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ICP-MS/MS as a tool to study abiotic methylation of inorganic mercury reacting with VOCs

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ABSTRACT

Methylmercury (CH_3Hg) has been registered as one of the most widespread toxic contaminants. Although the formation of CH_3Hg in aqueous environment has been widely investigated, little information was available on direct antropogenic or natural emissions of CH_3Hg to the atmosphere. In this work, ICP-MS/MS was chosen as a tool for the first time to study abiotic methylation of inorganic mercury reacting with VOCs in gas environment. We found that the gasous Hg^+ ions would be transformed to the more toxic species of CH_3Hg^+ ions instantaneously when collided with some VOCs. Several VOCs, e.g. methyl iodide (CH_3I), methylbenzene, acetic acid and ethyl acetate, exhibited good methylation of Hg^+ ions with productivities of 1.77%, 1.28%, 1.35% and 1.18%, respectively. Four isotope peaks of $CH_3{}^{199}Hg$ (M=214), $CH_3{}^{200}Hg$ (M=215), $CH_3{}^{201}Hg$ (M=216) and $CH_3{}^{202}Hg$ (M=217) were well identified when Hg^+ ions were collided with CH_3I, and the methyl group in CH_3Hg^+ had been validated by the source of CD_3I, indicated that the CH_3Hg^+ ions were formed. This study might reveal that the abiotic methylation of Hg^+ ions would potentially occur when contact with the VOCs in the atmosphere environment, leading to the secondary environment pollution.

1. Introduction

Mercury (Hg) compounds have long been of great public concern because of their adverse effect on wildlife and humans. It is well known that the toxicity of mercury compounds depends on their species, which include inorganic, methyl, ethyl and phenyl mercury. Among these compounds, methylmercury (CH_3Hg) is the most toxic form in the environment. The lipophilic nature of CH_3Hg enhances its ability to be bioaccumulated in comparison with inorganic Hg, and results in enhanced biomagnification of CH_3Hg in the food chain.[1]

Methylmercury can be formed naturally by two general pathways in environment: microbial metabolism (biotic processes) and chemical methylation (abiotic processes). Biotic methylation was shown to be carried out by sulfate-reducing bacteria,[2, 3] iron-reducing bacteria,[4] or other microbes.[5-8] Abiotic methylation of inorganic mercury can occur only if suitable methyl donors exist in the environment. Abiotic formation of CH_3Hg in aquatic systems has been widely investigated by a variety of environmental factors such as humic substances,[9] fulvic acids,[10] dissolved organic matter (DOM),[11] acetic acid,[12] methylcobalt (III),[13-15] methyltin (IV) compounds[15] and methyl iodide,[15, 16] etc. However, little information was reported on the abiotic methylation of atmosphere mercury. Although Hg^0 is the dominant mercury specie in the troposphere, the methylation productivity of Hg^0 is low,[17-19] perhaps attributed to the low reaction activity of Hg^0. Neverthless, the mercury ions with higher reaction activity also exist in the atmosphere,[20, 21] with the ions content in the magnitude of pg m^{-3},[22, 23] which are easily adsorbed on the surface of the fine particle matter or floating dust and following deposited to the ground. Munthe et al.[24] implied that atmospheric deposition can be an important source of CH_3Hg in terrestrial and aquatic ecosystems. While in today's society, more and more VOCs were emitted to the atmosphere by automobile exhaust, petrochemical industry, coal combustion and so on, such as alkanes and benzene series with the contents in the magnitude of μg m^{-3}.[25, 26] Whether the VOCs in the atmosphere contain methyl donor can be reacted with mercury ions to form the more poisonous CH_3Hg is of great significance to study.

In order to study the methylation reaction of mercury ions and VOCs in gas environment, we need to design a reactor to mix the gasous mercury ions and gasous VOCs together to generate a methylated reaction and then detect this product in time. Fortunately, an instrument called triple quadrupole ICP–MS/MS has been commercially available as the ideal reactor and detector. This configuration consists of a tandem mass spectrometer with an octopole reaction cell (ORS^3) located in-between two quadrupole mass analyzers. When Hg^{2+} standard solution was introduced to the ICP, the ions with m/z ratio different from the target nuclide of Hg^+ ions (e.g. m/z 202) were all removed by the first quadrupole mass analyzer (Q1). And then the gasous $^{202}Hg^+$ ions were entered into the ORS^3 mixed with the gasous VOCs introduced from another inlet of the ORS^3. After a controlled process of ion-molecules collision in the ORS^3, the products were promptly collected by the second quadrupole mass analyzer (Q2) and following detected online.

In this work, we demonstrate at the first time that the ICP-MS/MS is a useful tool to study the abiotic methylation of inorganic mercury reacting with VOCs. We used four mercury isotopes (^{199}Hg, ^{200}Hg, ^{201}Hg and ^{202}Hg) to examine the possible methylation of Hg^+ ions by CH_3I in gas environment. CD_3I was used to validate the source of the methyl group in CH_3Hg^+. The effects of experiment parameters on the methylation productivities of Hg^+ ions were also investigated. This study might reveal that the Hg^+ ions would be potentially transformed into more toxic species of CH_3Hg^+ ions when contact with the VOCs in the atmosphere, leading to the secondary environment pollution.

2. Experimental

2.1 Instrumentation

The Agilent 8800 triple quadrupole ICP–MS/MS instrument (Agilent Technologies, Japan) was chosen to model this methylation reaction. Fig.1 showed the schematic diagram of the instrumental system and the procedure for the methylation of gasous Hg^+ ion using VOCs. The helium (He) gas was used not only to accelerate the liquid VOCs reagent from the liquid phase vaporized to the gas phase, but also to carry the gas phase VOCs to the third inlet of the ORS[3] through a T-junction gas mixing system. The liquid phase VOCs was stored in a 1 mL injector and pushed to the T-junction gas mixing system by a micro-injection pump (Pump 11 Elite, Harvard) in a predetermined speed. The concentration of the VOCs was regulated according to the ratio of VOCs with He gas. The operational parameters of the instrument were shown in Table 1. In order to study the reactions between VOCs and Hg^+ ions, product ion scanning was used. In ICP-MS/MS, Q1 is set to the mass of the target nuclide itself and Q2 to that of the corresponding reaction product ion. For Hg, a ratio of m/z setting as 202 in Q1 is selected because this is the most abundant nuclide of Hg and m/z setting from 202 to 260 in Q2 are selected to identify the reaction products of Hg throughout this work, except mentioned specially.

2.2 Reagents and Standards

All chemicals used in this work were of analytical-reagent grade including CH_3I, CD_3I, ether, methylbenzene, acetaldehyde, acetic acid, hexane, methanol, ethyl acetate and acetone except of nitric acid with electronic grade. The stock standard solution of Hg^{2+} was purchased from SPEX Certiprep (USA). Stock solutions of Hg^{2+} was stored in pre-cleaned glass vials and kept at 4 ℃. Working standard solution was prepared daily by stepwise dilution of the stock solutions with 1% (v/v) nitric acid.

The nature gas with the main component of methane (≥90%) was collected from the household nature gas pipeline with a 4 L gas collecting bag. Then part of the nature gas was transferred to a 50 mL injector and pushed manually to the T-junction gas mixing system with He as the carrier gas to investigate the possibility of abiotic methylation of Hg^+ ions by the methane.

3 Results and discussion

3.1 Identification of CH_3Hg^+ ions

In order to identify the methylation reaction, four isotopic Hg^+ ions (^{199}Hg, ^{200}Hg, ^{201}Hg and ^{202}Hg) were reacted with CH_3I, a kind of VOC, which has been reported as a methylating reagent for inorganic Hg methylation in aqueous environment.[15, 16] The results of mass spectra of methylation of different Hg^+ isotope ions by CH_3I were shown in Fig.2. In Fig.2a-b, no methylation product was existed whether the CH_3I or the Hg^+ ions was absent. While when the CH_3I and Hg^+ ions were all existed in the ORS[3], the peaks with the m/z of M+15 (199->214, 200->215, 201->216 and 202->217) were all produced in the products of each Hg^+ isotope in Fig.2e-g and Fig.2c, indicated that a species of Hg-compound ion was produced with a 15 mass larger than Hg ion.

To further identify the species of Hg-compound was CH_3Hg^+, CD_3I was used to validate it with the same way as CH_3I. As shown in Fig.2d, a peak with the m/z of M+18 (202->220) was produced, indicated that the source of 15 mass in the Hg-compound was CH_3. Therefore, it can be confirmed that CH_3Hg^+ ions were produced when Hg^+ ions were reacted with CH_3I in gas environment.

In addition to the peak of CH_3Hg^+, another peak with the m/z of 204 with the signal intensity higher than CH_3Hg^+ had been always existed in Fig.2 e-g and Fig.2c. As can be seen that the peak with the m/z of 204 was also found in Fig.2a, but not found in Fig.2b, it could be deduced that this peak was only related to the methylating reagent of CH_3I or its impurity. At the same time, a peak with a m/z of 207 was appeared instead of 204 when CD_3I was used in Fig.2d. Therefore, it could be further speculated that the specie with the m/z of 204 had "H_3" in its component. Unfortunately, the synthesis process of the reagent of CH_3I used in this work was unknown, thus the definite component of this specie could not be given. Except the two peaks mentioned above, other peaks in Fig.2 always had lower signal intensities and appeared at random, which might be instrument noise.

3.2 Effects of the experiment parameters

The effects of the experiment parameters on the CH_3Hg^+ productivity were also investigated with CH_3I as methylation reagent, including concentrations of the Hg^{2+} ions, the flow rates of CH_3I and the carrier gas of He.

Fig.3 presented the effect of Hg^{2+} concentration settings on the signal intensities of $^{217}CH_3Hg^+$ and $^{202}Hg^+$. It was found that the signal intensities of $^{202}Hg^+$ and $^{217}CH_3Hg^+$ were increased synchronously with the increase of the Hg^{2+} concentrations from 0.01 to 20 μg L^{-1}. Therefore, the $^{217}CH_3Hg^+$ productivities (calculated by the signal intensity ratios of $^{217}CH_3Hg^+$ / $^{202}Hg^+$) were not affected by the Hg^{2+} concentrations. In addition, the lowest Hg^{2+} concentration with visible $^{217}CH_3Hg^+$ signal was found to be 0.5 μg L^{-1} in this system. For the purpose to compare the signal intensities of $^{217}CH_3Hg^+$ more clearly, a Hg^{2+} concentration of 10 μg L^{-1} was chosen for the further study.

The effect of CH_3I flow rate settings on $^{217}CH_3Hg^+$ productivity was also studied. As shown in Fig.4, the signal intensities of $^{217}CH_3Hg^+$ were increased when the CH_3I flow rates increased from 0.05 to 5 μL min^{-1} and then kept constant when the CH_3I flow rate increased from 5 to 7.5 μL min^{-1}, but finally reduced sharply when the CH_3I flow rate increased from 7.5 to 10 μL min^{-1}. The decrease of $^{217}CH_3Hg^+$ signal intensities with the higher flow rate of CH_3I might due to another mercury compound ion had been produced. In addition, it was found that the signal intensities of $^{202}Hg^+$ were not affected by the flow rates of CH_3I, so the $^{217}CH_3Hg^+$ productivity calculated by the signal intensity ratios of $^{217}CH_3Hg^+$ / $^{202}Hg^+$ were changed synchronously with the change of $^{217}CH_3Hg^+$ as shown in Fig.4. Moreover, the lowest flow rate of CH_3I with visible $^{217}CH_3Hg^+$ signal was found to be 0.1 μL min^{-1}. At last, a CH_3I flow rate of 5 μL min^{-1} was chosen with a $^{217}CH_3Hg^+$ productivity of 0.49%.

Bolea-Fernandez, et al[27] has reported that the productivities of $AsCH_2^+$ and $SeCH_2^+$ were significantly influenced by the collision gas flow rates in ICP-MS/MS. So another experiment was conducted to investigate the effect of He flow rate settings on $^{217}CH_3Hg^+$ productivity in this work. The He flow rates were only investigated from 0.05 to 0.3 mL min^{-1}, for the lowest He flow rate could be set was 0.05 mL min^{-1} and no signal intensity of $^{202}Hg^+$ and $^{217}CH_3Hg^+$ could be detected when the He flow rate was set up to 0.3 mL min^{-1}. It could be clearly seen from Fig.5 that the signal intensities of $^{202}Hg^+$ gradually decreased with the increase of He flow rates from 0.05 to 0.3 mL min^{-1}, which probably due to the diluting and collision effect. At the same time, the signal intensities of $^{217}CH_3Hg^+$ were nearly constant when the He flow rate increased from 0.05 to 0.15 mL min^{-1} and then reduced sharply with the He flow rates up to 0.3 mL min^{-1}. According to the signal intensities of $^{202}Hg^+$ and $^{217}CH_3Hg^+$, the productivities of $^{217}CH_3Hg^+$ calculated by the intensity ratios of $^{217}CH_3Hg^+$ / $^{202}Hg^+$

were shown in the inset picture of Fig.5. The productivities of $^{217}CH_3Hg^+$ were found to be increased with the increase of He flow rate from 0.05 to 0.15 mL min^{-1} and then reached a platform with the He flow rate between 0.15 and 0.25 mL min^{-1}, but finally reduced to zero with the He flow rate up to 0.3 mL min^{-1}. Therefore, a He flow rate of 0.15 mL min^{-1} with a $^{217}CH_3Hg^+$ productivity of 1.77% was chosen.

3.3 Methylating productivities of Hg^+ ions with individual VOCs

In order to confirm the fact that VOCs could methylate the Hg^+ ions in gas phase, the reactions between the Hg^+ ions and individual VOCs containing methyl donors were investigated, including ether, methylbenzene, acetaldehyde, acetic acid, hexane, methanol, ethyl acetate, acetone and methane with the same way as CH_3I. The results were shown in Table 2. The $^{217}CH_3Hg^+$ productivities (%) were calculated by the signal intensity ratios of $^{217}CH_3Hg^+$ / $^{202}Hg^+$ with individual VOCs as methylating reagent with the same Hg^{2+} concentration. Among the nine VOCs investigated, only three of them (methylbenzene, acetic acid and ethyl acetate) exhibited good methylation with productivities of 1.28%, 1.35% and 1.18%, respectively. No $CH_3{}^{202}Hg^+$ (M=217) signal was detected by other VOCs (ether, acetaldehyde, hexane, methanol, acetone and methane), which might due to the stable character of these VOCs themselves or other reasons. These results indicated that the abiotic methylation of the gasous Hg^+ ions could be realized by some VOCs species.

3.4 Possible mechanism for the methylation of Hg^+ ions by individually VOCs

According to the literature reported by Craig and Rapsomanikis,[28] methyl iodide (CH_3I) is expected to dissociate to $CH_3^{\cdot}/I^{\cdot}$ or CH_3^+/I^-, but not CH_3^-/I^+ in aqueous media and then the $CH_3^{\cdot}$ and CH_3^+ can methylate Hg^+ or Hg^0. And in our work, CH_3^+ (m/z=15) and CH_3I^+ (m/z=142) were all found in gas environment in the ORS[3]. However, since $CH_3^{\cdot}/I^{\cdot}$ did not have charges, they could not be detected in our work. For the reaction between CH_3I and Hg^+ ion in the ORS[3], collision in the He atmosphere would accelerate the decomposition of CH_3I into $CH_3^{\cdot}$ and CH_3^+ without UV irradiation. Then the group of $CH_3^{\cdot}$ was transferred to the Hg^+ ion to form the product ion of CH_3Hg^+ according to the following mechanism.

$$^{202}Hg^+(g) + {}^{15}CH_3\cdot(g) \rightarrow {}^{217}CH_3Hg^+(g)$$

Acetic acid with a good methylation effect was also reported by other groups in aqueous environment.[12, 29] The methylation property of acetic acid was explained by decarboxylated into CO_2 and a methyl group, which was transferred to the present Hg^{2+} in the solution to form CH_3Hg^+.[29] In this work, the reaction between acetic acid and Hg^+ in gas atmosphere was speculated to be realized with the same methylation property as in solution. The methylation process of methylbenzene was speculated to be decomposed by the collision in the He atmosphere into a benzene ring and a methyl group. While the methylation process of ethyl acetate might have two ways, which to be decomposed into CO_2 and two methyl groups or a carboxyl group and a single methyl group. These mechanism need to be further explored in the future.

3.5 Further discussion

Many literatures has reported that UV irradiation is a necessary condition for producing obvious CH_3Hg whether in aqueous environment[11, 16] or gasous environment.[18] However, our work demonstrated that the obvious gasous CH_3Hg^+ ions can be produced just through a collision reaction between the ions and molecules in a dark reactor, which had not been reported before. The productivities of the gasous CH_3Hg^+ ions by CH_3I in the dark reactor in our work is close to the productivities of the aqueous CH_3Hg^+ ions by CH_3I by UV irradiation reported by Yin, et al.[16]

In addition, our work had also demonstrated that this methylation reaction can be occurred even in an extremely low gas pressure, for the ORS[3] in the ICP-MS/MS is set in nearly vacuum condition. Therefore, it can be deduced that this methylation reaction can still occur even in the high altitude, although the gas pressure in the high altitude is much lower than the ground.

The triple quadrupole ICP-MS/MS is often used to convert the target ion not the interfering ion reacted with gas molecules in the ORS[3] to a novel ionic species that can be measured at a different mass/charge ratio to increase element selectivity and sensitivity.[27, 30-33] While in this study, we have used a ICP–MS/MS instrument as the tool to study the inorganic mercury methylation, which expand the application range of ICP-MS/MS for elements determination. However, since the contents of $^{202}Hg^+$ ions and CH_3I in the ORS[3] are calculated to be 2.72 pg m^{-3} and 152 mg m^{-3}, respectively, which are much higher than the real content of Hg^{+} ions[20] and CH_3I with a concentration of 1~4 ppt[34] in the atmosphere. Therefore, the otherness is still existed between the instrument model and the real atmosphere environment, although this instrument satisfies the requirement for the model study of element methylation.

4 Conclusion

In this work, ICP-MS/MS was chosen as a tool for the first time to study abiotic methylation of inorganic mercury reacting with VOCs in gas environment. It was demonstrated that the gasous Hg^{+} ions would be transformed to the more toxic species of CH_3Hg^{+} ions instantaneously when collided with some VOCs in gas environment using ICP-MS/MS. Several VOCs, e.g. methyl iodide, methylbenzene, acetic acid and ethyl acetate, exhibited good methylation of Hg^{+} ions. This study might reveal that the abiotic methylation of Hg^{+} ions in the atmosphere environment would potentially occur when contact with the VOCs in the atmosphere, leading to the secondary environment pollution.

Acknowledgments

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Figures and Tables

Fig.1 The schematic representation of ICP–MS/MS operation in the methylation of gasous Hg^{+} ion using VOCs / He as reaction gas.

Fig.2 The products scan results of methylation of the gasous Hg^{+} ions. a) The products scan mass spectrum of CH_3I only without $^{202}Hg^{+}$ ions; b) The products scan mass spectrum of $^{202}Hg^{+}$ ions only without CH_3I; c) The products scan mass spectrum of $^{202}Hg^{+}$ ions reacted with CH_3I; d) The products scan mass spectrum of $^{202}Hg^{+}$ ions reacted with CD_3I; e) The products scan mass spectrum of $^{199}Hg^{+}$ ions reacted with CH_3I; f)The products scan mass spectrum of $^{200}Hg^{+}$ ions reacted with CH_3I; g)The products scan mass spectrum of $^{201}Hg^{+}$ ions reacted with CH_3I. (Experiment conditions: Hg^{2+} concentration, 10 μg L^{-1}; CH_3I/CD_3I flow rate, 5 μL min^{-1}; He flow rate, 0.05 mL min^{-1})

Fig.3 The effect of Hg^{2+} concentration settings on the species of $^{217}CH_3Hg^{+}$ and $^{202}Hg^{+}$. All the tests were conducted in triplicate, and the error bars indicate the s.d. of three repeated measurements. (Experiment conditions: CH_3I flow rate, 5 μL min^{-1}; He flow rate, 0.05 mL min^{-1})

Fig.4 The effect of CH_3I flow rate settings on the species of $^{217}CH_3Hg^{+}$ and the ratios of $^{217}CH_3Hg^{+}$ / $^{202}Hg^{+}$. All the tests were conducted in triplicate, and the error bars indicate the s.d. of three repeated measurements. (Experiment conditions: Hg^{2+} concentration, 10 μg L^{-1}; He flow rate, 0.05 mL min^{-1})

Fig.5 The effect of He flow rate settings on the species of $^{217}CH_3Hg^{+}$ and $^{202}Hg^{+}$ and the ratios of $^{217}CH_3Hg^{+}$ / $^{202}Hg^{+}$ (inset). All the tests were conducted in triplicate, and the error bars indicate the s.d. of three repeated measurements. (Experiment conditions: Hg^{2+} concentration, 10 μg L^{-1}; CH_3I flow rate, 5 μL min^{-1})

Table 1 Instrument settings for the Agilent 8800 ICP–MS/MS instrument.

Table 2 The results of the methylation experiments of gasous Hg^{+} ions with individually VOCs. (Experiment conditions: Hg^{2+} concentration, 10 μg L^{-1}; VOCs flow rate, 5 μL min^{-1}, He flow rate, 0.15 mL min^{-1})

Table 1 Instrument settings for the Agilent 8800 ICP–MS/MS instrument.

Parameter	Value
Reaction gas	VOCs/He
Scan type	MS/MS
RF power(W)	1550
Extract 1 (V)	0
Q1 bias (V)	1.0
Q1→Q2	202→202~260
Octopole bias (V)	-5.0
Octopole RF (V)	150
Energy discrimination (V)	-7.0
Extract 2 (V)	-165
Wait time offset (ms)	2
Sweeps / replicate	10
Integration time / mass (s)	0.1
Replicates	3

Table 2 The results of the methylation experiments of gasous Hg^{+} ions with individually VOCs. (Experiment conditions: Hg^{2+} concentration, 10 μg L^{-1}; VOCs flow rate, 5 μL min^{-1}, He flow rate, 0.15 mL min^{-1})

Species	Productivities of $^{217}CH_3Hg^{+}$ (%)
Methyl iodide	1.77±0.14
Ether	ND[1]
Methylbenzene	1.28±0.06
Acetaldehyde	ND[1]
Acetic Acid	1.35±0.09
Hexane	ND[1]
Methanol	ND[1]
Ethyl Acetate	1.18±0.14
Acetone	ND[1]
Methane	ND[1]

[1]ND: not detected.

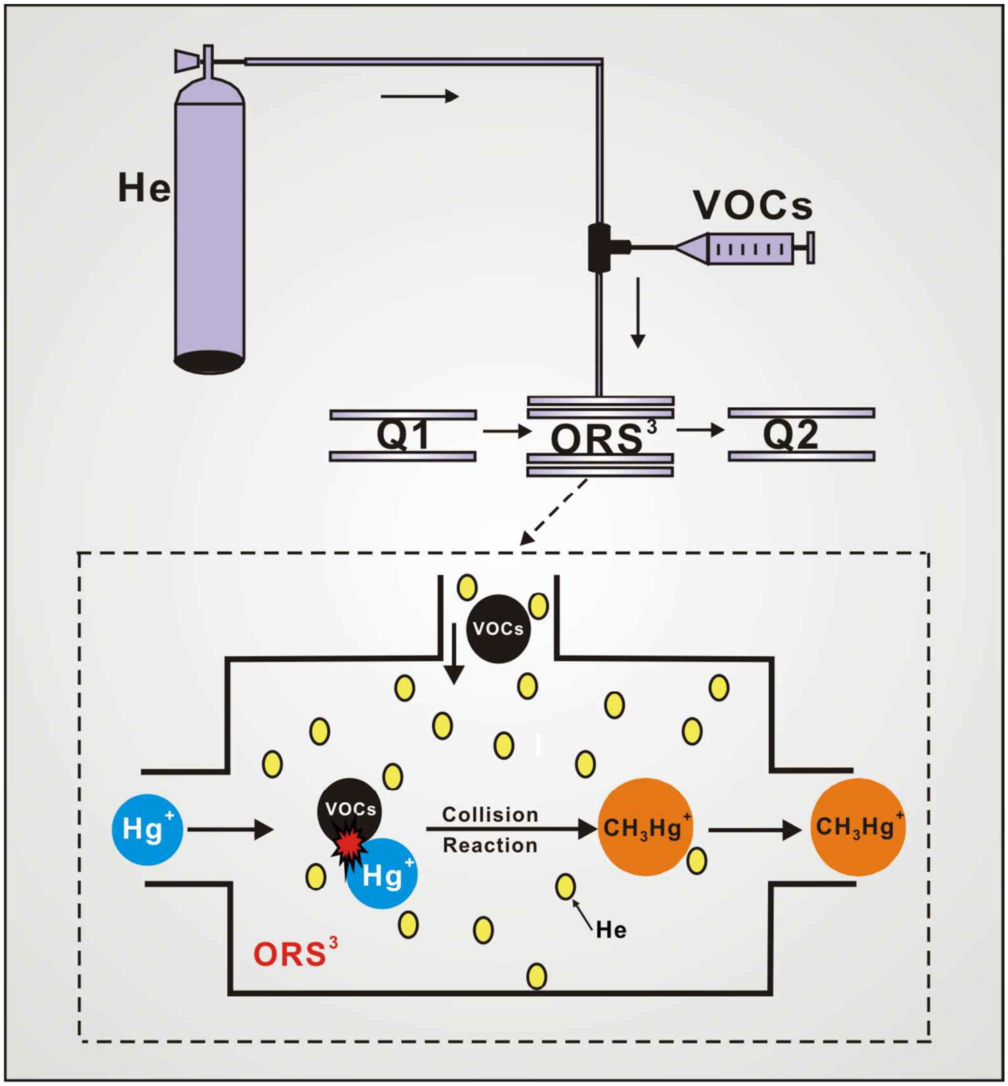

Fig.1 The schematic representation of ICP–MS/MS operation in the methylation of gasous Hg+ ion using VOCs / He as reaction gas.
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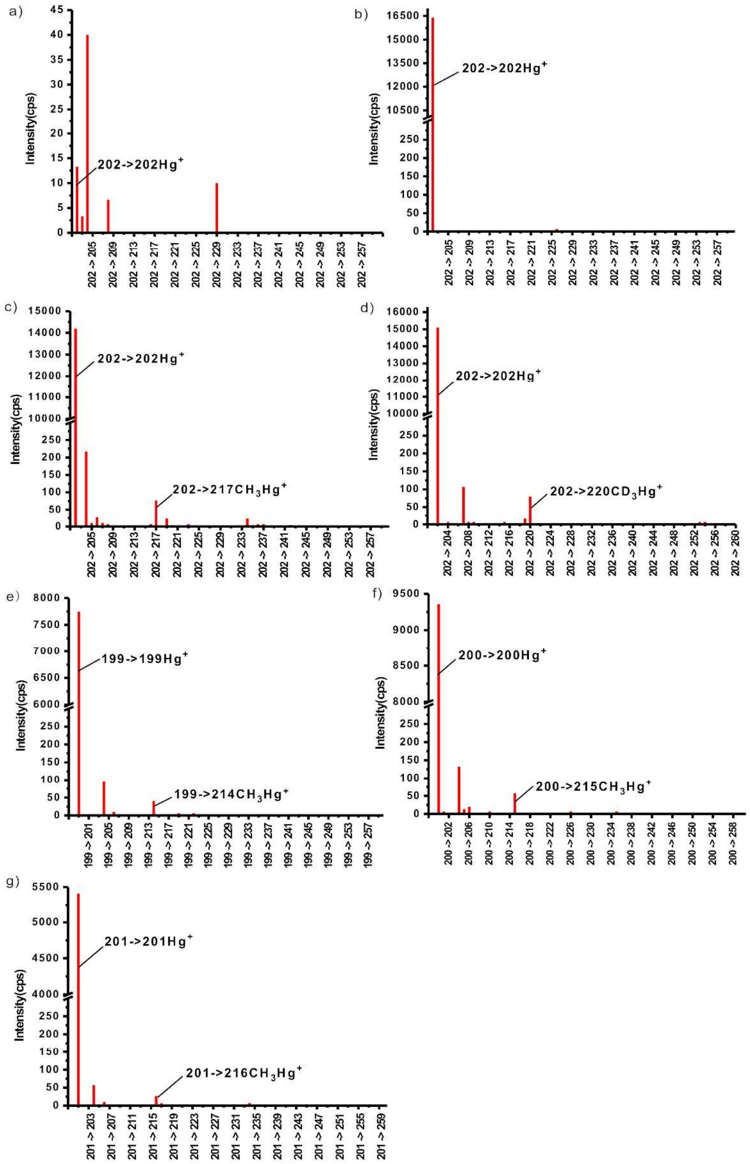


Fig.2 The products scan results of methylation of the gasous Hg+ ions. a) The products scan mass spectrum of CH3I only without 202Hg+ ions; b) The products scan mass spectrum of 202Hg+ ions only without CH3I; c) The products scan mass spectrum of 202Hg+ ions reacted with CH3I; d) The products scan mass spectrum of 202Hg+ ions reacted with CD3I; e) The products scan mass spectrum of 199Hg+ ions reacted with CH3I; f)The products scan mass spectrum of 200Hg+ ions reacted with CH3I; g)The products scan mass spectrum of 201Hg+ ions reacted with CH3I. (Experiment conditions: Hg2+ concentration, 10 μg L-1; CH3I/CD3I flow rate, 5 μL min-1; He flow rate, 0.05 mL min-1)
301x457mm (200 x 200 DPI)

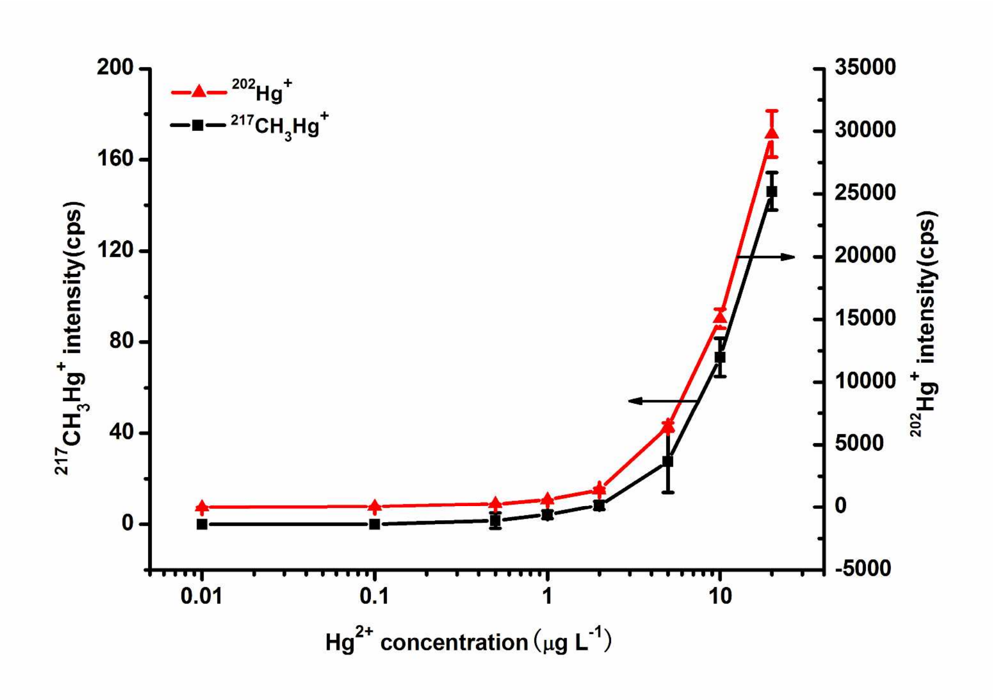


Fig.3 The effect of Hg2+ concentration settings on the species of 217CH3Hg+ and 202Hg+. All the tests were conducted in triplicate, and the error bars indicate the s.d. of three repeated measurements. (Experiment conditions: CH3I flow rate, 5 μL min-1; He flow rate, 0.05 mL min-1)
297x209mm (300 x 300 DPI)

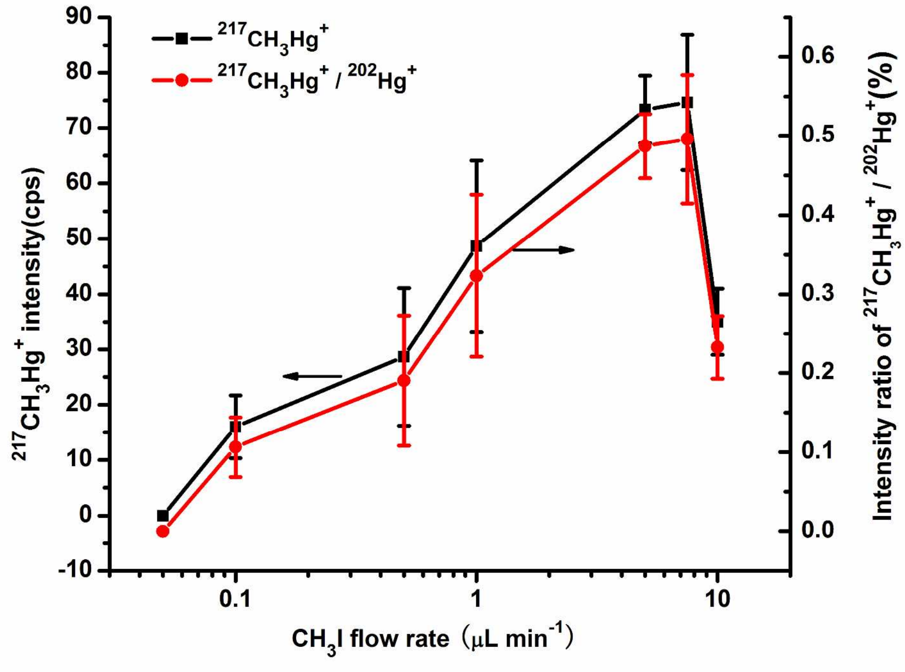


Fig.4 The effect of CH3I flow rate settings on the species of 217CH3Hg+ and the ratios of 217CH3Hg+ / 202Hg+. All the tests were conducted in triplicate, and the error bars indicate the s.d. of three repeated measurements. (Experiment conditions: Hg2+ concentration, 10 μg L-1; He flow rate, 0.05 mL min-1)
279x215mm (300 x 300 DPI)

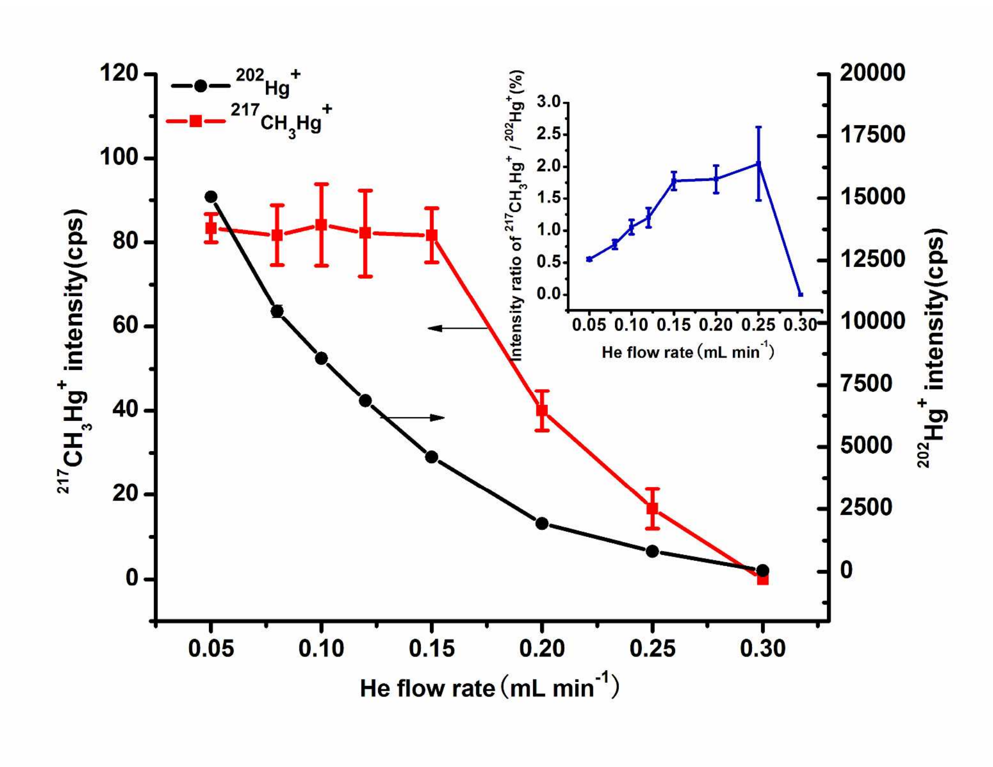
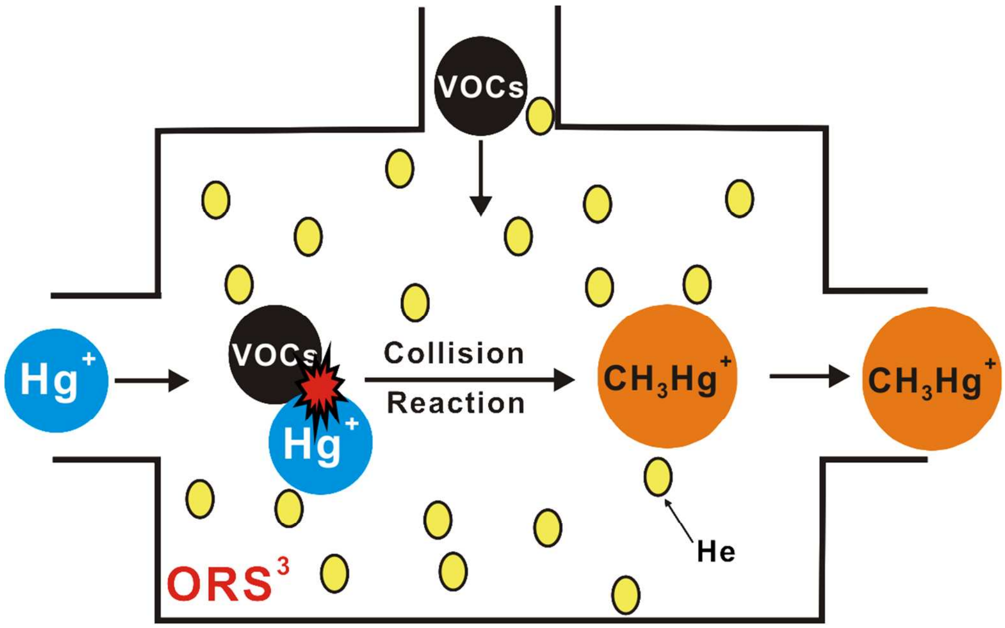


Fig.5 The effect of He flow rate settings on the species of 217CH3Hg+ and 202Hg+ and the ratios of 217CH3Hg+ / 202Hg+ (inset). All the tests were conducted in triplicate, and the error bars indicate the s.d. of three repeated measurements. (Experiment conditions: Hg2+ concentration, 10 µg L-1; CH3I flow rate, 5 µL min-1)
279x215mm (300 x 300 DPI)



In this work, ICP-MS/MS was chosen as a tool for the first time to study abiotic methylation of inorganic mercury reacting with VOCs in gas environment.
108x67mm (300 x 300 DPI)