp current	(nA)	7.5	12.5	12.5	7.5
Spectral band path	(nm)		0.8		
Time constant	(sec)		0.1		

Ar sheath gas flow-rate :	3.0 L/min
Ar carrier gas flow-rate: Atomization step; 30 mL/min	

Furnace	Cup cuvette + Mini-cup
Mode	Peak area (Integration)
Background correction	Zeeman-effect

Table 2. Optimum Heating programs

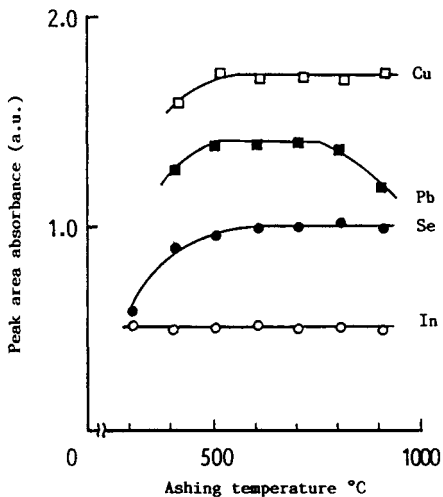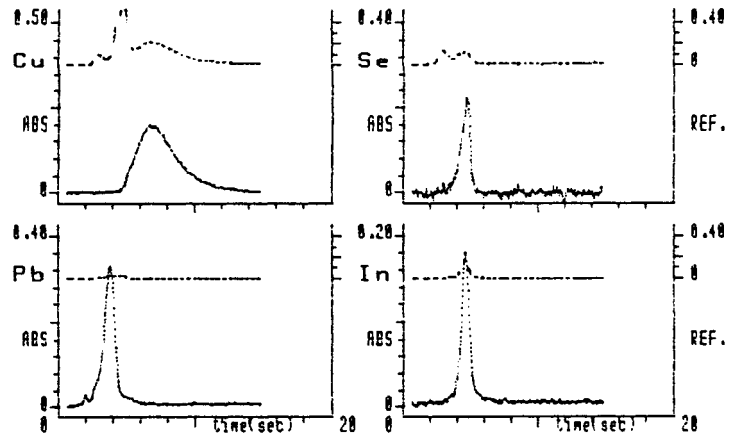|	Temperature (°C)	Time (sec)
Drying	200	30
Ashing	600	30
Atomization	2600	14
Cooling	—	30

Fig. 1 Effect of ashing temperature on absorbance of Cu, In, Pb, and Se

Fig. 2 Absorption profils Cu, In, Se, and Pb in $Ni(PDC)_2$

Absorption profiles

In order to ascertain the heating conditions and determine the atomization time, the absorption profile for each element was investigated. Typical absorption patterns of the lead, selenium, copper and indium in nickel/APDC complex are shown in Fig.2, and it was found that the atomizing time at 2600 °C requires 6 sec for lead 8 sec for selenium and indium, but the atomizing time for copper requires 14 sec because relatively large amounts of copper were added as the internal standard element for eliminating the effect of copper contamination. Thus an atomizing time of 14 sec was determined, and the optimum heating conditions for this method are summarized in Table 2.

Effects of pH on the coprecipitation and recoveries

The effects of pH on the coprecipitation of lead, selenium, copper and indium with the nickel/APDC complex were examined.

As shown in Fig.3, the optimum pH for the coprecipitation of lead, selenium, copper and indium was in the range of 1-5, so that a range of 2-3 was used.

The recovery tests for lead and selenium were examined at pH 2-3 when known amounts of the metals were spiked into 100 ml of water samples.

Table 3. Recoveries of Se(IV) and Pb(II) by coprecipitation with $Ni(PDC)_2$

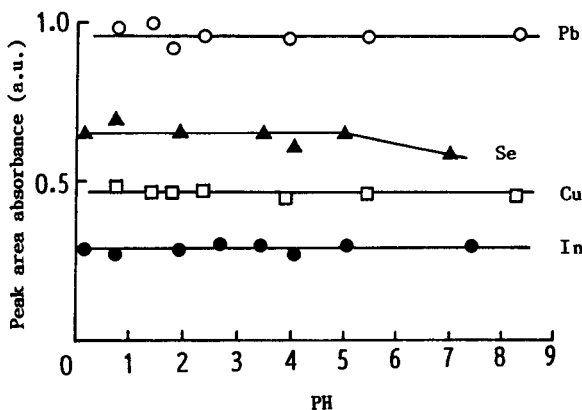| Sample (100 g)	Element added[μg]	Ni added [mg]	Recovery [%]* Se(IV)	Pb(II)
Pure water	10.0	3	100	98
Tap water	5.00	3	99	99
Sea water	5.00	3	100	99
Tap water	1.00	1	100	100
Sea water	1.00	1	100	100

Sample taken: 100 g   *3 determinations (RSD 5%)

Fig. 3 Effect of pH on recoveries of Pb, Se, Cu, and In by coprecipitation with Ni(PDC)$_2$

Table 4. Sensitivities, detection limit and precision for Se and Pb

		Se	Pb
Sensitivity (absorbance 0.0044)	[ng]	0.5	0.2
Detection limit (3 times of RSD for 5 determinations)	[ng]	7	3
Precision (RSD of 10 determinations)	[%]	6.9	4.5

Concentration factors, detection limits and precision

The concentration factor is defined as a weight ratio of the aqueous sample to the precipitate on the filter, because it is unnecessary to redissolve the chelating precipitates in the proposed method.

Therefore, the concentration factor depends on the amounts of nickel as the carrier metal in this case. Adding 3 mg of nickel to 100 g of waters a concentration factor was reached of about 5000. It is possible to increase the sample volume to at least 300 g.

The detection limit is defined as the value of three times relative standard deviation : RSD of the analytical blank values calculated from the calibration curves for each element. Based on this definition, the detection limits and analytical precision were calculated as shown in Table. 4.

Selection of the internal standard elements and calibration graph for lead and selenium

It has been pointed out that the use of a microbalance is laborious and expensive in the solid sampling technique with AAS. This problem was overcome by the use of the internal standard method. In the proposed method, various restrictive conditions for choosing an internal standard such as in emission spectrometry with d-c arc analysis [18] need not be considered since the specimen had the same matrix as the chemical species, and the analytes in Ni/APDC are quite stable (Fig.1). Therefore the internal standard element was selected depending on the conditions of the coprecipitation with Ni/APDC.

In the present work, copper and indium as the internal standard were examined. The concentration of copper in water samples is usually below 10 µg/kg level, but copper may be apt to be contaminated. Therefore 14 µg of copper were added as the internal standard, and in this case, the spectral line of λ =222.6 nm was used.

As the concentrations of indium in water samples was very low, and this element was not apt to be contaminated, 1.0 µg of indium was added, and the spectral line of λ =410.5 nm was used. It was also possible to use tellurium as an internal standard, because tellurium used spectral line of λ =214.3 nm showed the same behavior as indium. Calibration curves for lead and selenium could be used in the range 1-10 ng for lead and selenium whether the internal standard method was used or not, as shown in Figs.4 and 5.

Determination of tap water and secondary effluent water

The above method was applied to tap water and secondary effluent water from Kitami city. Results for the determination of lead and selenium are listed in Table 5. Though µg/kg level of lead could be determined, selenium was not detected. In this case, the standard addition method for both the elements was applied in order to ascertain the results.
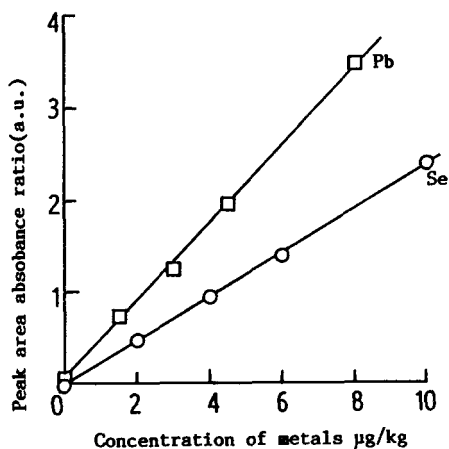
Fig 4. Calibration curves for Se and Pb
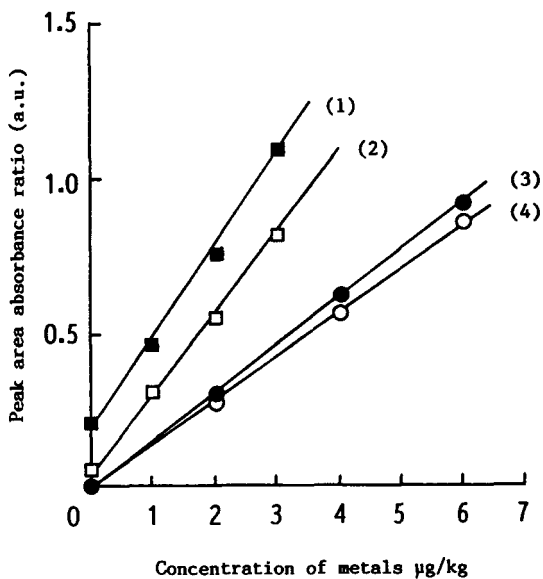Internal standard: In (1.0 μg)

Fig. 5 Calibration curves for Se and Pb in waste
and pure water (Standard addition method)

Internal standard: Cu(14 μg) Sample taken: 100 g
(1)and(3): Pb (■) and Se (●) in waste water
(2)and(4): Pb (□) and Se (○) in Pure water

Table 5. Results for Se and Pb in tap water
determinations

Internal standard	Concentration[μg/L]	
Element	Se	Pb
Cu	N.D.	0.41±0.05
In	N.D.	0.47±0.07

Ni added: 3.0mg.　　Enrichment factor: 5500.
Sample taken: 100g.　　N.D.: not detected

Results for Se and Pb in secondary effluent water
determinations

Internal standard	Concentration[μg/L]	
Element	Se	Pb
Cu	N.D.	0.52±0.08
In	N.D.	0.54±0.02

Ni added: 2.0mg.　　Enrichment factor: 8300.
Sample taken: 100g.　　N.D.: not detected

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