Determination of Ag and Cd in Soil and Sediment Samples by Graphite Furnace Atomic Absorption Spectrometry (GFAAS)

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INTRODUCTION

Silver (Ag) occurs in nature as sulphides, tellurides, arsenides, antimonides, and halides. It also occurs as native state and is associated with native gold and copper. The only oxygen compound of Ag known to occur in nature is argentojarosite, a sulphate of silver and iron. The crustal abundance of silver is 0.070 ppm and of cadmium it is 0.1 ppm. Cadmium (Cd) is a relatively rare metal and found in association with zinc (Zn) (1). It occurs usually as green ockite associated with sphalerite. The Geological Survey of India has taken up the National Geochemical Mapping (NGCM) program and 68 elements are to be determined in soil and sediments at their crustal abundance level or below. The 68 elements are divided into 10 different packages, i.e., from Package A to Package J. The elements Ag and Cd come under Package F and the required detection limits were set as 20 and 100 ppb, respectively. These elements are very useful in geochemical exploration.

Elemental analysis by graphite furnace atomic absorption spectrometry (GFAAS) is normally carried out in the solution phase (2). Geological samples, e.g., soils, sediments, rocks, ores, minerals, etc., are usually brought into solution by mineral acid digestion. Dissolution of geological samples to bring Ag and Cd in solution is an important part of the analysis. Matrix and background absorbance

ABSTRACT**

An extensive study has been made for the determination of silver (Ag) and cadmium (Cd) in soil and sediment samples using different decomposition procedures. A simple and rapid method has been developed for the accurate determination of Ag and Cd at ppb levels by graphite furnace atomic absorption spectrometry (GFAAS). In the present study, -200 mesh size samples were digested in a 100-mL glass beaker using 1:1 HNO₃ for measurement of Ag and Cd by GFAAS. A bulk calibration standard of 20 ppb of Ag and 10 ppb of Cd was used for the measurement of silver and cadmium, respectively. The method was proposed for the determination of Ag and Cd in soil and sediment samples collected according to the guidelines of the National Geochemical Mapping (NGCM) program and is being followed by the Geological Survey of India with an objective for Geochemical Mapping. The precision of the proposed method was investigated by analyzing 10 soil and sediment samples, and the estimated value of the RSD (%) was found to be <10%. The efficiency of the method was also compared by analyzing 10 international soil and sediment reference samples. Very good agreement and excellent precision were observed for the certified values. The limit of quantitation (10 σ) achieved for Ag was 5.0 ng/g and for Cd it was 2.0 ng/g, with a recovery of 95–103%

play a vital role for the estimation of elements by GFAAS at such a low level of concentration. Viets et al. (3) determined these elements by flame atomic absorption spectrometry (FAAS) using alkaline fusion, followed by hydrochloric acid dissolution and pre-concentration in an organic solvent resulting in a detection limit of 100 ppb. Zongshou Yu et al. (4) reported different digestion techniques such as HF/HClO₄, HF/HNO₃, and HF/H₂SO₄ to dissolve geological samples for trace element determination. Silver and cadmium were also estimated in geological samples with the help of FAAS and GFAAS by several authors using different acid and fusion mixtures (3, 5–8). There are some complete dissolution and some partial decomposition techniques. But an accurate, precise, simple, and rapid method is required to fulfill the requirement as per the National Geochemical Mapping (NGCM) program.

In this paper, a simple and rapid dissolution procedure has been developed for the determination of Ag and Cd in geological samples collected according to the guidelines of the NGCM program. The samples were pulverized to -200 mesh sizes to reduce the probability of leaving the silver trapped in the silicate phase. The proposed method consists of two parts: dissolution and GFAAS measurement.

For geochemical mapping, the total concentration of the elements is required. These data have a multi-purpose use, e.g., for mineral exploration and environmental investigative study of basic geology (9). Nitric acid digestion has been most commonly used in exploration

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**The abstract of this article was published in the 43rd Chemist Convention conducted by the Indian Chemical Society.

geochemistry for many years, but it does not always provide a total extraction as reported by Chao and Sanzolone (10). Balaram et al. (11) studied *aqua regia* digestion and extraction for some base metals resulting in 95–99% extraction. Saha et al. (5) reported a comparative study using a different dissolution procedure for the measurement of copper, lead, zinc, nickel, cobalt, silver, and cadmium and concluded that HF-HClO₄-HNO₃ digestion is most suitable for the complete extraction of the metals. The present authors observed that complete extraction of Ag and Cd from soil and sediment samples is possible with 1:1 HNO₃. The dilution factor is also very important for low level determination of the elements in geological samples. Flame AAS has been widely used for the trace element determination in geochemical samples (12). However, the detection limits required in NGCM samples for Ag and Cd are very low, and FAAS has not been able to achieve such low detection limits even though some authors have reported such detection limits for one or two elements, e.g., lithium and zinc (13).

Nowadays, GFAAS, inductively coupled plasma atomic emission spectrometry (ICP-AES), and inductively coupled plasma mass spectrometry (ICP-MS) are the most commonly used techniques for the determination of trace amounts of Cd and Ag (14–17). GFAAS is simple, sensitive, and cost-effective in comparison to ICP-AES and ICP-MS, but it is a great challenge to achieve the very low detection limits required for Ag and Cd in geological samples. In most cases, detection limits at the ppb level are achieved only using pre-concentration methods such as ion exchange separation, solvent extraction, etc. Sometimes it is required to digest more samples to reach detection limits at the ppb level, but interferences from high concentrations of

other elements provide erroneous results. The present dissolution technique overcomes almost all possibilities of error. The limit of quantitation (10σ) achieved for the estimation of Ag and Cd is much less than the crustal abundance level, which is also the required detection level for the NGCM program. The validity of the method was checked with 10 certified reference materials (CRMs).

EXPERIMENTAL

Instrumentation

All analyses were performed using a Varian 220 FS atomic absorption spectrophotometer (Varian, Palo Alto, CA, USA). The analytical parameters used for the determination of Ag and Cd by GFAAS are listed in Table I. The temperature profile for measurement of Ag and Cd is depicted in Tables II and III, respectively.

TABLE I
Instrumental Parameters for GFAAS Measurement of Ag and Cd

	Ag	Cd		Ag	Cd
Sampling Mode	Auto Mix	Auto Mix	Calibration Mode	Concentration	Concentration
Measurement Mode	Peak Height	Peak Height	Wavelength	328.1 nm	228.8 nm
Slit Width	0.5 nm	0.5 nm	Lamp Current*	4.0 mA	4.0 mA
Background Corrector	ON	ON	Conc. Decimal Places	2	2
Sample Volume	20 µL	10 µL	Total Volume	25 µL	15 µL
Bulk Conc.	20 µg/L	10 µg/L	Calibration Standards (µg/L)	2, 10, 20	2, 5, 10

* Parameter may change depending on the model of the instrument.

TABLE-II
Temperature Profile for Ag Measurement

Step	Temp. (°C)	Time (sec)	Flow (L/min)	Gas Type	Read	Signal Storage
1	85	5.0	3.0	Normal	No	No
2	95	30.0	3.0	Normal	No	No
3	120	10.0	3.0	Normal	No	No
4	700	25.0	3.0	Normal	No	No
5	700	2.9	3.0	Normal	No	No
6	750	2.9	0	Normal	No	Yes
7	2100	0.8	0	Normal	Yes	Yes
8	2100	2.0	0	Normal	Yes	Yes
9	2150	2.0	3.0	Normal	No	Yes

Reagents and Standard Solutions

All reagents used were of analytical reagent (AR) grade. Distilled 1:1 HNO₃ was preferred for the procedure.

Silver and cadmium standards were prepared from silver nitrate and cadmium nitrate (obtained from Johnson and Matthey Chemical Ltd., Royston, U.K.).

Stock solutions were made of 100 ppm Ag and 100 ppm Cd solution.

100 ppm Ag: 0.17 g of AgNO₃ (SpecPure®) was dissolved in 25 mL 5% HNO₃, and the volume was made up to 1000 mL, maintaining 5% HNO₃ concentration.

100 ppm Cd: 0.236 g of Cd(NO₃)₂ was dissolved in 25 mL of 5% HNO₃, and the volume was made up to 1000 mL, maintaining 5% HNO₃ concentration.

Sub-standard solutions: 1.0 and 0.5 ppm solutions of Ag and Cd, respectively, were prepared by successive serial dilution of the 100 ppm stock solution.

Mixed calibration standard (bulk): 20 ppb and 10 ppb mixed standard solutions of Ag and Cd were prepared with 5% HNO₃ by dilution of the 1.0 ppm and 0.5 ppm Ag and Cd solutions, respectively.

High purity Milli-Q® water (18 MΩ·cm) was used for all of the sample and standard preparation procedures. All glassware and digestion vessels were acid-washed and rinsed with Milli-Q water.

Certified Reference Materials (CRMs)

For this study, the authors have selected 10 CRMs obtained from the China National Analysis Centre for Iron and Steel, Beijing, P.R. China. There are five certified soil reference samples (GSS-1, GSS-2, GSS-3, GSS-5, and GSS-8) and five certified sediment reference samples (GSD-3, GSD-4, GSD-5, GSD-6, and GSD-10).

Dissolution Procedure for the Geological Samples and CRMs

A 2.0-g sample (~200 mesh) was taken into a 250-mL glass beaker, and 80 mL (1:1) HNO₃ (AR) was added. The beaker was covered with a glass lid, placed on a hot plate, and boiled gently for 2.0–2.5 hours. The lid was removed and the solution evaporated slowly to a pasty mass. Then, 10 mL of 5% HNO₃ was added, warmed for 5 minutes, removed from the hot plate, and cooled. The contents were transferred to glass-stoppered graduated test tubes, and the volume was made up to 20 mL with demineralized water. The

solution was kept aside undisturbed overnight to settle down, and then the appropriate volume of the supernatant solution was taken by auto-pipette for its subsequent measurement by GFAAS using the parameters listed in Tables I, II, and III. A process blank was prepared for each batch of samples, following the same procedure as for the original processed sample solution.

RESULTS AND DISCUSSION

This study was made using 10 Chinese CRMs of soil and sediments for the determination of Ag and Cd. Excellent agreement was found with the certified values. The results of these 10 CRMs are listed in the Table IV and demonstrate that 1:1 HNO₃ effectively extracts Ag and Cd present in the soil and sediment samples. In order to investigate the precision of the proposed method, six separate sets of each CRM were dissolved using 1:1 HNO₃, and measurement of the solutions was performed by GFAAS taking the mean of three replicates. As can be seen from Table IV, the percentage RSD (relative standard deviation x 100/mean reading) for the determination of Ag and Cd was in the 4–6% range, except for a few cases where it was estimated to be around 8–9%.

Ten soil and stream sediment samples collected under the NGCM program were also analyzed by the proposed methodology, and uniform recovery of Ag and Cd was observed. The results of these 10 samples are listed in Table V. The precision of the proposed method for the analysis of these samples was checked by following the same procedure as for the CRMs. The estimated RSD value was in the range of 3–8%, confirming good precision of the proposed method. The limit of quantitation (LOQ, 10 times the standard deviation of the digestion procedure blank solution) was expressed as the concentration

TABLE III
Temperature Profile for Cd Measurement

Step	Temp. (°C)	Time (sec)	Flow (L/min)	Gas Type	Read	Signal Storage
1	85	5.0	3.0	Normal	No	No
2	95	30.0	3.0	Normal	No	No
3	120	10.0	3.0	Normal	No	No
4	300	30.0	3.0	Normal	No	No
5	300	2.5	3.0	Normal	No	No
6	400	2.5	3.0	Normal	No	Yes
7	2000	0.8	0	Normal	Yes	Yes
8	2000	2.0	0	Normal	Yes	Yes
9	2100	2.0	3.0	Normal	No	Yes

TABLE IV
Results of Ag and Cd Determination in CRMs by GFAAS

Sample	Ag (ng/g)			Cd (ng/g)		
	Observed	Determined mean $\pm$ SD	Certified	Observed	Determined mean $\pm$ SD	Certified
GSS-1	366,381,400,389,406,398	390 $\pm$ 14.68	350 $\pm$ 70	4375,4500, 4213,4555, 4183,4424	4375 $\pm$ 150.69	4300 $\pm$ 600
GSS-2	53,59,52,56, 57,47	57 $\pm$ 4.28	54 $\pm$ 10	71,78,76, 82,73,64	74 $\pm$ 6.22	71 $\pm$ 22
GSS-3	87,93,86,83, 81,80	85 $\pm$ 4.77	91 $\pm$ 11	49,47,54, 46,53,57	51 $\pm$ 4.33	59 $\pm$ 20
GSS-5	4200,4486, 4314,4050, 4005,3965	4170 $\pm$ 202.55	4400 $\pm$ 600	460,449,435,443,403,390	430 $\pm$ 27.51	450 $\pm$ 90
GSS-8	50,46,48,56, 59,53	52 $\pm$ 4.94	60 $\pm$ 14	122,130,112,103,109,120	116 $\pm$ 9.82	130 $\pm$ 50
GSD-3	570,560,588,555,612,565	575 $\pm$ 21.39	590 $\pm$ 70	97,95,92, 87,83,86	90 $\pm$ 5.51	100 $\pm$ 20
GSD-4	90,98,103, 100,96,89	96 $\pm$ 5.55	84 $\pm$ 26	177,194,186,173,165,167	178 $\pm$ 11.22	190 $\pm$ 30
GSD-5	372,350,395,370,365,380	372 $\pm$ 15.03	360 $\pm$ 40	820,840,828,808,780,784	810 $\pm$ 24.10	820 $\pm$ 70
GSD-6	355,378,375,336,341,346	355 $\pm$ 17.70	360 $\pm$ 40	409,435,402,416,390,420	412 $\pm$ 15.50	430 $\pm$ 30
GSD-10	261,252,240,287,280,246	261 $\pm$ 18.89	270 $\pm$ 30	1174,1067, 1140,1096,1125,1130	1122 $\pm$ 36.88	1120 $\pm$ 120

SD = standard deviation of six determinations.

TABLE V
Results of Ag and Cd Determination of 10 Soil and Sediment Samples by GFAAS

Sample ID		Sample Type	^a Determined mean $\pm$ SD ^b RSD(%)	
			Ag (ng/g)	Cd (ng/g)
1.	14935-1	Soil	21 $\pm$ 1.34 (6.38)	59 $\pm$ 2.13 (3.61)
2.	14935-10	Soil	26 $\pm$ 1.55 (5.96)	63 $\pm$ 1.98 (3.14)
3.	14935-21	Soil	44 $\pm$ 1.87 (4.25)	125 $\pm$ 1.87 (1.49)
4.	14935-31	Soil	20 $\pm$ 1.42 (7.10)	50 $\pm$ 1.74 (3.48)
5.	14935-41	Soil	5 $\pm$ 0.46 (9.20)	9 $\pm$ 0.43 (4.78)
6.	14849-1	Stream Sediment	24 $\pm$ 1.43 (5.96)	41 $\pm$ 1.21 (2.95)
7.	14849-4	Stream Sediment	33 $\pm$ 1.63 (4.94)	49 $\pm$ 1.33 (2.71)
8.	14849-11	Stream Sediment	27 $\pm$ 1.59 (5.89)	46 $\pm$ 1.56 (3.39)
9.	14849-18	Stream Sediment	23 $\pm$ 1.26 (5.48)	42 $\pm$ 1.37 (3.26)
10.	14849-19	Stream Sediment	11 $\pm$ 0.78 (7.09)	27 $\pm$ 1.19 (4.41)

^a Mean of six determinations.

^b %RSD = relative standard deviation values listed in parentheses..

in the samples, thereby accounting for the dilution factor used. The standard calibration curves obtained for the measurement of Ag and Cd are shown in Figures 1 and 2. The absorbance value of a 10-ppb Ag solution was 0.1974, whereas for a 4-ppb Cd solution it was 0.2253. The characteristic concentration for Ag and Cd was 0.222 ng/mL and 0.0781 ng/mL, respectively. Thus, a solution containing 0.222 ng/mL Ag and 0.0781 ng/mL Cd will give 1% absorption. The LOQ (10 σ) observed for the quantification of Ag was 5 ng/g and for Cd 2 ng/g, which is below the crustal abundance level; the RSD was <10%. These results confirm that this methodology may be used very effectively for the determination of Ag and Cd in soil and sediment samples for geochemical exploration work.

CONCLUSION

The proposed method is very simple and rapid in comparison to other dissolution techniques followed by preconcentration, it uses

Fig.1: Calibration Curve of Silver by GF-AAS.

Fig.2: Calibration Curve of Cadmium by GF-AAS.

a single acid decomposition procedure, and allows complete extraction of Ag and Cd. The most striking advantages of the nitric acid decomposition method are simplicity, smaller background value, and direct injection of the aqueous solution into the graphite tube with the auto-injection procedure. The method is less hazardous in comparison to the *aqua regia* and HF-HClO_4 dissolution processes which produce harmful chlorine and hydrogen fluoride gases. There is no probability of loss of the analyte element during evaporation using the proposed dissolution procedure since no volatile chlorides are formed, which is a common phenomenon in the case of *aqua regia* digestion methods. The crustal abundance of Ag is 70 ppb and of Cd it is 100 ppb. The limit of quantification achieved by the proposed method is much below the crustal abundance for these elements. Due to its simplicity, rapid estimation, low cost, and achievement of a much lower detection limit, this method is routinely followed by the Geological Survey of India for the quantitative determination of Ag and Cd in soil and sediment samples collected under the NGCM program. The limit of quantitation (10σ) achieved for Cd was 2.0 ng/g and for Ag 5.0 ng/g, with a recovery of 95–103%.

ACKNOWLEDGMENT

The authors are highly grateful to the Director General, Geological Survey of India, for giving permission to publish this work. Thanks are also due to Dr. N.K. Roy, Retired Senior Deputy Director General (STSS), Geological Survey of India, for his keen suggestions and providing the facilities for this work.

Received January 29, 2015.

REFERENCES

1. K.H. Wedepohl, *Geochem. et Cosmochem. Acta* 59(7), 1217 (1995).
2. H.M. Kingston and S.J. Haswell (Eds.), *Microwaves enhance chemistry. Fundamentals, sample preparation and applications*, AES, Washington, DG, USA (1997).
3. John G. Viets, Richard M. O'Leary and J. Robert Clark, *Analyst* 109, 1589 (1984).
4. Zongshou Yu, Philip Robinson, and Peter McGoldrick, *Geostd. Newsl.* 25(2-3), 199 (2001).
5. M.C. Saha, T. Bhattacharya and N.K. Roy, *Indian Minerals* 59, 123 (2005).
6. Anindya Das and Manik C. Saha, *At. Spectrosc.* 34(2), 60 (2013).
7. J.G. Sengupta and J.L. Bouvier, *Talanta* 42(2), 269 (1995).
8. Zhongxi Li, Liping Zhou, and Feng Tan, *Microchim. Acta* 156, 263 (2007).
9. X. Xueijing, *Analyst* 120, 1497 (1995).
10. T. T. Chao and R. F. Sanzalone, *J. Geochem. Expl.* 44, 65 (1992).
11. V. Balaran, P.V.S. Raju, S.L. Ramesh, K.V. Anjaiah, B. Dasaram, C. Manikyamba, V.R. Mohan, and D.S. Sarma, *At. Spectrosc.* 20(4), 155 (1999).
12. John G. Viets, *J. Geochem. Expl.* 42, 107 (1992).
13. P.J. Potts, *A Handbook of Silicate Rock Analysis*, Blackie Academy and Professional, London, U.K., 187 (1987).
14. M.A. Rahman, S. Kaneco, and M. Amin, *Talanta* 62, 1047 (2004).
15. J.B. Borba da Silva, M.A. Mesquita da Silva, A.J. Curtius, and B.J. Welz, *Anal. At. Spectrom.* 14, 1737 (1999).
16. A. Vaisanen, R. Suontamo, J. Silvonen, and J. Rintala, *Anal. Bioanal. Chem.* 373, 93 (2002).
17. L.P. Zhou and Z. Li, *Chin. J. Anal. Lab.* 24(9), 20 (2005).