ICP-MS Determination of Sub- $\mu\text{g g}^{-1}$ Levels of Iodine in Soil and Sediments Using Purified Ammonia Reagent for Sample Decomposition

Lu Luo, Qin Shuai, Lanlan Jin, and Shenghong Hu*

State Key Laboratory of Biogeology and Environmental Geology, School of Earth Sciences, China University of Geosciences, Wuhan, 430074, P. R. China

INTRODUCTION

Iodine (I) is an essential element for humans and all biological species, and is widely distributed in the atmosphere, hydrosphere, biosphere, and lithosphere, a cycle that is constantly repeated (1). Studies of I content in geological samples provide important information on the magmatic, metamorphic, and sedimentary processes (2). However, the content of I in soils and sediments is at low $\mu\text{g g}^{-1}$ levels (3), thus requires accurate and precise analytical techniques for the analysis of geological materials.

Inductively coupled plasma mass spectrometry (ICP-MS) has been widely applied for the measurement of I in various biological samples (4-8), but few reports have been published on the analysis of geological materials (9-10). The main problems in ICP-MS for the accurate determination of I in geological samples are as follows (11): (a) difficulty in the quantitative extraction of trace levels of I from the geological materials; (b) its volatility causes serious memory effects during sample preparation and analysis; (c) the relatively high first ionization energy (>10 eV) results in a limited ionization in the ICP plasma ($\sim 33\%$). Many efforts have been made to improve the sample preparation procedure and memory effects in ICP-MS analysis (12-15). Schnetger et al. described a pyrohydrolysis technique in which 100-1200 mg of solid powder with V_2O_5 was heated to 1100°C under a wet oxygen flow, and the separated I

ABSTRACT

Iodine is the most informative element with regard to the geochemical composition of crustal material. In this work, a rapid and high sensitivity method was developed to analyze the sub- $\mu\text{g g}^{-1}$ levels of iodine in soil and sediment certified reference materials (CRMs). Iodine was completely extracted by heating a mixture of 4 mL of 5% ammonia solution for 6 hours in a closed PTFE bomb at 190°C . Two strategies were involved in obtaining high analytical performance: (a) decreasing the reagent background up to 27 times by purifying AR grade ammonia ($\text{NH}_3\cdot\text{H}_2\text{O}$) and (b) increasing iodine sensitivity by about 2 times by using methane as the matrix modifier. The total signal background ratio (SBR) was improved about 50 times compared to methods without combining a purification procedure and methanol addition.

The limit of detection (LOD) of this study was low at $0.0061 \mu\text{g L}^{-1}$. The proposed method was used to analyze 27 soil and 26 sediment CRMs. The measured results of 47 of these samples were in good agreement with the certified or reference values. Analysis of the six CRMs (GBW07317, GBW07358, GBW07361, GBW07362, GBW07428, and GBW07446) showed large relative errors ($\sim -30\%$), probably because some of the iodine could not effectively be extracted with ammonia.

gas was collected in 10 mL of a $50 \mu\text{g mL}^{-1}$ Na_2SO_3 trapping solution (12). Alkali fusion and sintering is another method for extracting I from geological samples. Li et al.

(13) mixed 250 mg of geological powders with 1.5 g of flux (sodium carbonate and zinc oxide), then heating to 650°C for 40 minutes in a muffle furnace, and dissolving in hot water (13). However, it was necessary to separate the interfering components from the matrix solution using the cation-exchange resin because of the high flux-to-sample ratio (6:1). Alkali extraction is a simple method whose efficiency depends on the solubility of the analyte in alkaline solutions (i.e., tetramethylammonium hydroxide or $\text{NH}_3\cdot\text{H}_2\text{O}$). Li et al. (14) used a 10% (v/v) ammonia solution for the direct extraction of iodine in screw top PTFE-lined stainless steel bombs at 185°C in 18 hours. Recently, Luo et al. (15) reported a rapid acid digestion ($\text{HNO}_3 + \text{HF}$) with ammonia dilution for the simultaneous determination of Br and I in soils and sediments. However, some low content sediments were 35-73% lower than the reference values. A possible explanation for this situation is that I was lost in the form of I_2 during the acid digestion procedures. In addition, volatilization of iodine leads to severe memory effects in ICP-MS analysis, which could be due to the evaporation of iodine as HI or I_2 from aerosol droplets in the sample introduction system. To overcome the memory problems, one strategy is the use of perchloric acid as the wet ashing agent to convert volatile iodine to nonvolatile species (16). Another strategy (14, 17) is to prepare the sample in alkaline media to prevent the reduction of I^- to I_2 or the formation of HI, or use alkaline solutions to wash out the introduction systems of the ICP-MS. Based on the above methods

* Corresponding author.
Email: shhu@cug.edu.cn
Tel: +86-027-67848602

described, only at relatively high concentration of I ($>1 \mu\text{g g}^{-1}$) in soils and sediments can be successfully measured. However, the ultra-trace levels of I ($0.1\text{--}1.0 \mu\text{g g}^{-1}$) present in geological samples requires an analytical method with high sensitivity and low background.

The aim of this paper was to develop a sensitive method for measuring the sub- $\mu\text{g/g}$ levels of I in soils and sediments by ICP-MS using ammonia for sample decomposition. A combination technique to improve the performance of the analytical ICP-MS method is proposed based on purifying the ammonia reagent by increasing the I sensitivity with methane as the matrix modifier in the ICP. The optimization of the digestion parameters, methane gas flowing rate, selection of the rinsing solutions, and the internal standard element for ICP-MS analysis are described in detail. The developed method was also used to determine the I concentrations in 53 soil and sediment certified reference materials (CRMs).

EXPERIMENTAL

Instrumentation, Reagents, and Standards

An Agilent 7700X ICP-MS (Palo Alto, USA) (18, 19), equipped with an aerosol dilution system, a MicroMist nebulizer, and a Peltier-cooled Scott-type double pass spray chamber (2°C), was used for this work. CH_4 gas (99.999%, $1\text{--}5 \text{ mL min}^{-1}$) was added using an aerosol dilution system before the sample aerosol reached the ICP. The optimized operating parameters for ICP-MS analysis are listed in Table I.

High-purity water (resistivity of $18.2 \text{ M}\Omega\cdot\text{cm}$) obtained with a Millipore® Milli-Q® water purification system (Darmstadt, Germany) was used for preparation of the samples and standard solutions. AR grade ammonia (Alfa Aesar, Ltd., Tianjin, P.R. China) was purified

twice with a sub-boiling distillation. A stock solution of iodide (1000 mg L^{-1}) was made up by dissolving KI (Sinopharm Chemical Reagent Co., Ltd., P.R. China) with deionized water, and further diluted gradually with $0.4\text{--}1\%$ m/m NH_4OH to a series of working iodine stock solutions in the range of $0\text{--}25 \mu\text{g L}^{-1}$. For this study, a total of 53 soil and sediment CRMs were purchased from the Institute of Geophysical and Geochemical Exploration of China (IGGE, Langfang, P.R. China) were obtained: 27 soil CRMs (GBW07401-08, GBW07423-30, GBW07446-49, GBW07452-57) and 26 sediment CRMs (GBW07301-06, GBW07308-12, GBW07317-18, GBW07358, GBW07360-64, GBW07366, GBW0731a-5a, and GBW0737a-8a).

Sample Preparation

A 50-mg dried sample was weighed into a 10-mL PTFE vessel, and then mixed with 4 mL of 5% NH_4OH solution. The PTFE vessel was closed tightly and put into a sealed stainless steel canister, then heated in an electric dry oven at 190°C for 6–18 hours. After cooling, the solution in the vessel was poured into a 50-mL polypropylene centrifuge tube, diluted up to $20\text{--}50 \text{ g}$ with deionized water, then centrifuged at 8000 r/min for five minutes. The supernatant was used

TABLE I
Instrumental
Operating Parameters

Instrument	Agilent 7700x ICP-MS
RF Power	1450 W
Plasma gas flow	15 L min^{-1}
Nebulizer gas flow	1.05 L min^{-1}
CH_4	0.6 mL min^{-1}
Sampling depth	7.0 mm
Sample uptake rate	0.3 mL min^{-1}
Dwell time	30 ms
Sweeps	300
Replicates	3
Monitored ion	^{127}I

for iodine determination by ICP-MS. Each sample analysis was replicated three times. ^{128}Te was used as an internal standard during ICP-MS analysis to correct for signal drift.

RESULTS AND DISCUSSION

Purification of Ammonia Reagent

In order to analyze the low concentrations of I in geological samples accurately, a high signal background ratio (SBR) is required. Generally, decreasing the background signal and/or increasing the analyte signal could meet this goal. In this study, the background signal of ammonia was first checked because it was the main reagent used in both the sample preparation and the ICP-MS analysis. As listed in Table II, the background equivalent concentration (BEC) of I in 1% (v/v) ammonia (AR grade) was high at up to $0.19 \mu\text{g L}^{-1}$ of I. Since it is difficult to measure the trace levels of I in real samples, the ammonia (AR grade) should be purified before it is used. A simple and low-cost PFA distillation bottle (Savillex, USA) was employed to purify the ammonia reagent. As shown in Table II, the BEC of I in distilled ammonia decreased from 0.19 to $0.022 \mu\text{g L}^{-1}$. It was surprising to note that with a secondary distillation, the BEC was up to $0.0075 \mu\text{g L}^{-1}$ (Table II). Thus, the calculated SBR of this method increased by about 25 times (from 5.3 to 133).

TABLE II
Background Equivalent Concentration (BEC) of I in 1% Ammonia Reagent With or Without Purifying Procedures

1% Ammonia	BEC, I Concentration ($\mu\text{g L}^{-1}$)
Initial ammonia (AR)	0.19
First distillation	0.022
Second distillation	0.0075

Signal Increase With CH₄ Matrix Modifier

Unlike other metal elements, such as Rh, the sensitivity of I in ICP-MS is only one-tenth of that for Rh because of the low ionization efficiency of I in the ICP. Addition of 3–5% carbon-containing compounds could increase the ICP-MS signal intensity of the high ionization energy elements (e.g., As, Se, and Hg) (20–24). To improve the poor sensitivity of I, a carbon source, CH₄ gas, was directly introduced into the plasma by an additional port on the connector tube between the cyclonic spray chamber and the ICP torch. Signal intensities of I⁺ as a function of CH₄ gas flow rate, after blank corrections, are illustrated in Figure 1. The results show that the maximum sensitivity for I⁺ with 0.6 mL min⁻¹ CH₄ was four times greater than without CH₄ addition. A higher RF power (1450 W) and lower nebulizer gas flow rate (1.05 L min⁻¹ instead of the normal value 1.10 L min⁻¹) were used to compensate the plasma cooling effect of carbon addition (Figure 2a+b). Compared to the addition of a carbon source

(i.e., methanol) into the digested solution, the proposed method (addition of CH₄) is simpler, avoids contamination, and is free of operation error. This signal enhancement can be explained by a charge transfer reaction occurring between the positively charged carbon species and the high ionization potential (10.08 eV) in the central channel of the plasma (24).

Optimization of Purified Ammonia for Sample Decomposition

In this study, I was extracted from the geological samples using the preparation procedure of purified ammonia for sample decomposition. Therefore, the effects of

ammonia concentration, digestion temperature, and digestion time on the extraction rate of I in the sample preparation procedure were studied in detail. Figure 3a shows the trend of I extraction with different concentrations of ammonia. It can be seen that the iodine in the representative samples (soil GBW 07404 and sediment GBW07311) can be quantitatively extracted with over 2.5% m/m ammonia solution. Considering the volatility of the aqueous ammonia solution and the background of the reagent blank, 5% m/m ammonia was chosen for sample digestion. Figure 3b shows that the I recovery improved with an increase in digestion tem-

Fig. 1. Effects of CH₄ gas flow rate on the ICP-MS signal intensity for 10 ng mL⁻¹ iodine.

Fig. 2. Effects of RF power and carrier gas flow rate on the ICP-MS signal intensity for 10 ng mL⁻¹ iodine: (a) without addition of CH₄, (b) with 0.6 mL min⁻¹ of CH₄.

Fig. 3. Effect of the different digestion conditions (a: ammonia concentration, b: digestion temperature, c: and d: digestion time) on the extraction of iodine in geological samples using purified ammonia for the sample decomposition method.

perature. A temperature of 190 °C can complete the quantitative recovery (99%), thus it was selected as the final digestion temperature. Figure 3c shows the effect of different digestion times on the iodine extraction rate in the selected CRMs. The results indicated that the recovery was over 95% for extraction times of two hours or more. Further verification of the method for six other geological CRMs (GBW07404, GBW07407, GBW07408, GBW07310, GBW07311 and GBW07312) is shown in Figure 3d. The results indicate that most of the CRMs were completely extracted (>93%) after two hours of digestion; however, the recovery of I for GBW07312 was less than 85%. Therefore, an extended digestion time of six hours was used for subsequent experiments to obtain satisfactory analytical results.

Study of Memory Effect

Memory effect is a phenomenon that introduces positive errors in the ICP-MS determination of volatile elements, such as I. Although iodine does not produce volatile I_2 in alkaline digestion procedures as easily as in acidic digestion procedures, the memory effect in ICP-MS analysis should be studied in order to obtain a high analysis throughput. As shown in Figure 4, the I washout curves were constructed by use of different concentrations of ammonia solution to eliminate different concentrations of iodine. In Figure 4, it seems that the trend of washing different concentrations of iodine with different concentrations of ammonia (0.2–0.8%) is almost the same. The washout time (I signal return to baseline) using ammonia is less than 150 seconds; however, it requires more than 300 seconds with deionized water.

Analytical Performances

Calibration curves for the I standard solutions (0.1 to 50 $\mu\text{g L}^{-1}$) were constructed and satisfactory results of the linear correlation coefficient ($R^2 = 0.999$) with a limit of detection (LOD, 3 SD) at 0.006 $\mu\text{g L}^{-1}$ were obtained. The precision, expressed as the relative standard deviation (RSD) obtained for six replicate determinations at 0.1 $\mu\text{g L}^{-1}$ analytes, was 2.3–4.2%.

Sample Analysis

The developed method was used to measure 27 soil CRMs and 26 sediment CRMs. As shown in Figure 5, most of the results obtained were in good agreement with the certified or reported values and are within analytical uncertainty of the data. Moreover, the relative errors for the selected CRMs between the determined values and the certified values were 10% (Figure 6), except

Fig. 4. Washout curves for different concentrations of I using ammonia and deionized water.

for the six geological samples with a low weathering degree (quartz sand area sediment GBW07317, multi-metal mining area sediment GBW07358, metamorphic rock area sediment GBW07361, granite area sediment GBW07362, copper and nickel mine sediment GBW07428, and sandy soil GBW07446). Further studies should be conducted for these samples.

CONCLUSION

A rapid and high sensitivity method based on using purified ammonia reagent for sample decomposition and ICP-MS analysis of soil and sediment CRMs, was developed to measure the sub- $\mu\text{g g}^{-1}$ levels of iodine. This combination technique increased the sensitivity of I by using methane as the matrix modifier in the ICP and improved the analytical performance. The low detection limit ($0.006 \mu\text{g L}^{-1}$), good accuracy (recovery, 80–120%) and

Fig. 5. Comparison of measured values and certified values for the geological CRMs.

reproducibility make this method a powerful tool for studying the trace levels of iodine in geochemical samples.

ACKNOWLEDGMENT

This work was supported by the National Key Research and

Development Program of China (No. 2017YFD0800304 and 2017YFD0801202) and the National Natural Science Foundation of China (No. 41773013 and 41703132).

Received February 20, 2019.

Fig. 6. Relative errors between measured and certified values for the geological CRMs.

REFERENCES

1. D.C. Whitehead, *Environ. Inter.* 10, 321 (1984).
2. J. Selverstone and Z.D. Sharp, *Earth Planet. Sci. Lett.* 417, 120 (2015).
3. The China Geological Reference Materials Data Sharing Service System. <http://geodata.geoscience.cn/bzwz/bzwz.action>.
4. K. Leppanen, M. Niemela, and P. Peramaki, *Food Anal. Methods* 7, 1103(2013).
5. M. Haldimann, A. Eastgate, and B. Zimmerli, *Analyst* 125, 1977 (2000).
6. J.T.P. Barbosa, C.M.M. Santos, L. dos Santos Bispo, F.H. Lyra, J.M. David, M.d.G.A. Korn and E.M.M. Flores, *Food Anal. Methods* 6, 1065 (2012).
7. E.H. Larsen and M.B. Ludwigsen, *J. Anal. At. Spectrom.* 12, 435 (1997).
8. M.F. Mesko, V.C. Costa, R.S. Picoloto, C.A. Bizzi, and P.A. Mello, *J. Anal. At. Spectrom.* 31, 1243 (2016).
9. L.S.F. Pereira, A.C. Frohlich, F.A. Duarte, R.A. Burrow, E.I. Muller, and E.M.M. Flores, *J. Anal. At. Spectrom.* 31, 1243 (2015).
10. A. Michel and B. Villemant, *Geostand. Newsletter: J. Geostandard Geoanal.* 27, 163 (2003).
11. W. Guo, Y.X. Wang, Y.E. Peng, L.L. Jin, Q.G. Guo, and S.H. Hu, *At. Spectrosc.* 37(1), 7 (2016).
12. B. Schnetger, Y. Muramatsu, and S. Yoshida, *Geostand. Newsletter: J. Geostandard Geoanal.* 22, 181 (1998).
13. B. Li, H.L. He, S.Y. Shi, X.R. Ma, H.L. Wen, and C.F. Lu, *J. Anal. At. Spectrom.* 17, 371 (2002).
14. B. Li, X.R. Ma, L.R. Han, and H.X. Yang, *Geostand. Geoanal. Res.* 28, 317 (2004).
15. T. He, J. Xie, Z. Hu, T. Liu, W. Zhang, H. Chen, Y. Liu, K. Zong, and M. Li, *Geostand. Geoanal. Res.* 42, 309 (2018).
16. K.L. Ackley., J.A. Day, and K.L. Sutton, *Anal. Commun.* 36, 295 (1999).
17. A.Al-Ammar, E.Reitznerova, and R.M. Barnes, *Fresenius J. Anal. Chem.* 370, 479 (2001).
18. Y. T. Li, W. Guo, Z. C. Hu, L. L. Jin, S. H. Hu, and Q. H. Guo, *J. Agric. Food Chem.*, 67, 935(2019).
19. W. Guo, L.L. Jin, S.H. Hu, and Q.H. Guo, *J. Agri. Food Chem.* 65, 3406 (2017).
20. P. Allain, L. Jaunault, Y. Mauras, J.M. Mermet, and T. Delaporte, *Anal. Chem.* 63, 1497(1991).
21. W. Guo, S.H. Hu, X.F. Li, J. Zhao, S.S. Jin, W.J. Liu, and H.F. Zhang, *Talanta* 84, 887 (2011).
22. W. Guo, S.H. Hu, Y.X. Wang, L.Y. Zhang, Z.C. Hu, and J.Y. Zhang, *Microchem. J.* 108, 106 (2013).
23. W. Guo, S.H. Hu, J.Y. Zhang, L.L. Jin, X.J. Wang, Z.L. Zhu, and H.F. Zhang, *J. Anal. At. Spectrom.* 26, 2076 (2011).
24. Z.C. Hu, S.H. Hu, S. Gao, Y.S. Liu, and S.L. Lin, *Spectrochim. Acta B*, 59, 1463 (2004).