DETERMINATION OF SILVER IN SOILS BY ATOMIC ABSORPTION SPECTROMETRY

SATOSHI SAEKI, MASATSUGU KUBOTA and TERUO ASAMI

School of Agriculture, Ibaraki University, Ami, Ibaraki 300–03, Japan

Abstract. A method for the determination of Ag in soils using atomic absorption spectrometry is described. The method involves the extraction of Ag from soil by boiling with 6 M HCl followed by separation of the extracted Ag into methylisobutylketone (MIBK) using sodium N, N-diethyldithiocarbamate (DDTC) as a complexing agent. Silver is determined in the MIBK by direct aspiration into a flame atomic absorption spectrophotometer. The detection limit (S/N=2) for this method is 0.0001 mg L^{-1} for aqueous solution and 0.002 mg kg^{-1} for soil. The Ag content of even unpolluted soils can be determined by this method.

The determination of Ag using this method was shown to be unaffected by the presence of various ions in the soil. The method was able to recover nearly 100% of Ag added to soil and approximately the same amounts of soil Ag were determined using this method as with HF-H_2SO_4 decomposition. For 3 reference soils of the Canadian Certified Reference Materials Project (CCRMP), the Ag values obtained by this method were the same as the values determined by Ebarvia *et al.* (1988).

The amounts of Ag in the soils sampled in the Ichi River basin and the Ichi River sediments were determined using this method. This area has been polluted by Cd, Cu, Pb, and Zn discharged from the Ikuno Mine and Smelter. The Ag values ranged from 0.27 to 6.89 mg kg^{-1} which were much higher than the values of the unpolluted soils.

1. Introduction

Silver is known to be very toxic to bacteria, and has been used as an antimicrobial agent and for water purification. For human beings, Ag accumulation in the body leads to a grayish blue discoloration of skin and a disturbance of the dark adaptation of eyes. These conditions are known as argyria and argyrosis. (Smith and Carson, 1977).

A threshold value for Ag in working environments has been recommended in many countries. The Japan Association of Industrial Health (1992) reported such values as follows. In the USA, the recommended values are 0.1 mg m^{-3} in dust and fumes, and 0.01 mg m^{-3} as soluble Ag compounds. In Germany, they are 0.01 mg m^{-3}. In Finland they are 0.1 m^{-3} in dust and insoluble Ag compounds, and 0.01 mg m^{-3} as soluble Ag compounds. In Australia, Berlgium, the Netherlands, Switzerland, and Yugoslavia, the value is 0.01 mg m^{-3} as total Ag. In Rumania, the value is 0.005 mg m^{-3} as a median and 0.015 mg m^{-3} as a threshold value. The Japan Association of Industrial Health recommended an Ag value 0.01 mg M^{-3} as total Ag. This limit is more severe than for Cd (0.05 mg m^{-3}) in the same recommendations.

Silver co-exists in Cu, Pb, and Zn ores besides Ag ores. Silver is scattered in the environment by mining and smelting these metals. Silver is also dispersed

by various industries such as photographic film, medicinal chemicals, tableware, electroplating, mirror, and jewelry etc. Only 7% of the domestic Ag supply is recycled Ag, and a large amount of Ag is dispersed not only during production but also by use and abandonment of the above products. This suggests that Ag pollution may be extensive and that an accurate method for determining Ag in the environment is required.

Silver pollution in soils was reported by Jones *et al.* (1983, 1984), and Ward *et al.* (1977) who used atomic absorption spectrometry to determine Ag. However these workers did not describe in detail the methods used to determine the amount of Ag in soil. We have investigated and established a method to determine soil Ag by using flame atomic absorption spectrometry.

2. Materials and Methods

2.1. 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 these recommended by the manufacturers. An air-C_2H_2 flame was used.

2.2. REAGENTS

Silver standard solutions: Ag standard solution in 1 M HCl was prepared from Silver Standard Solution (1 mg mL^{-1}. Kanto Chemical Co. Ltd.).

Tetrasodium ethylendiaminetetraacetate (EDTA·4Na) (50%,w/v) solution: 500 g of EDTA·4Na (Dojin Chemical Laboratory) was dissolved in 1 L of distilled water.

Sodium N, N-diethyldithiocarbamate (DDTC) (2%) solution: A 2% solution of DDTC (Wako Pure Chemical Industries, Ltd.) was made up in distilled water.

The DDTC and methylisobutylketone (MIBK) used, were of analytical-reagent grade.

2.3. SOIL SAMPLES

Four soil samples were used of which 2 samples were from polluted soils and the other 2 from unpolluted soils.

Annaka soil (Mollic Gleysol) was sampled near the Annaka Smelter, and Fuchu soil (Eutric Gleysol) was sampled in the Jinzu River basin, where Itai-Itai disease had occurred. Konosu soil (Eutric Gleysol) was sampled from a paddy field of the Central Agricultural Experiment Station, and Nagano soil (Eutric Cambisol) was sampled from a paddy field of the Nagano Agricultural Experiment Station.

2.4. PROPOSED METHOD FOR DETERMINATION OF SOIL Ag

Soil samples were air-dried and passed through a 2 mm aperture sieve, and were ground fine with a glass mortar if necessary. Five g of soil sample was weighed into a 100 mL Erlenmyer flask fitted with a Liebig condenser and boiled gently with 20 mL of 6 M HCl for 1 hr on a sand bath. The extract was then filtered and made up to 100 mL with distilled water in a volumetric flask. This is referred to as the sample solution.

Fifty mL of the sample solution was placed into a 100 mL beaker. While stirring the solution with a magnetic stirrer, 10 mL of 50% 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 to a 200 mL squib separating funnel, then 5 mL of MIBK was added, and shaken thoroughly for 3 min 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 phase into flame.

EDTA was added to prevent some metals other than Ag from being extracted into the MIBK phase. The amount of EDTA added was calculated to be able to complex up to $5000 \, mg \, L^{-1}$ of Fe in sample solutions. Iron was extracted from soils as Fe^{2+} and Fe^{3+} into the sample solution and interfered with the measurement of Ag because the viscosity of the MIBK phase was increased by Fe thus causing variation in aspiration rates into the flame. Adjusting the pH of the solutions to 9.5 was also necessary to prevent Fe from being extracted in the MIBK phase.

3. Results and Discussion

3.1. DETECTION LIMIT OF Ag

The detection limit (the Ag concentration when the signal peak of Ag is as twice as the noise width; S/N=2) for Ag using the proposed method was evaluated. The detection limit was $0.0001 \, mg \, L^{-1}$ for aqueous solutions and $0.002 \, mg \, kg^{-1}$ for soils, therefore even the Ag contents of unpolluted soils could be determined by this method.

3.2. EFFECTS OF VARIOUS IONS

The effects of 30 different ions in solution on the determination of Ag were investigated (Table I). In this experiment 2.5 μg of Ag together with the various ions were dissolved in 50 mL of 1 M HCl solution. This was equivalent to sample solutions prepared by hot 6 M HCl extraction. The added Ag was then determined by the proposed method.

Almost 100% of Ag was recovered in the presence of all ions examined except for Al^{3+}. A positive effect was given by $8\,000 \, mg \, L^{-1}$ or more of Al^{3+} in solution.

TABLE I

Effect of various ions on the recovery of Ag

Element	Compound	Added		Ag recovered (%)	Median of unpolluted soil[a] (mg kg^{-1})
		For solution (mg L^{-1})	For soil (mg kg^{-1})		
–	–	–	–	100	–
Al^{3+}	$AlCl_3$	10 000	200 000	111	71 000
		8 000	160 000	107	
		7 000	140 000	103	
		6 000	120 000	101	
Fe^{2+}	$FeSO_4$	5 000	100 000	99	40 000
Fe^{3+}	$FeNH_4(SO_4)_2$	5 000	100 000	98	
Ca^{2+}	$Ca(NO_3)_2$	1 500	30 000	99	15 000
K^+	KCl	1 500	30 000	100	14 000
Mg^{2+}	$MgSO_4$	500	10 000	97	5 000
Na^+	$NaNO_3$	500	10 000	99	5 000
Ti^{3+}	$TiCl_3$	500	10 000	100	5 000
Mn^{2+}	$Mn(NO_3)_2$	200	4 000	101	1 000
Cu^{2+}	$CuSO_4$	200	4 000	99[b]	30
Zn^{2+}	$Zn(NO_3)_2$	200	4 000	99	90
Pb^{2+}	$Pb(NO_3)_2$	200	4 000	100	35
Cr^{3+}	$CrCl_3$	100	2 000	100	70
Cr^{6+}	$K_2Cr_2O_7$	100	2 000	102	
Ni^{2+}	$Ni(NO_3)_2$	100	2 000	102	50
Sn^{2+}	$SnSO_4$	100	2 000	98	4
Ba^{2+}	$Ba(NO_3)_2$	50	1 000	100	500
Zr^{4+}	$ZrO(NO_3)_2$	50	1 000	102	400
Sr^{2+}	$Sr(NO_3)_2$	50	1 000	100	250
As^{3+}	As_2O_3	50	1 000	99	6
V^{5+}	NH_4VO_3	10	200	100	90
La^{3+}	$La(NO_3)_3$	10	200	101	40
Li^+	$LiNO_3$	10	200	98	25
Ga^{3+}	$Ga(NO_3)_3$	10	200	98	20
Co^{2+}	$Co(NO_3)_2$	10	200	101	8
Cd^{2+}	$Cd(NO_3)_2$	10	200	101	0.35
Sb^{3+}	$SbCl_3$	10	200	99	1
Ge^{4+}	K_2GeO_3	10	200	99	1
Bi^{3+}	$Bi(NO_3)_3$	10	200	101	0.2
Tl^+	$TlNO_3$	10	200	101	0.2

2.5 μg Ag was added to each 50 mL sample solution.
[a] Data from Bowen (1979).
[b] 10mL of DDTC solution (2%) was added.

TABLE II

Effect of acids on the recovery of added Ag

Acid	Concentration (M)	Recovered (%)
HCl	1	100
HNO_3	1	98
H_2SO_4	0.5	98
$HClO_4$	1	64
	0.1[a]	71
	0.01[a]	90
	0.001[a]	100

2.5 μg Ag was added to each 50 mL sample solution.
[a] HCl was added to make the concentration of acid 1 M.

However the amounts of Al^{3+} extracted from soils by hot 6 M HCl were much less than this value, and thus no effect of Al^{3+} is considered likely in ordinary soils.

In the case of an addition of 200 mg L^{-1} Cu^{2+}, 10 mL of DDTC solution was added instead of 5 mL, because too much DDTC was preferentially complexed by Cu^{2+}. If the Cu^{2+} concentration is less than 150 mg L^{-1}, 5 mL of DDTC is sufficient.

3.3. EFFECTS OF ACIDS

The effects of different acids on the determination of Ag were investigated. In this experiment 2.5 μg of Ag was added to 50 mL of 1 M HCl, 1 M HNO_3, 0.5 M H_2SO_4, or 1 M $HClO_4$ respectively, and Ag was determined using the proposed method. The results are shown in Table II.

The same Ag concentrations were determined in HNO_3 and H_2SO_4 solution as in HCl solution. However a substantially lower Ag concentration was obtained in $HClO_4$ solution. Therefore it would appear that $HClO_4$ is not suitable for Ag extraction from soils.

3.4. COMPARISON OF METHODS FOR EXTRACTING Ag FROM SOIL

The HF-H_2SO_4 decomposition method is used for the extraction of heavy metals from soil (Geological Survey of Japan, 1976). The proposed hot 6 M HCl extraction was compared with the HF-H_2SO_4 method. As shown in Table III, approximately the same amounts of Ag were obtained for the 4 soils using both methods. Since hot 6 M extraction is easier and faster than the HF-H_2SO_4 method, the proposed method is appropriate for the extraction of Ag from soils.

TABLE III

Comparison to HF-H$_2$SO$_4$ decomposition (mg kg^{-1} dry soil)

Soil	Determined value	
	HF-H$_2$SO$_4$	6 M HCl
Annaka	1.963	1.640
Fuchu	1.405	1.410
Konosu	0.145	0.138
Nagano	0.105	0.100

TABLE IV

Recoveries of Ag added to soils

Soil	Ag added (μg 5g^{-1})	Ag found (μg 5g^{-1})	Recovery (μg 5g^{-1})	(%)
Annaka[a]	0	8.20	–	–
	1.00	9.18	0.98	98.0
	5.00	13.06	4.86	97.2
Fuchu	0	7.04	–	–
	1.00	8.00	0.96	96.0
	5.00	12.04	5.00	100.0
Konosu	0	0.69	–	–
	1.00	1.69	1.00	100.0
	5.00	5.52	4.83	96.6
Nagano	0	0.50	–	–
	1.00	1.50	1.00	100.0
	5.00	5.22	4.72	94.4

[a] Sample was ground fine.

3.5. RECOVERY OF Ag ADDED TO SOIL

The recovery of Ag added to 4 soils is shown in Table IV. Silver was added to each soil (0, 1, or 5 μg per 5 g soil) and determined by the proposed method. The recoveries of Ag from the soils ranged from 94.4% to 100.0%.

3.6. DETERMINATION OF Ag IN REFERENCE SOILS

In order to determine the accuracy of proposed method, Ag in 4 reference soils of Canadian Certified Reference Materials project (CCRMP) were determined by the

TABLE V

Ag content in reference soils (mg kg^{-1} dry soil)

Reference soil	Ag content	
	This method	Ebarvia *et al.*
SO-1	0.098	0.100
SO-2	0.047	0.080
SO-3	0.010	<0.050
SO-4	0.117	0.120

TABLE VI

Silver and other heavy metal contents in paddy soils derived from the Ichi River basin and the Ichi River sediments

No.	Soils and sediments	Heavy metal contents (mg kg^{-1} dry soil)				
		Ag	Cd	Zn	Pb	Cu
1	Paddy soil	2.95	1.71	378	239	62
2	River sediment	1.22	4.79	731	157	65
3	River sediment	4.60	4.05	1950	418	473
4	Paddy soil	1.96	1.55	922	285	128
5	Paddy soil	0.61	0.62	142	26	42
6	Paddy soil	6.89	9.30	1670	609	402
7	Paddy soil	1.15	5.20	1370	169	121
8	Paddy soil	0.27	0.41	133	47	23
9	Paddy soil	1.50	5.10	839	245	144
10	Paddy soil	1.96	2.24	1040	160	149
11	River sediment	1.81	2.94	1350	144	187

proposed method. The results are shown in Table V. The Ag values obtained in this work were in good agreement with the values determined by Ebarvia *et al.* (1988) for reference samples SO-1, SO-3 and SO-4, but a lower value was obtained for sample SO-2.

3.7. THE AMOUNTS OF Ag IN PADDY SOILS IN THE ICHI RIVER BASIN AND THE ICHI RIVER SEDIMENTS

The Ikuno Mine (Hyogo Prefecture, Japan) has been famous for its Ag mining for a long time. It has produced Ag since 1542 and has also produced Cu, Pb, and Zn, and in the process polluting the Ichi River ans its basin. Though mining ended in 1976, old waste heaps and drainage of the mine are still polluting this area. The
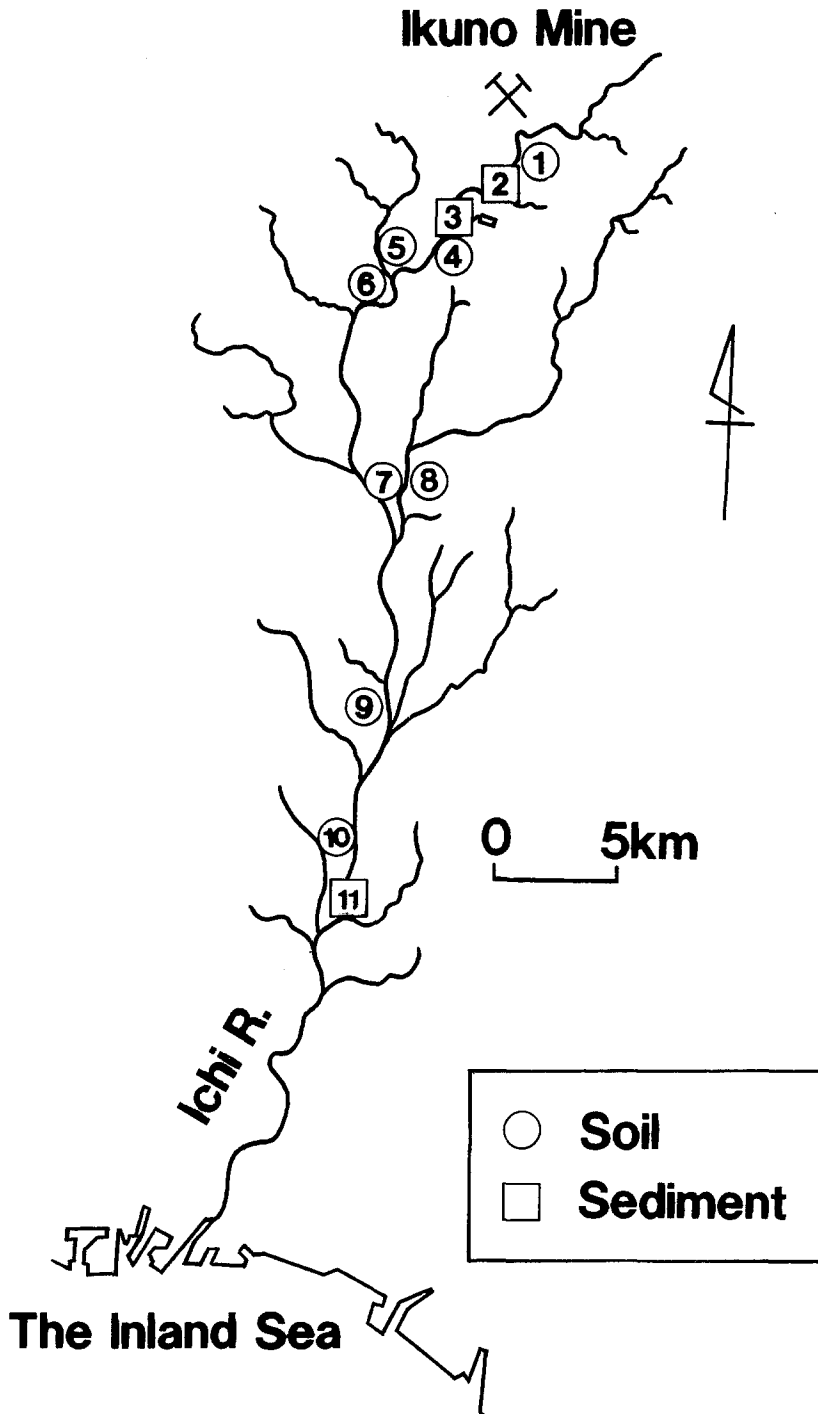
Ikuno Mine

Fig. 1.   Sampling location in the Ichi River and the Ichi River basin.

Cd, Cu, Pb and Zn pollution of soils and sediments in this area were reported by Asami *et al.* (1981,1982) and Asami (1988).

The amounts of Ag in 8 paddy field plow-layer soils in the Ichi River basin and 3 Ichi River sediments were determined by the proposed method. The sampling locations are shown in Figure 1 and the results are shown in Table VI. The Ag values ranged from 0.27 to 6.89 mg kg^{-1} dry soil. The Ag values of unpolluted Konosu and Nagano soils were 0.14 and 0.10 mg kg^{-1}, respectively, and the median of reported Ag values in soils compiled by Bowen (1979) was 0.05 mg kg^{-1}. The Ag values of the Ichi River sediments and paddy soils of the basin were much higher than these values.

The Ag contents in these samples showed high correlations with Cu and Pb contents. The correlation coefficient between Ag and Cu was 0.857, and between Ag and Pb was 0.954. The correlations were significant at the 0.1% level.

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