

and MT-like proteins from *A. marina* that would help understand the role of MTs in heavy metal tolerant plants.

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ACKNOWLEDGEMENT. We thank the Department of Biotechnology, New Delhi for the grants.

Received 15 March 2007; revised accepted 4 September 2007

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## Rapid determination of iodine in soils using inductively coupled plasma mass spectrometry

Iodine plays a pivotal role in many of the geological, chemical and biological processes because of its litho-, bio-, atmo-, hydro- and chalcophilic nature. Speciation of iodine in the form of inorganic iodine (iodides and iodates), molecular iodine and organically bound iodine provides its chemical signature in diverse forms. The secondary environment (soil) has high iodine content compared to the primary environment (parent rocks) from which it is derived as a result of weathering. On an average, the igneous rocks contain an average of 0.25 mg per kg of iodine, the sedimentary rocks, including shales, have 2.3 mg per kg iodine and the metamorphic rocks have 0.81 mg per kg iodine<sup>1,2</sup>. Organic matter is the major concentrator of iodine in sedimentary basins. Hence increase in iodine concentration is considered as an anomaly, indicating the presence of hydrocarbons in an area<sup>3</sup>. Oil-field brines, especially those of the Anadarko basin, Oklahoma, have been found to contain more than 500 ppm of iodine and the origin is considered to be organic<sup>4</sup>.

Iodine was also known to be the first element essential to humans and is a major

constituent of the thyroid hormone, the deficiency of which leads to endemic goitre<sup>5</sup>. The WHO has recommended a daily intake of 100–150 µg iodine in the diet. Similarly, for the prevention of health hazards due to radioactive forms of iodine (<sup>129</sup>I and <sup>131</sup>I), potential sorbents of iodine like organic matter are under study<sup>6</sup>. Iodine plays an important role in bio-geochemical cycles of nature and the main source of iodine supply is from the oceans in the form of I<sub>2</sub> and CH<sub>3</sub>I. Iodine is transferred back to the land surface through wet and dry precipitation<sup>7</sup>.

To study all these natural and anthropogenic phenomena involving iodine in any of its bio-geochemical forms on land surface, a suitable method is required for the extraction and accurate determination of iodine in different kind of soils. Different analytical techniques have been developed to extract and measure iodine concentration from the soil. Pyrohydrolysis sample preparation followed by analysis using inductively coupled plasma mass spectrometry (ICP-MS)<sup>8</sup>, hexane extraction of the iodo-derivatized sample and subsequent analysis by gas chromatography-mass spectrometry (GC-MS)<sup>9</sup>,

spectrophotometric determinations based on Sandell-Kolthoff reaction<sup>10</sup>, isotope dilution mass spectrometric determination (IDMS)<sup>11</sup>, neutron activation analysis (NAA)<sup>12</sup>, accelerator mass spectrometry (AMS)<sup>13</sup>, etc. have been described earlier. All these methods have their own advantages and disadvantages. Extraction of iodine using tetra methyl ammonium iodide (TMAH) as a chemical modifier in iodine determination is now being widely utilized<sup>8,14–17</sup>. However, the sample preparation requires specialized combustion apparatus and trapping systems for iodine. For plant samples and biological materials, halogen extraction using TMAH under mild conditions has proved to be effective<sup>17</sup>. For the determination of iodine in soil samples by ICP-MS, we have adopted and modified this procedure<sup>17</sup>. The iodine extraction efficiency in soils has been improved by optimization of reaction conditions and reagents, the details of which are presented here.

Ten per cent TMAH solution was prepared by diluting 25% TMAH solution (in water from Qualigens Fine Chemicals, India). Internal standard, antimony, of 250 ppb concentration, was prepared

by diluting 1000 ppb antimony stock solution (Reagecon, Ireland). All working standards and solutions were prepared in Elix Millipore water with conductivity <0.2 µS/cm.

100 mg of soil standards were taken in closed Savillex pressure decomposition vessels, to which 5 ml of 10% TMAH was added and the vessel was kept in a uniformly heated oven at 80°C for 6 h. After cooling to room temperature, the solution was diluted with water and 1 ml of 250 ppb antimony was added to act as an internal standard and the volume was made up to 25 ml. The final solution containing 2% TMAH and 10 ppb antimony was centrifuged at 3000 rpm for 20 min and filtered through Wattman's No. 1 paper to get a clear solution. Blank and duplicate of samples were also prepared using similar procedure.

A Labtech LDO-140E oven was used for treating the samples at 80°C; a Hermle Z 300 Centrifuge was used at 3000 rpm to get clear solutions. Samples were digested in PTFE Savillex Pressure Decomposition Vessel (capacity 60 ml; M/s Savillex Corporation, USA). Analyses were performed using Perkin-Elmer Sciex Elan DRC II ICP-MS. A Philips MagiX PRO model PW2440 X-ray fluorescence spectrometer coupled with an automatic sample changer PW 2540 was used to support the ICP-MS for measuring iodine concentration.

In the procedure mentioned, SO-1, being a matrix matching international soil standard reference material was used to calibrate the ICP-MS. Several studies have revealed that a single internal stan-

dard is sufficient for the accurate measurement of trace and ultra trace elements in geological materials<sup>18,19</sup>. SO-1 was prepared under similar experimental conditions stated above and used for calibration of the ICP-MS. To evaluate the accuracy of the methodology, two different dilutions of soil reference materials SO-1 (25 and 50 mg), SO-2, SO-3 and SO-4 were analysed as unknown samples and compared with the certified values. Procedural blank was also prepared and analysed in a similar way. The operating conditions of the mass spectrometer are listed in Table 1 and other details are provided elsewhere<sup>18</sup>.

The measured concentrations of iodine in soil standards are reported in Table 2, along with the certified values. The values obtained are in good agreement with the certified values, except for standard SO-2. The relative standard deviation (% RSD) is <1%. The concentration obtained for SO-2 during repeat measurements in our experiment is 18.84 ppm, whereas the value reported in the literature is 15 ppm<sup>20</sup>. This value may be uncertain and can be confirmed using

different procedures. Similar extraction procedure was also carried out for the geochemical exploration samples GXR-1, GXR-3, GXR-4, GXR-5, GXR-6 and the marine sediments reference materials MESS-1, HISS-1, PACS-2, GSMS-2 and GSMS-3 for which the literature values of iodine are not available (except for GXR-5 = 3.1 ppm (ref. 20) and GXR-5 = 11.4 (ref. 21)). Six constant reproducible observations for each of these standards were obtained using ICP-MS and are proposed as the expected iodine concentrations in these reference materials. For two samples GXR-3 and GXR-5, the iodine concentration is determined using the X-ray fluorescence spectrometer (XRF) to support the values obtained by ICP-MS. The XRF values of iodine are shown in Table 3 and are in close agreement with the ICP-MS values. Due to the constraints of relatively larger amounts (~1 g) of sample required for XRF analysis compared to smaller amounts (~100 mg) required for ICP-MS analysis, only two samples were selected for the former analysis. Details of XRF measurements are not given here. The

**Table 1.** Instrumental and data acquisition parameters of ICP-MS

Instrumental parameter	
RF power	1150 W
Argon gas-flow (l/min)	
Nebulizer	0.86
Auxillary	1.20
Plasma	15
Lens voltage	9.00
Sample uptake rate	0.80 ml/min
Data acquisition parameter	Quantitative mode
Measuring mode	Peak-hopping
Point per peak	1
Number of sweeps	60
Dwell time	50 ms
Replicates	6
Internal standard	<sup>121</sup> Sb

**Table 2.** Certified and measured concentrations of iodine with %RSD using ICP-MS in soil reference materials

Reference material	Certified value (ppm)	Measured value (ppm)	%RSD
Soil standard			
SO-1* (25 mg)	3	3 ± 0.00	0.00
SO-1* (50 mg)	6	6.388 ± 0.69	0.83
SO-2*	15(?)	18.841 ± 0.66	0.38
SO-3*	3	2.719 ± 0.17	0.58
SO-4*	1	0.585 ± 0.32	0.59

\*Replicates of six analyses; (?) Value uncertain.

**Table 3.** Measured values of geochemical exploration samples and marine sediment reference samples using ICP-MS and XRF

Reference material	Certified value (ppm)	Measured value (ppm)		
		ICP-MS	XRF	%RSD
Geochemical exploration samples				
GXR-1*	—	0.89 ± 0.1	—	0.49
GXR-3*	—	11.580 ± 0.85	10.60	1.1
GXR-4*	—	0.378 ± 0.3	—	0.26
GXR-5*	—	20.749 ± 1.9	20.07	0.18
GXR-6*	—	10.499 ± 0.42	—	0.29
Marine sediments				
MESS-1*	—	29.063 ± 3.3	—	0.57
HISS-1*	—	13.511 ± 4	—	0.95
PACS-2*	—	34.353 ± 2.2	—	0.44
GSMS-2*	—	27.069 ± 3.9	—	0.86
GSMS-3*	—	15.598 ± 0.0	—	0.57

\*Replicates of six analyses.

%RSD for these samples is <1, except for GXR-3, where it is 1.1. The limit of detection calculated as three times the standard deviation of the blank was about 0.027 mg per kg, indicating that the sensitivity of the method stated is satisfactory for the measurement of iodine concentration in the soil and sediment. For GXR-5, two values have been reported in the literature. From our six repeat measurements in which the experimental conditions were optimized for the sample preparation as well as for the instrument, we report a consistent value of 20.749 ppm, which has been supported by iodine concentration determination using XRF. TMAH being a strong base prevents iodine losses through volatilization, as it forms tetra methyl ammonium iodate salt in the reaction mixture. It has been seen that high matrix loading of TMAH may produce carbon black when oxidized in the plasma. To prevent any such blocking, diluted samples having 1% TMAH are recommended for analysis<sup>17</sup>. When carrying out extraction of iodine with 1% TMAH, yields obtained were less compared to certified values. Increasing the overall concentration of TMAH to 2% in the present method resulted in better extraction yields. During optimization of the procedure, rhodium was also used as internal standard for analyses over ICP-MS, as it was found to be at negligible levels in the samples investigated and is a mono-isotopic element like antimony. It is observed that use of antimony as an internal standard gave better results, which are much closer to the recommended values. The stability period of the prepared alkaline extract of soil samples since the day of preparation, was also observed under cold conditions (3°C). It was found that the extract can be stored for a week from the day of preparation,

after which the concentrations are susceptible to variation. Hence immediate analysis is preferred.

This study provides an improved method for the extraction and determination, iodine in soil using TMAH and ICP-MS. The measured values are in good agreement with the certified values and %RSD is <1%. The concentration of iodine determined in soil standards was significantly close to the certified values, wherever available for comparison. For the geochemical exploration samples and marine sediments, for which certified values are not available, the concentration of iodine has been proposed supported by XRF determination for some selected samples. The method involves a simplified procedure for rapid analyses of iodine concentration in soils and can be reliably applied to a large number of samples, especially in oil-exploration studies.

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ACKNOWLEDGEMENTS. We thank to Dr V. P. Dimri, Director, NGRI, Hyderabad for permission to publish this work. The Oil Industrial Development Board is acknowledged for funds to pursue this work. We also thank Mr Keshav Krishna for help with XRF analysis. D.M. thanks to NGRI-CSIR for research internship.

Received 23 November 2006; revised accepted 3 September 2007

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## Road deposited sediment characteristics of Middle Brahmaputra Plain, India

Pollution of the environment by anthropogenic activities is a ubiquitous phenomenon today in the entire globe. Preventing pollution and assessment of the environmental quality has become an important challenge to the scientific community. In the fast-moving world, vehicular mode of transport is growing at

a rapid pace and thus the vehicular contribution to pollution.

Road deposited sediment (RDS) is a good indicator of environmental quality of an area, especially pollution that originates from vehicular source. RDS originating from the interaction of solid, liquid and gaseous materials produced

from different sources<sup>1</sup> has become an increasingly important environmental sampling medium for assessing anthropogenic metal levels<sup>2,3</sup>. The ubiquitous nature of RDS, its easy sampling, strong association with automobile emission and relationship with non-point pollution source makes it a valuable archive of