Quantitative Determination of Antimony, Bismuth, and Tellurium in Geological Samples by Inductively Coupled Plasma Mass Spectrometry and Flow Injection Hydride Generation Atomic Absorption Technique

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INTRODUCTION

The determination of hydride-forming elements (As, Sb, Bi, Se, and Te) in geological materials is often required due to their industrial importance along with their toxic effects. They are used as a pathfinder for the exploration of ores (1-2). These elements tend to form dispersion halos around and above some less mobile ore-forming elements, and their presence in anomalies may indicate targets of mineral potential. Their use as a pathfinder or indicator of certain types of deposits containing Ag, Au, Ni, Co, W, Sn, Mo, and Cu has been reported (3) and may also find "signature" elements for primary non-ferrous metal smelting (4).

The determination of these elements in soil has been a great analytical challenge since geological samples are complex in nature and also due to the absence of sufficiently sensitive and robust analytical methods (5). Geological samples, e.g., soils, sediments, rocks, ores, minerals, etc., are normally brought into solution either by a fusion technique or using mixtures of mineral acids. Complete dissolution is recommended for geochemical exploration and geochemical mapping (6). Different dissolution techniques have been adopted to bring the geological samples in solution and measurement was carried out using several instrumental techniques. Halls et al. (5) studied the mutual interferences in the determination of these elements using hydride

ABSTRACT

An extensive study has been made for the accurate determination of antimony (Sb), bismuth (Bi), and tellurium (Te) in soil and sediment samples at the ng/g level by inductively coupled plasma mass spectrometry (ICP-MS). A comparison was made with the flow injection hydride generation accessory coupled with atomic absorption spectrometry (FI-HG-AAS). Samples of -200 mesh size were completely decomposed by a combination of hydrofluoric and perchloric acids, followed by extraction with 1:1 nitric acid for estimation of Sb, Bi, and Te by ICP-MS. The hydrochloric acid medium was maintained for estimation of the above elements by FI-HG-AAS.

The accuracy of the proposed method was verified by analyzing 10 international soil and sediment reference samples. In addition, 20 soil and sediment samples, collected as per the guidelines of the National Geochemical Mapping Programme of the Geological Survey of India, were also analyzed. In order to investigate the precision of this method. Three sets of samples were digested separately and the mean of three replicates was considered for this study. A comparative study for the precision, accuracy, and quantification limits between the two techniques was also made. The limit of quantitation (10σ) achieved for Sb, Bi, and Te was in the ng/g level for both techniques.

generation inductively coupled mass spectrometry (HG-ICP-MS) by following two acid digestion procedures commonly used for geological materials and recommended the addition of KI and ascorbic acid for analysis, free from mutual interferences. Hydride-forming elements were estimated in geological samples with the help of flame atomic absorption spectrometry (FAAS) and flow injection hydride generation atomic absorption spectrometry (FI-HG-AAS) using a different combination of acids and fusion mixtures (7-8). Analytical techniques, such as instrumental neutron activation analysis (INAA), graphite furnace atomic absorption spectrometry (GFAAS), quartz tube atomic absorption spectrometry (QTAAS), inductively coupled plasma atomic emission spectrometry (ICP-AES), hydride generation atomic fluorescence spectrometry (HG-AFS), and the recently used sector field inductively coupled plasma mass spectrometry (SF-ICP-MS), have been developed for the determination of these elements in environmental samples (9-14). To determine trace amounts of these elements in geological samples, the enrichment and separation of these elements from the matrix are often required, which is time-consuming and increases the risk of losses (15-17). Although hydride generation improves the limits of detection, problems associated with the gen-

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eration of the hydride species, plasma stability, and memory effect still exist and interferences from transition metals and hydride-forming elements have been reported (18). Methods for the determination of several of these elements in soil and sediment samples from a single sample are less well developed. Previous work on the analysis of geological materials includes the determination of various elemental groupings of As-Se, As-Sb, Se-Te, As-Sb-Te, As-Sb-Se, etc., using a combination of chemical procedures of separation and concentration which are time-consuming (19-22).

Several solvent extraction and precipitation methods have also been used for the pre-concentration and determination of these elements in geological samples at the nanogram level (23-26). The mutual interference warranting attention in the determination of Te by HG-ICP-MS is that of As on Te, where an excess of As of 5000-fold can suppress the signal by 35% (27). In case of HG-QTAAS, in the presence of As at 300-fold excess, only 50% Te signal is reported (27). These drawbacks make them unsuitable for the routine analysis of trace amounts of Sb, Bi, and Te in geological samples. Hence, an accurate, precise, simple, and rapid method is required to fulfil these requirements.

In this work, it is proposed to establish a suitable, accurate, and precise methodology for the determination of these elements in geological samples and also to achieve detection limits at crustal abundance levels or below using the ICP-MS technique. It is a great challenge to achieve the detection limits at such a level for Sb, Bi, and Te without the use of pre-concentration. Interferences from high concentrations of other elements give erroneous results and the selection of isotopes may play a major role. ICP-MS, being a rapid multi-element detec-

tion technique with very low detection limits, high sensitivity, small quantities, less interference, and a wide range of detection has been employed for this study. The presented dissolution and instrumentation technique overcomes almost all the possibilities of error. The limit of quantitation (10σ) achieved for the estimation of Sb, Bi, and Te is much less than the crustal abundance level and is also the required detection level for the Indian National Geochemical Mapping Programme. The validity of the method was checked for 10 standard reference materials (SRMs).

EXPERIMENTAL

Instrumentation

All analyses were performed using the PerkinElmer® ELAN® DRC™-e ICP-MS and the AAnalyst™ 700 FIAS instruments. The instrumental operating parameters for ICP-MS and FI-HG-AAS are listed in Tables I and II, respectively. The data acquisition parameters and isotopes used for ICP-MS measurement are listed in Tables III and IV, respectively.

TABLE I. Instrumental Parameters for ICP-MS

RF Power	1150 W	Plasma Gas Flow	17 L/min
Nebulizer Gas Flow	0.9 L/min	Lens Voltage	Auto Lens
Auxiliary Gas Flow	1.25 L/min	Sample Uptake Rate	1.0 mL/min

TABLE II. Instrumental and Data Acquisition Parameters for HG-FI-AAS

Conditions	Bi	Sb	Te
Light Sources	EDL	EDL	EDL
Lamp Current (mA)	360	380	380
Wavelength (nm)	223.1	217.6	214.3
Slit (nm)	0.7 L	0.7 L	0.7 L
Quartz Cell Temperature	900 °C	900 °C	900 °C
Sample Volume (μL)	500	500	500
Carrier	10% HCl	10% HCl	10% HCl
Pre-reductant	-	10% (w/v) KI and Ascorbic Acid	-
Reductant	0.2% NaBH ₄	0.2% NaBH ₄	0.2% NaBH ₄
Measurement Mode	Peak Height	Peak Height	Peak Height
Solution Flow Rate	2 mL/min	2 mL/min	2 mL/min

TABLE III. Data Acquisition Parameters

Measuring Mode	Peak Hopping	Integration Time	1000 ms
Point per Peak	1	Replicates	3
Number of Sweeps	20	Internal Standard	¹¹⁵ In
Dwell Time	50 ms		

TABLE IV. Isotopes for ICP-MS Analysis

Element	Sb	Te	Bi
Isotope	121	128	209

Reagents

All reagents used were of AnalR[®] grade. The Sb, Bi, and Te standards were prepared from Sb₂O₃, Bi₂O₃, and TeO₂ which were obtained from Johnson and Matthey Chemical Ltd., Royston, U.K.

Standard Solutions (100 ppm)

The Sb, Bi, and Te standards (100 ppm) were prepared by dissolving 0.0599 g of Sb₂O₃, 0.0557 g of Bi₂O₃, and 0.0625 g of TeO₂ in (1:1) distilled HNO₃. They were then made up to 500-mL volume with Milli-Q[®] water (Millipore Corporation, USA).

Calibration Standards

Amounts of 1 ppb and 10 ppb calibration standard solution of Sb, Bi, and Te were prepared by appropriate dilution of the 100-ppm solution.

High purity Milli-Q[®] water (18 mΩ-cm) and distilled nitric acid were used in all of the sample preparation procedures. All glassware and digestion vessels were acid-washed and rinsed with Milli-Q water.

Certified Reference Materials (CRMs)

The authors have chosen 10 CRMs obtained from the China National Analysis Centre for Iron and Steel, Beijing, P.R. China. The six certified sediment reference samples were GSD-3, GSD-4, GSD-5, GSD-6, GSD-11, and GSD-12, and the four certified soil reference samples were GSS-1, GSS-2, GSS-3, and GSS-7.

Dissolution of Samples

ICP-MS

A sample amount of 0.200 g was accurately weighed and transferred into a 30-mL Teflon[®] vessel, followed by addition of 8 mL of HF and 4 mL of HClO₄. The beaker was covered and heated for about one hour and then the HF was evapo-

rated slowly. The contents were heated at about 280 °C under covered conditions for two hours. The solution was then evaporated slowly to incipient dryness. The temperature was properly monitored at this stage in order to prevent loss of analyte. The contents were extracted with 25 mL of 8% HNO₃ (8 mL concentrated HNO₃ diluted to 100 mL by Milli-QTM water) and made up to 100-mL volume with Milli-Q water. The solution was used for measurement of Sb, Bi, and Te by ICP-MS as per parameters shown in Table I, Table II, and Table III. A process blank was carried out following the same procedure as for the CRMs.

FI-HG-AAS

An accurate amount of 0.500 g sample was transferred into a Teflon[®] beaker and 4 mL nitric acid added, followed by addition of 4 mL perchloric and 8 mL hydrofluoric acid. The contents were kept standing overnight at ambient temperature. The next day, the sample was digested on a hot plate under covered conditions for one hour at a temperature of about 150 °C, and then at about 250 °C until dissolution was completed. The solution was then evaporated to a pasty mass and extracted with 10 mL of 1:1 HCl. The solution was made up to 50-mL volume maintaining 10% HCl. Measurement was made for Bi and Te using FI-HG-AAS as per parameters listed in Table II.

For the determination of Sb, 2 mL of the above solution was separately reduced by adding 2 mL of KI-ascorbic acid, and measurement was made after appropriate dilution to a volume of 25 mL.

RESULTS AND DISCUSSION

The present authors have chosen 10 soil and sediment reference materials for this study. Determination of Sb, Bi, and Te was made using ICP-MS together with FI-HG-AAS. The isotopic masses of 121,

209, and 128 were selected for ICP-MS measurement. The mass no. 128 has potential interferences from the inert gas element Xenon (Xe). A correction factor of $-0.072617 \cdot \text{Xe}$ 129 was used to minimize the interference. There is no interference on mass nos. 21 and 209 for Sb and Bi, respectively. In case of FI-HG-AAS, the hydrides of the elements are generated using 0.2% NaBH₄. A mixture of 10% KI and ascorbic acid was used as the pre-reductant for the reduction of Sb-V to Sb-III. The values observed by ICP-MS and HG-FI-AAS of the 10 CRMs are listed in the Table V. It can be seen that the analytical data obtained by ICP-MS for all elements is very close to the certified values, thus confirming the accuracy of the methodology. The values observed by FI-HG-AAS are also close to the certified values, but the RSD (%) is on the higher side due to interference of the sample matrix on the rate and quantity of the hydride formation.

The limit of quantitation (LOQ), defined as 10 times the standard deviation (10σ) of the process blank solution, was expressed as the concentration in the samples, thereby accounting for the dilution factor used, and was calculated as 20 ng/g for Sb, 20 ng/g for Bi, and 5 ng/g for Te by ICP-MS measurement. The values of the LOQ, obtained without the need of any complicated separation and pre-concentration steps, were comparable with or even better than the previously achieved detection limits using tedious separation and pre-concentration steps (15-17). Quantification by FI-HG-AAS of Sb, Bi, and Te could only be done above 100 ng/g, 100 ng/g, and 50 ng/g, respectively. In order to investigate the precision of the methodologies, three separate sets of solutions were prepared for instrumental measurement and the mean of three replicate measurements was taken. The relative stan-

dard deviation (RSD), was calculated as <5% for the ICP-MS measurements, whereas for FI-HG-AAS it was found to be about 10%. The results in Table V show that the detection limits, precision, and accuracy for ICP-MS are better than of the FI-HG-AAS technique using a very simple and rapid method. Hence, the ICP-MS measurement is preferred over FI-HG-AAS.

In addition, 20 soil and stream sediment samples collected from the Phek district, Nagaland, India (Toposheet No. 83K/10) under the NGCM program were also studied. These samples were analyzed by the proposed methodology and uniform recovery of Sb, Bi, and Te was observed and the results are listed in Table VI. The precision of the proposed method was also checked by analysis of these samples following the same procedure as for the CRMs. The estimated RSD value was found to be <5% for Sb and Bi, whereas for Te, it was <10% confirming good precision of the proposed methodology.

CONCLUSION

The developed method using ICP-MS is simple, fast, sensitive, and promising for routine ICP-MS analysis of trace amounts of Sb, Bi, and Te in geological samples. A comparative study of precision, accuracy, and the limit of quantitation (10σ) between two techniques has also been made. It was observed that the ICP-MS technique is superior to FI-HG-AAS. This method is adopted by the Geological Survey of India for routine analysis of Sb, Bi, and Te in geological samples at crustal abundance levels collected under the National Geochemical Mapping Programme. The LOQ for Sb, Bi, and Te was found to be 20 ng/g, 20 ng/g, and 5 ng/g, respectively.

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TABLE V
Results of Sb, Te, and Bi in SRMs by FI-HG-AAS and ICP-MS

Sample ID	Sb (ppm)		Certified	Te (ppm)		Certified	Bi (ppm)		Certified
	Observed FI-HG-AAS	ICP-MS		Observed FI-HG-AAS	ICP-MS		Observed FI-HG-AAS	ICP-MS	
GSD-12	26.83	22.77	24±4	0.25	0.27	0.29±0.07	12.25	10.4	10.9±1.3
GSD-11	13.16	14.23	14.9±1.8	0.32	0.34	(0.36)	44.68	51.4	50±5
GSD-6	1.96	1.35	1.25±0.33	0.17	0.12	(0.13)	7.3	5.16	5.0±0.6
GSD-5	3.35	3.73	3.9±0.7	0.10	0.12	0.12±0.03	1.98	2.30	2.4±0.
GSD-4	2.42	1.85	1.84±0.27	0.05	0.067	(0.07)	0.72	0.69	0.64±0.15
GSD-3	6.7	5.15	5.4±0.8	0.17	0.15	0.14±0.03	0.98	0.79	0.79±0.14
GSS-7	0.39	0.47	0.42±0.13	0.052	0.046	(0.047)	0.16	0.19	0.20±0.07
GSS-3	0.64	0.46	0.45±0.15	0.051	0.041	0.040±0.015	0.15	0.16	0.17±0.06
GSS-2	1.58	1.25	1.3±0.3	n.d.	0.031	(0.035)	0.38	0.37	0.38±0.06
GSS-1	1.62	0.88	0.87±0.32	0.055	0.047	(0.047)	1.4	1.26	1.2±0.2

n.d. = not detected.

TABLE VI
Results of Sb, Bi, and Te by ICP-MS

Sample No.	Sample I.D.	Sample Nature	Observed Values (µg/g)		
			Sb	Bi	Te
15564-7	83K10/019/S/14	Stream Sediment	0.53	0.37	0.03
15564-8	83K10/020/S/14	Stream Sediment	0.57	0.46	0.02
15564-9	83K10/030/S/14	Stream Sediment	0.72	0.97	0.03
15564-13	83K10/043/S/14	Stream Sediment	0.77	0.52	0.02
15564-14	83K10/044/S/14	Stream Sediment	0.51	0.40	0.03
15564-15	83K10/045/S/14	Stream Sediment	1.42	0.42	0.02
15564-20	83K10/069/S/14	Stream Sediment	0.49	0.57	0.03
15564-25	83K10/085/S/14	Stream Sediment	0.63	0.53	0.03
15564-26	83K10/096/S/14	Stream Sediment	0.75	0.59	0.04
15564-27	83K10/097/S/14	Stream Sediment	0.81	0.54	0.04
15564-28	83K10/098/S/14	Stream Sediment	0.66	0.52	0.05
15564-29	83K10/099/S/14	Stream Sediment	0.73	0.60	0.03
15564-30	83K10/111/S/14	Stream Sediment	0.62	0.55	0.02
15564-31	83K10/112/S/14	Stream Sediment	0.53	0.46	0.02
15564-33	83K10/144/S/14	Stream Sediment	0.80	0.53	0.02
15564-34	83K10/087/S/14	Stream Sediment	0.15	0.05	0.03
15564-35	83K10/088/S/14	Stream Sediment	0.79	0.53	0.05
15564-36	83K10/101/S/14	Stream Sediment	0.19	0.10	0.04
15564-38	83K10/114/S/14	Stream Sediment	0.49	0.37	0.05
15564-39	83K10/117/S/14	Stream Sediment	0.81	0.56	0.04

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