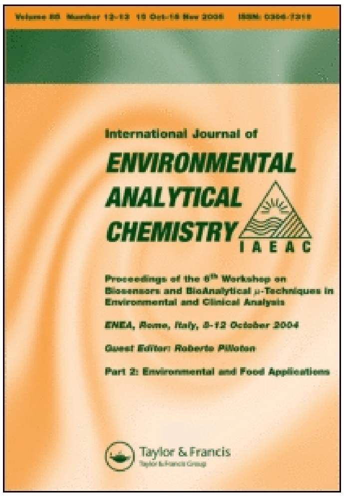

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DETERMINATION OF SILVER IN PLANTS BY FLAME ATOMIC ABSORPTION SPECTROMETRY

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A precise method to determine Ag in plants using flame atomic absorption spectrometry is described. This method consists of the wet digestion of plant samples using conc. HNO_3 and conc. H_2SO_4, and of the separation of Ag into methylisobutylketone (MIBK) using sodium N,N-diethyldithiocarbamate (DDTC) as a complexing agent. Silver in the MIBK was determined by direct aspiration into flame atomic absorption spectrophotometer.

By this method, we could recover almost 100% of added Ag to plants. The Ag content in a reference material determined by this method was in good agreement with the certified value.

The amounts of Ag in plants taken near the Hitachi Mine and Smelter was determined by this method. The Ag contents ranged from 0.066 to 2.41 $\mu g\ g^{-1}$, which were higher than uncontaminated rice blade or spinach.

KEY WORDS: Silver, plants, flame atomic absorption spectrometry

INTRODUCTION

Silver has been found to be toxic to bacteria, algae, or fishes. The Japan Association of Industrial Health[1] has recommended the maximum permissible content of Ag in the working environment to be 0.01 mg m^{-3}, which is a stricter value than that of Cd or Hg (0.05 mg m^{-3}).

We have established a determination method of Ag in soils using flame atomic absorption spectrometry by extracting Ag into methylisobutylketone (MIBK) with sodium N,N-diethyldithiocarbamate (DDTC) after digesting with 6 M HCl, and have shown that no ions in soils or acids other than perchloric acid influenced the Ag determination[2]. We have also established a determination method of Ag in water[3]. Furthermore a precise Ag determination method for plants is required to investigate the contamination of Ag and its behavior in plants.

Some data about the Ag contents in plants has been reported. Bowen[4] showed the content of Ag in vascular plants to be 0.01–0.8 $\mu g\ g^{-1}$. Horovitz *et al.*[5] used neutron activation analysis to determine Ag in plants and reported the contents to be 0.02–0.1 $\mu g\ g^{-1}$. Jones *et al.*[6] reported the usefulness of furnace atomic absorption spectrometry to determine Ag in plants, and showed the Ag contents in vascular plants to be 0.015 (0.008–0.99) $\mu g\ g^{-1}$.

We investigated the method of using more reliable flame atomic absorption spectrometry with a preconcentration of Ag by the organic solvent extraction method we adopted for the determination of Ag in soils[2].

EXPERIMENTAL

Apparatus

A Shimadzu model AA610S atomic absorption spectrophotometer was used with a Hamamatsu Photonics Ag hollow-cathode lamp and a Shimadzu model U-125MN recorder. The instrumental and operating conditions were those recommended by the manufactures.

Reagents

Silver standard solution in 1 M HNO_3 was prepared from Silver Standard Solution (1 mg mL^{-1}. Kanto Chemical Co. Inc.). A 10% solution of tetrasodium ethylenediaminetetraacetate (EDTA · 4Na. Dojin Chemical Laboratory) and a 2% solution of sodium N,N-diethyldithiocarbamate (DDTC. Wako Pure Chemical Industries, Ltd.) were made up in distilled water.

The DDTC and methylisobutylketone (MIBK. Wako Pure Chemical Industries, Ltd.) used were of analytical-reagent grade, and the other reagents were of special (GR) grade.

Plant samples

To evaluate the determination method, 3 plant samples were used. Two samples were unpolluted plants of which rice (*Oryza sativa* L.) blade was taken in the Experimental Farm of Ibaraki University and spinach (*Spinacia oleracea* L.) was purchased in a market. Hebinonegoza (*Athyrium yokoscense* Christ) was taken near the Hosokura Mine and Smelter. The Hosokura Mine and Smelter had produced mainly Pb, Zn and Ag.

Plants were washed thoroughly with distilled water and dried at 80°C for more than 48 hours, then ground in an electric grinder.

THE EVALUATION OF THE DETERMINATION METHOD OF Ag IN PLANTS

Proposed method

The concentration of Ag in plants was so small that it should be preconcentrated for determination. We examined the method of using DDTC-MIBK extraction, which we adopted for the determination of Ag in soils[2], after wet digestion of plant samples. The existence of perchloric acid in sample solution was shown to prevent the extraction of Ag into MIBK phase[2]. Therefore, we adopted a wet digestion of using HNO_3 and H_2SO_4.

The Ag determination method we proposed was as follows. Two g of plant sample were weighed into a 500 mL Kjeldahl flask and 20 mL of conc. HNO_3 and 10 mL of conc. H_2SO_4 were added. The flask was gently heated until the evolution of NO_2 had ceased and the evolution of white gaseous H_2SO_4 had occurred. If the solution in the flask was still black or brown, it was cooled at room temperature and 5 more mL of conc. HNO_3 were added, then heated again. This procedure was repeated until the solution became clear or faintly yellow. The solution was then made up to volume in a 100 mL volumetric flask.

Fifty mL of the sample solution was placed in a 100 mL beaker. While stirring with a magnetic stirrer, 5 mL of 10% EDTA.4Na solution was added and the pH was adjusted to 9.5 using conc. NH_4OH solution, then 5 mL of 2% DDTC solution was added. The solution was transferred into a 200 mL squib separating funnel, then 5 mL of MIBK was added, and shaken thoroughly for 3 minutes with a shaker. The MIBK phase was separated into a 10 mL stoppered test tube. The Ag concentration was determined using atomic absorption spectrometry by direct aspiration of the MIBK into flame.

The detection limit (S/N = 2; the concentration for signal peak twice as large as the noise width) for Ag using the method was 1 μg L^{-1} for the MIBK phase, which corresponded to detect 0.005 μg Ag in 1 g of plant sample.

Recovery of Ag added to plants

The recovery of Ag added to plant samples was investigated. In this experiment, 1 mL of 0, 0.1 or 0.5 μg mL^{-1} $AgNO_3$ solution was added to 2 g of each sample. These correspond to the addition of 0, 0.05 or 0.25 μg Ag for 1 g of each sample, respectively. The recoveries were nearly 100%, and ranged from 96.0 to 102.0%, as shown in Table 1.

The determination of Ag in the reference material

To evaluate the accuracy of the method, Ag in a reference material was determined. The reference material used was the NIES (National Institute for Environmental Studies) No. 1 pepperbush (*Clethra barbinervis* Sieb. et Zucc.). The experiment was made in triplicate. The determined Ag content was 0.033 μg g^{-1}, while the certified value was 0.034 μg g^{-1}, as shown in Table 2. The certified value had been determined by using isotope dilution surface ionization mass spectrometry by Murozumi *et al.*[7].

Table 1 Recovery of Ag added to plants.

Plants	*Ag addition* *(μg g^{-1})*	*Ag found* *(μg g^{-1})*	*Ag recovery*	
			(μg g^{-1})	*(%)*
Rice	0.000	0.020	–	–
	0.050	0.068	0.048	96.0
	0.250	0.269	0.249	99.6
Spinach	0.000	0.018	–	–
	0.050	0.069	0.051	102.0
	0.250	0.266	0.248	99.2
Hebinonegoza	0.000	1.750	–	–
	0.250	1.990	0.240	96.0

The determination was made in triplicate.

Table 2 Ag content in a reference sample.

Reference plant	*Ag content (μg g $^{-1}$ DW)*	
	This method	*Murozumi et al.*
Pepperbush	0.033 ± 0.003	0.034

The determination was made in triplicate.

DETERMINATION OF Ag IN PLANTS TAKEN NEAR THE HITACHI MINE AND SMELTER

By using this method, the Ag contents of 11 plants were determined, of which 9 were Hebinonegoza (*Athyrium yokoscense* Christ) and 2 were mugwort (*Artemisia princeps* Pamp.). These plants were taken in the vicinity of the Hitachi Mine and Smelter, which had produced mainly Cu. The location of the Hitachi Mine and Smelter, and the sampling points are shown in Figure 1. The soils near the Hitachi Mine and Smelter are contaminated by Ag (unpublished data), or Cu. etc.[8].

The contents of Ag and the other heavy metals in these plant samples are shown in Table 3. The arithmetic mean of Ag contents was 0.557 μg g^{-1}, ranging from 0.066 to 2.41 μg g^{-1}. These values are extremely high compared with the content in uncontaminated rice blade or spinach shown in Table 1. The result shows that the plants grown on the Ag contaminated soil contain a considerable amount of Ag, nevertheless the amount of "soluble and exchangeable" Ag in the soil was less than 1% of total soil Ag[9].

The correlation coefficient between Ag and Cu contents was 0.960 which was significant at the 0.1% level, but those between Ag and other metals were not significant.

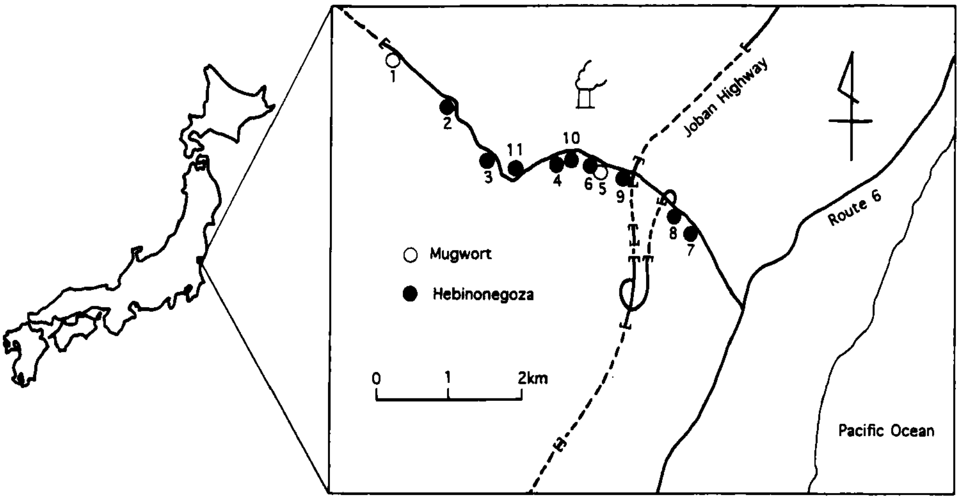

Figure 1 Sampling location near the Hitachi Mine and Smelter.

Table 3 Silver and other heavy metal contents in plants grown on the soils polluted by the heavy metals discharged from the Hitachi Mine and Smelter.

No.	*Plants*	*Heavy metal contents ($\mu g\ g^{-1}$ DW)*				
		Ag	*Cd*	*Pb*	*Zn*	*Cu*
1	Mugwort	0.074	1.48	3.95	86.6	13.5
2	Hebinonegoza	0.096	1.33	1.98	34.4	9.8
3	Hebinonegoza	0.066	1.99	5.05	77.5	9.1
4	Hebinonegoza	0.654	24.8	37.5	141	24.3
5	Mugwort	0.151	2.93	13.8	81.7	32.0
6	Hebinonegoza	0.252	4.16	18.6	48.0	28.2
7	Hebinonegoza	2.41	4.31	36.5	158	198
8	Hebinonegoza	0.676	19.0	13.6	302	51.7
9	Hebinonegoza	0.954	1.96	7.73	65.8	115
10	Hebinonegoza	0.567	45.3	51.6	141	55.6
11	Hebinonegoza	0.230	53.2	2.73	142	15.5

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