

Reduction of Matrix Effect and Volatilization Loss for Iodine Detection in Marine Carbonates by NH_4HF_2 digestion ICP-MS

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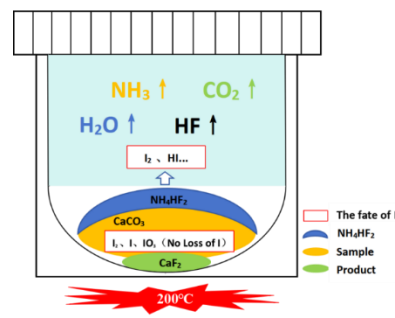
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Received: February 28, 2026; Revised: April 24, 2026; Accepted: April 24, 2026; Available online: April 24, 2026.

DOI: 10.46770/AS.2026.006

ABSTRACT: As a valid seawater oxygen proxies, trace iodine in marine carbonates is crucial for reconstructing the redox conditions of the paleoceanography. Although highly sensitive inductively coupled plasma-mass spectrometry (ICP-MS) is often used for the determination of iodine, the accurately determining trace iodine of marine carbonates remains challenging due to its high volatility loss during the sample digestion and the matrix effect of coexisting high-calcium (Ca) in ICP-MS analysis. In this study, an ammonium bifluoride (NH_4HF_2) sample digestion ICP-MS method was evaluated for analyzing sub- $\mu\text{g/g}$ levels of I in marine carbonate rocks. Results show that more than 97% of the target iodine can be well retained in the digestion solution, while simultaneously achieving the removal of the coexisting calcium matrix (over 86% of the calcium remains in the residue). The limit of detection (LOD, 3 sigma) the established method is $0.024 \mu\text{g g}^{-1}$ (taken into 250-fold dilution) with the relative standard deviation (RSD, N=5) ranging from 3.1 % to 8.0 %. The proposed method was applied to determination of I in a series of carbonate rock reference materials (RMs) and the satisfactory results (recovery, 87-104%) indicate that it has great potential for the determination of trace level I in various marine carbonate rocks.



INTRODUCTION

In-depth research into the patterns of change in ancient oceanic dissolved oxygen concentrations is not only of great scientific significance for reconstructing ancient oceanic environments and elucidating the relationship between life evolution and geological events, but also provides critical evidence for modern marine resource development, ecological environment assessment, and global change prediction.¹⁻³ Iodine is a highly redox-sensitive element with unique geochemical properties. In marine environments, iodine primarily exists as iodate (IO_3^-) and iodide (I^-). Iodate concentrations increase when dissolved oxygen concentrations in the marine environment rise.⁴ Only iodate ions can enter the carbonate lattice during the deposition of marine carbonate, which allows the I in carbonate to monitor seawater oxidation levels throughout Earth history.⁵⁻⁷ Unlike other redox-sensitive elements, the I in marine carbonate reflects only changes

in seawater oxygen and organic carbon burial. It is lightly affected by continental weathering (river input), carbonate precipitation or dissolution, or mantle-derived hydrothermal activity.⁸⁻¹⁰ Based on this unique chemical property, the I in marine carbonates is a reliable paleo-redox proxy and it has been increasingly used in recent years to trace paleo-oceanic redox changes.^{6,11} Thus, accurately determining trace iodine ($\sim 0.1 \mu\text{g/g}$) in marine carbonates is of great significance.

It is well-known that the inductively coupled plasma-mass spectrometry (ICP-MS) method has the advantages of high sensitivity, low detection limits, fast sample analysis, wide linear range, and the ability to analyze multiple elements simultaneously.¹²⁻¹⁵ It has been widely applied to measure I and other elements in the fields of geological samples, material

samples, environmental samples, and biological samples.^{16,17} The dilute acid dissolution ICP-MS method was firstly proposed by Lu *et al.*,⁴ who involve weighing approximately 4 mg of powdered carbonates and 3% HNO₃ is added to completely dissolve the samples. It has been applied for determining iodine in marine carbonate samples from Turkey and South China across the Permian–Triassic boundary, aiming to constrain shallow-marine redox conditions during the end-Permian mass extinction.¹⁸ Sun *et al.*¹⁹ also applied this method to measure I in modern deep-sea scleractinian and bamboo corals collected from global oceans, to explore the incorporation mechanisms of iodate into coral skeletons and to assess the potential of coral I as a proxy for seawater oxygenation.

Although the dilute acid dissolution ICP-MS method has widely employed, there are still significant variances in the I value measured by different research groups for the same carbonate reference material (*e.g.*, JCP-1 coral powder), the reported values of I/Ca ranged from 3.7 to 4.5 $\mu\text{mol/mol}$.^{20–23} Volatile loss of iodine and coexisting high-calcium (Ca) matrix effect could be considered the main reasons for the inaccurate measurement of trace iodine, occurring respectively during sample pretreatment and ICP-MS detection.¹⁶ Glock *et al.* used stabilizer tetramethylammoniumhydroxide (TMAH) and used ICP-MS detection within 120 min after sample processing to slightly improve volatile loss.²⁴ However, the organic reagent TMAH could induce more complex matrix effects for I detection in ICP-MS, such as signal increasing effects leading to positive errors for I results.¹⁶ Currently, the main method to reduce the calcium matrix effect on I detection is to dilute the digest solution by higher dilution times (*e.g.*, >2000-fold) for carbonates before ICP-MS analysis. However, excessive dilution (*e.g.*, >2000) could reduce the Ca matrix effect, the target element iodine in final solution (<0.25 $\mu\text{g/L}$) is almost impossible to measure accurately by ICP-MS (iodine content in marine carbonates is approximately 0.05–0.5 $\mu\text{g/g}$).

In previous works, an efficient and green efficient ammonium bifluoride (NH₄HF₂) digestion procedures was proposed for the determination of trace elements and halogens in geological materials.^{25,26} Compared to conventional mineral acids (HF, HNO₃, *etc.*), NH₄HF₂ elevates the digestion temperatures in open vessels because of its higher boiling point (240 °C), which is beneficial to the rapid decomposition of refractory minerals in silicate materials.²⁵ This decomposition method avoids the disadvantages of both open acid digestion (*e.g.*, long digestion time) and the commonly used fusion methods (high temperature and furnace required), which have been recognized as novel and practical methods in analytical chemistry for geological sample decomposition.²⁵ However, compared to silicate materials, the reaction mechanisms between the carbonate materials and NH₄HF₂ reagents are completely different, and whether it can be used for the analysis of trace iodine in carbonates requires further

study.

Herein, the feasibility of NH₄HF₂ digestion ICP-MS method for trace iodine quantitation in marine carbonates is evaluated in detail. The potential reaction mechanisms of carbonate material and NH₄HF₂ reagent in closed vessel, the degree of iodine volatilization, the removal efficiency of coexisting high-Ca matrix, analytical performance of the method, as well as its application to the determination of trace iodine in a series of carbonate rock reference materials (RMs) are described.

EXPERIMENTAL

Instrumentation. An inductively coupled plasma mass spectrometer (Agilent 7700x, Agilent Technologies, USA) was used to analyze the I (target), Te (as the internal standard for correcting signal drift), and matrix Ca contents. Instrumental parameters were optimized using a 1 $\mu\text{g/L}$ tuning solution to obtain the maximum signal intensity and stability. Under the optimized ICP-MS conditions (See in Table S1), the intensity of the ¹²⁷I signal was >10000 cps ng⁻¹ mL⁻¹. The background signal in ultrapure Milli-Q water was less than 600 cps.

Reagent and carbonate reference materials. High-purity argon gas (99.999%) was supplied by Wuhan Heyuan Qingsheng Gas Co., Ltd. NH₄HF₂ (98% metals basis; Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) was purified using a 120 mL PFA sub-boiling system (Savillex Eden Prairie, MN). The ammonia solution (5% v/v) was prepared from Aladdin (Shanghai, China) ammonia hydroxide (Chromatographic grade, 25%), which used for preparation the I calibration standards. Individual stock standard solutions (1000 mg L⁻¹ I, Te, and Ca were purchased from the National Center for Analysis Testing of Steel Materials, China. A serial of carbonate rocks reference materials (RMs, GBW07118 (GSR-12), GBW07127(GSR-21), GBW07128(GSR-22), GBW07129(GSR-223), GBW07133(GSR-27)) was use to evaluate the accuracy of the developed method, which were purchased from the China National Institute of Metrology (NIM, China).

Sample preparation. The optimized digestion method is as follows: (1) A total of 500 mg of NH₄HF₂ with a 125 mg carbonate sample was weighed into a 15 mL Teflon vial (Savillex, Eden Prairie, MN); (2) The electric oven was reheated to 200 °C, and then the capped vials were heated at 200 °C for 2 h.; (3) The digest supernatant was diluted by 5% v/v NH₄OH solution to 50 g after cooling; one mL sample of the supernatant solution together with 10 μL of internal standard solution of Te (10 $\mu\text{g mL}^{-1}$) was transferred to a polyethylene tube after centrifugation. The detailed optimization parameters of the amount of NH₄HF₂, the digestion temperature and time are shown in supporting information (Fig. S1).

RESULTS AND DISCUSSION

Target iodine loss and memory effect. Previous studies^{16,17} have demonstrated that during the pretreatment process of geological samples, iodine, due to its high volatility, is prone to loss; additionally, during ICP-MS detection, iodine easily contaminates various components of the sample introduction system (such as the nebulizer, spray chamber, and sample introduction tube), leading to iodine loss, and the residual iodine can cause serious positive interference in the analysis of the next sample, known as the “memory effect”.

To evaluate the effectiveness of this procedure in preventing iodine loss and eliminating memory effects, we designed a simple experiment: a single-element iodine solution (1 mL) containing 2000 ppb was used as the sample, subjected to the digestion process described above (in the section of “Sample preparation”), and analyzed by ICP-MS. The results showed an iodine recovery of 97–98%, and the iodine ICP-MS signal in digest solution could be quickly (35s) eluted to 0.1% using the Milli-Q water as rinse solution. The results indicate that the proposed procedure can effectively inhibit both the iodine loss and the memory effects. The reason may be that this digestion process creates an alkaline environment, in which iodine is neither easily lost through volatilization nor easily adsorbed onto the components of the sampling system of ICP-MS; the possible mechanism will be discussed in detail later in the text.

Reduction of Ca matrix effect. It is well-known that the coexistence of a high-calcium matrix in carbonate decomposition solutions can seriously interfere the ICP-MS determination of trace iodine. In our previous work, we found that when the Ca concentration exceeds 100 µg/g, partial Ca deposition occurs on the sampling cone surface, reducing ion transmission efficiency and compromising signal stability. This effect becomes particularly significant in high-Ca matrices and is one of the primary causes of ICP-MS signal attenuation and poor reproducibility.^{27,28,29} In the digested solution of real carbonate rocks, which are characterized by high Ca content (approximately 40%) and low I content (<0.5 µg/g), even after 1000-fold dilution, the Ca concentration often exceeds 300 µg/g, leading to significant deviations of the measured iodine values from their real values.

An interesting phenomenon is that when using the proposed procedure to digest the carbonate samples, the calcium content in the digest is less than 10% of its theoretical value. As showed in Fig. 1, the reference calcium value for the two carbonate standard materials high up to ~40%, while the proportion of the measured calcium content in final digest solution is less than ~14%. Such a low concentration of calcium in the digest indicates that most of the calcium matrix (>86%) has been effectively separated from the target element (I). The residue of calcium (<14%) in digest solution has a negligible impact on the I measurement during

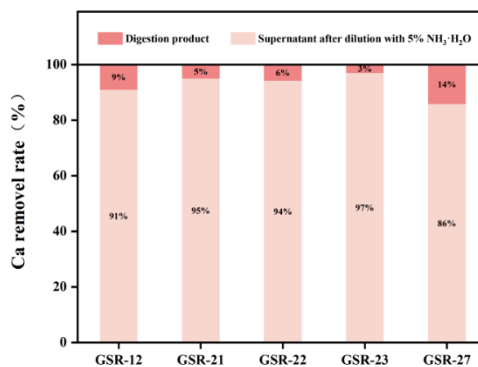


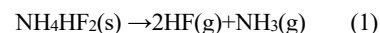
Fig. 1 Removal rate of calcium in carbonate samples using the NH₄HF₂ digestion ICP-MS method. Deep red: proportion of calcium in the supernatant; Light red: proportion of calcium in the precipitate.

ICP-MS analysis, ultimately allowing for accurate analytical results.

Potential decomposition mechanism. Obviously, our results indicate that the proposed digestion procedure has the advantages of high Ca matrix removal capacity, low iodine volatilization loss, and rapid elimination of memory effects. The chemical reactions involved in this procedure need to be investigated.

The main speculated reactions could be as follows: hydrofluoric acid (HF) generated by the thermal decomposition of NH₄HF₂ rapidly destroys the lattice of carbonate minerals and releasing iodine, while the ammonia (NH₃) produced forms stable ammonium salts with iodine, dissolving in the solution phase, and the calcium ions released from calcium carbonate combine with F ions to form CaF₂ precipitate. The potential reaction equations are as follows:

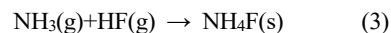
- (1) Thermal decomposition reaction of ammonium fluoride:



$$\Delta H = 194.14 \text{ kJ/mol}, \Delta S > 0$$

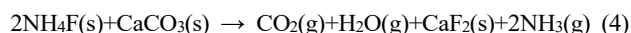


$$\Delta H = 47.39 \text{ kJ/mol}, \Delta S > 0$$



$$\Delta H = -146.75 \text{ kJ/mol}, \Delta S < 0$$

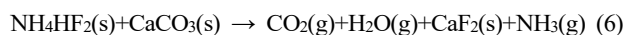
- (2) Destroy the carbonate lattice:



$$\Delta H = 187.693 \text{ kJ/mol}, \Delta S > 0$$



$$\Delta H = -105.807 \text{ kJ/mol}, \Delta S > 0$$



$$\Delta H = 88.333 \text{ kJ/mol}, \Delta S > 0$$

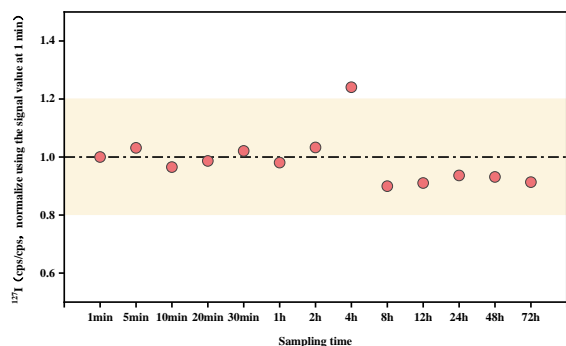


Fig. 2 Variations of ^{127}I signal intensity (ICP-MS) in digestion solution of the calcium carbonate RM (GBW07129) with NH_4HF_2 digestion procedure.

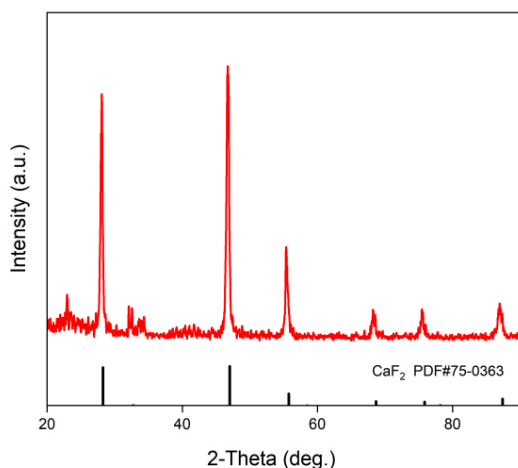


Fig. 3 XRD test results of the precipitated product after digesting carbonate rock RM (GBW07129) with NH_4HF_2 digestion procedure.

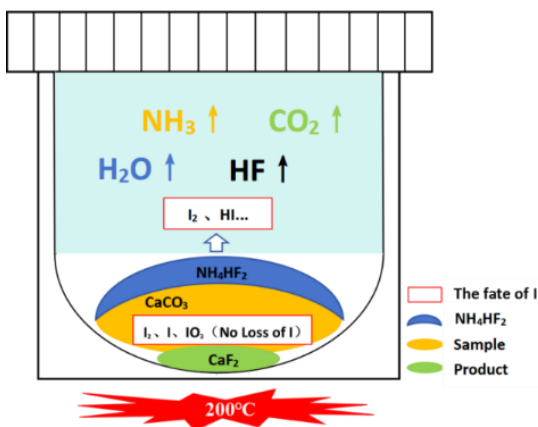
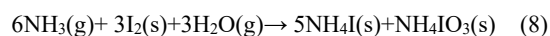
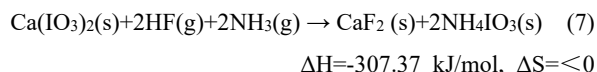
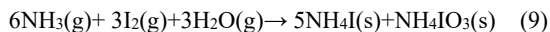


Fig. 4 Potential pathway of the reactions during the NH_4HF_2 digestion procedure.

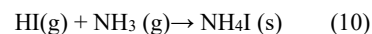
(3) Cracked iodine is captured in an ammonia atmosphere:



$$\Delta H = -290.196 \text{ kJ/mol}, \Delta S < 0$$



$$\Delta H = -477.51 \text{ kJ/mol}, \Delta S < 0$$



$$\Delta H = -168.07 \text{ kJ/mol}, \Delta S < 0$$

The I species (IO_3 , I_2 or I) released from the calcium carbonate lattice and/or adsorbed on the sample surface, could be captured by the ammonia solution (and does not exist in the gas or solid phase), while the calcium ions released from the decomposition of calcium carbonate form CaF_2 that is insoluble in ammonia solution and precipitates in the solid phase. As shown in Fig. 2, the ICP-MS signal of iodine in the solution phase remained almost constant (>72 h), confirming that the target iodine can be stably preserved in an alkaline environment. Fig. 3 showed the XRD pattern of the precipitate for GBW07129 in the digestion bomb (Teflon vial), and the results are consistent with the standard CaF_2 Database (PDF#75-0363), which verified above speculation.

Overall, we outlined the potential pathway of the reactions during the ammonium fluoride digestion process as shown in Fig. 4. Although it is not yet perfect and requires further verification, we believe that it can be used to explain why the proposed ammonium hydrogen fluoride digestion technique can reduce iodine volatilization and high-calcium matrix problems.

Carbonate RM analysis. The calculated detection limit of I for the method is $0.024 \mu\text{g/g}$, which is lower than that of most reports ($0.025\text{--}0.1 \mu\text{g/g}$).^{6,24,27,28} The detection capability of this method adequately covers the range of I values previously reported for marine carbonate rocks ($0.05\text{--}2.5 \mu\text{g/g}$).^{2,6,29,30} The precision, expressed as the relative standard deviation (σ) from five replicate determinations, ranged from 3.1% to 8.0%. The proposed method was used to analyze five marine carbonate RMs: GBW07118, GBW07127-29, and GBW07133, which originating from Southwest China. As listed in Table 1, the iodine measured concentrations for four RMs using the proposed method agreed well with the reference values (recoveries ranging from 94% to 104%). Although the iodine measured value ($0.20 \pm 0.02 \mu\text{g/g}$) in the GBW07118 is 13% lower than its reference value, it is still within the allowable deviation range ($0.23 \pm 0.08 \mu\text{g/g}$).

Table 1. Measured results for five carbonate RMs (N=5)

Carbonate RMs	Reference values ($\mu\text{g/g}$)	Measured values ($\mu\text{g/g}$) $\pm 2\sigma$	Recovery (%)
GBW07118	0.23 ± 0.08	0.20 ± 0.02	87
GBW07127	0.5	0.52 ± 0.05	104
GBW07128	0.3	0.31 ± 0.05	103
GBW07129	0.5	0.47 ± 0.03	94
GBW07133	0.5	0.48 ± 0.03	96

CONCLUSION

The feasibility of the method using NH_4HF_2 digestion and ICP-MS analysis of trace iodine in marine carbonate rocks was evaluated. This method can effectively avoid the loss of target iodine and enable the efficient separation of coexisting high-calcium matrices, which will greatly promote the development of iodine as the seawater oxygen proxies for reconstructing the redox conditions of the paleoceanography. Before measurement, sample selection may also important, as coexisting components (e.g., organic matter, clay, phosphate, and silicate) may affect the results.

ASSOCIATED CONTENT

The supporting information (Table S1 and Fig. S1) is available at <https://www.at-spectrosc.com>

AUTHOR INFORMATION



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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This research was funded by the Research Funding of the State Key Laboratory of Geomicrobiology and Environmental Change Laboratory (GKZ25Y66).

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