Journal of Chromatography A, 1218 (2011) 1260–1265

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

A reliable method to determine methylmercury and ethylmercury simultaneously in foods by gas chromatography with inductively coupled plasma mass spectrometry after enzymatic and acid digestion

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ARTICLE INFO

Article history:
Received 10 September 2010
Received in revised form
25 December 2010
Accepted 30 December 2010
Available online 6 January 2011

Keywords:
Methylmercury
Ethylmercury
Enzymatic digestion
Acid digestion
Phenylation
GC-ICP/MS

ABSTRACT

A reliable and sensitive method for determination simultaneously of monomethylmercury (MeHg) and monoethylmercury (EtHg) in various types of foods by gas chromatography inductively coupled plasma mass spectrometry (GC-ICP/MS) was developed and validated. Samples were digested with pancreatin and then hydrochloric acid. MeHg and EtHg in the extract were derivatized in an aqueous buffer with sodium tetraphenylborate. After phase separation, the extract was directly transferred to analysis. The analyses were conducted by GC-ICP/MS with monopropylmercury chloride (PrHgCl) as surrogate standard. Concentrations of 254 ± 5.1, 13.7 ± 0.69 and 162 ± 6.2 μg Hg kg^{-1} (one standard deviation, $n = 3$) were obtained for MeHg in NIST SRM 1947 (Superior Lake fish), SRM 1566b (oyster tissue) and NRC Tort-2 (lobster Hepatopancreas), respectively. These are in good agreement with the certified values of 233 ± 10, 13.2 ± 0.7 and 152 ± 13 μg Hg kg^{-1} (as 95% confidence interval), respectively. The method detection limits (3σ) for MeHg and EtHg are 0.3 μg Hg kg^{-1}. The method detection limit was estimated by using a 0.5 g of subsample, sufficiently low for the risk assessment of MeHg and EtHg in foods. The spiked recoveries of MeHg and EtHg in different food matrices were between 87 and 117% and the RSDs were less than 15%. When isotopic dilution mass spectrometry (IDMS) analysis was performed with a commercial available ^{201}Hg-enriched monomethylmercury (Me^{201}Hg) solution as internal standard, concentrations of 244 ± 13.4, 13.9 ± 0.25 and 161 ± 1.3 μg Hg kg^{-1} were obtained for MeHg in NIST SRM 1947, SRM 1566b and NRC Tort-2, respectively. It shown clearly that IDMS analysis got improvement in precision and accuracy, however, EtHg cannot be analyze simultaneously and the cost of analysis is higher.

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1. Introduction

Food is usually the main source of human exposure to heavy metals. Amongst the heavy metals present in foods, methylmercury (MeHg) is of particular concern in terms of food safety and public health. Mercury exists naturally in abundance in the environment. It enters the environment by both natural and human means. Mercury in the environment can be oxidized to inorganic bivalent mercury with the presence of organic matters in waters. Inorganic mercury can also be converted to methylated form by microorganisms especially in aquatic systems [1].

In food, mercury can exist in inorganic form and the more toxic organic forms such as MeHg in fish and shellfish. Mercury present in other foods mainly in inorganic form. Dietary inorganic mercury is of little toxicological concern [2]. Fish and other seafood products are the main source of MeHg, especially large predatory species such as tuna and swordfish. Chung et al. [3] reported MeHg levels of different fish species and generally confirmed that more than 75% (w/w) of the total mercury content in the edible portion of fish is in form of MeHg. However, fish provide a healthy source of dietary protein and are relatively low in cholesterol and high in omega-3 fatty acids [4].

As Hong Kong is going to conduct its first total diet study on different chemicals including MeHg and EtHg, a sensitive method for testing the content of MeHg and EtHg in different food matrices, including mixed food, is required.

A number of analytical methods have been developed for monitoring organo-mercury compounds, especially MeHg, in the marine environment. However, there was few literature reported the determination of MeHg and EtHg simultaneously in foods. The most frequently used procedures for the extraction of mercury species from solid samples were based on alkaline [5–10], acidic leaching [11–14], aqueous distillation [15–19], ultrasonic extraction [20],

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0021-9673/$ – see front matter © 2011 Published by Elsevier B.V.
doi:10.1016/j.chroma.2010.12.112

supercritical fluid extraction (SFE) [21] and microwave-assisted extraction (MAE) [22–26]. Though MAE can shorten the sample extraction time, extreme care about the extraction condition is required as significant amount of MeHg could be lost. Lemes and Wang [27] recently reported that enzymatic hydrolysis with trysin could release methylmercuric cysteinate or glutathionate from fish protein.

Amongst the reported literatures, different analytical techniques have been developed for speciation of mercury [28]. They usually combined of a separation and a detection technique, such as gas or liquid chromatography coupled with element-selective detectors, such as atomic emission, atomic absorption, atomic fluorescence, or inductively coupled plasma mass spectrometry (ICP/MS). Amongst the methods mentioned, the coupling of GC to ICP/MS combines high sensitivity with the possibility of speciated isotope dilution measurements [29].

In view of the difficulties of fast extraction methods and the possibility of determining MeHg and EtHg simultaneously in foods at background level for risk assessment, a new method was developed. This present work describes the development and validation of an analytical method for the determination of MeHg and EtHg at parts-per-billion level simultaneously in various types of food items to be tested in the total diet study. For the analysis of both MeHg and EtHg, monopropylmercury chloride (PrHgCl) was used as surrogate standard. Good recovery and precision values were obtained for analyte in certified reference samples. For more accurate measurement of MeHg, a commercial available isotopic-labelled standard, was used as internal standard. Better precision, accuracy and recovery data were obtained for MeHg.

2. Experimental

2.1. Reagents and solutions

All the chemicals and solvents used were of analytical-reagent grade or higher, unless otherwise specified. Ultra-pure deionized water (18.2 MΩ cm; Milli-Q, Millipore Corp., Bedford, MA) was used throughout. Pancreatin solution of 1.5% (w/v) was prepared by dissolving pancreation (Sigma–Aldrich, St. Louis, USA) in water. A 0.08 mol L^{-1} phosphate buffer was prepared by dissolving appropriate amount of sodium phosphate dibasic and sodium phosphate monobasic in water and adjusted the pH value to 7.5 with sodium hydroxide solution. Sodium tetraphenylbroate (1.5%, w/v) solution, prepared by dissolving $NaBPh_4$ (Sigma–Aldrich) in water, was used as a derivatization reagent. A 2 mol L^{-1} sodium acetate buffer was prepared by dissolving an appropriate amount of sodium acetate in water and adjusted the pH to 4.5 with acetic acid.

MeHg and EtHg chloride were purchased from Acros (Geel, Belgium). PrHgCl was purchased from Fluka (Buchs, Switzerland). Individual stock solutions of 100 mg Hg L^{-1} were prepared in methanol with 1% (v/v) hydrochloric acid (1% HCl) and kept refrigerated until used. Working solutions were obtained by dilution of the stock solution with 1% HCl and prepared daily before use. A 250 μg Hg L^{-1} PrHgCl solution was prepared daily by diluting the stock solution in 1% HCl for use as surrogate standard.

^{201}Hg-enriched MeHg in acetic acid/methanol (3:1), 5.494 mg Hg kg^{-1}, was purchased from ISC Science (Oviedo, Spain). ^{201}Hg-enriched MeHg spike solution at a nominal concentration of 1.5 μg Hg kg^{-1} was prepared by diluting the stock solution with a solution of 12% (v/v) methanol in 1% HCl. All dilutions were achieved by mass.

The SRM 1947 (Superior Lake fish) and SRM 1566b (oyster tissue), obtained from the NIST (Boulder, USA), were used for method validation. The CRM Tort-2 (lobster Hepatopancreas) was obtained from the National Measurement Standards of the Research Council of Canada (Ottawa, Ontario, Canada).

Calibration standard solutions, 0.0, 0.01, 0.05, 0.1, 0.5, 1.0 and 5.0 μg Hg L^{-1} were prepared by transferred appropriate volume of mixed intermediate MeHg and EtHg standard solution into individual 50 mL centrifuge tube. Pipetted 0.13 mL of working surrogate/internal standard solution, 3 mL pancreatin solution, 7 mL water and 5 mL phosphate buffer solution into each centrifuge tube. Diluted to the volume of 30 mL with concentrated HCl.

Table 1
GC-ICP/MS operating conditions.

GC	
Column	DB-5MS, 30 m × 0.25 mm, 0.25 μm film thickness
Injection	Splitless
Injection volume	1 μL
Injector temperature	220 °C
Oven temperature programme	50 °C hold 1 min; ramp to 280 °C at 20 °C/min; hold 3 min
Carrier gas	1% Xenon in Helium
Flow rate	1 mL/min
Transfer line temperature	280 °C
ICP-MS	
Rf power	1440 W
Plasma Ar gas flow rate	15 L min^{-1}
Carrier gas (1% Xenon in Helium) flow rate	1.2 L min^{-1}
Sampling cone	Nickel
Skimmer cone	Nickel
Acquisition mode	Full quantitation
Dwell time	100 ms

2.2. Instrumentations

An Agilent 6890 gas chromatograph (Agilent Technologies, Santa Clara, CA), with autosampler, fitted with a DB-5MS column (Agilent Technologies) was used for the separation of the mercury species. The 7500ce inductively coupled plasma-mass spectrometer (Agilent Technologies) equipped with ChemStation software (Version B.03.02) was used for the detection of the mercury species. Helium containing 1% (w/w) Xenon (Linde Canada Limited, Alberta, Canada) was used as carrier gas. The isotopic masses of mercury of 200, 201 and 202 were measured. Typical GC-ICP/MS operating conditions are summarized in Table 1.

2.3. Sample extraction

Weighed approximately 0.5–1 g of a sample in a 40 mL-glass vial. Added 25 mL acetone, capped tightly and shook vigorously for 15 s. Centrifuged (Falcon 6/300, Measuring and Scientific Equipment, London, UK) at 2000 rpm (or 900 × *g*) for 5 min and then discarded acetone carefully with a Pasteur pipette. If the tissue formed clots, broke up with a glass rod. Repeated the fat removal procedure two more times with acetone and toluene respectively. Spiked 0.06 mL of surrogate standard or weighted appropriate amount of internal standard of ^{201}Hg-enriched MeHg spike solution into the sample for mercury speciation and isotopic dilution analysis respectively. Added 3 mL 1.5% (w/v) pancreatin solution and 5 mL phosphate buffer to the residue. Screwed the cap and kept the solution in a shaking water bath at 37 ± 2 °C overnight. Transferred the extract to a 50 mL centrifuge tube. Added appropriate amount of water to 15 mL and finally made up to 30 mL with concentrated HCl. Screwed the cap tightly. Shook vigorously to disperse the solid into the solution and maintained shaking for 3 h with a shaker. Centrifuged the tubes at 3000 rpm (or 2000 × *g*) for 20 min.

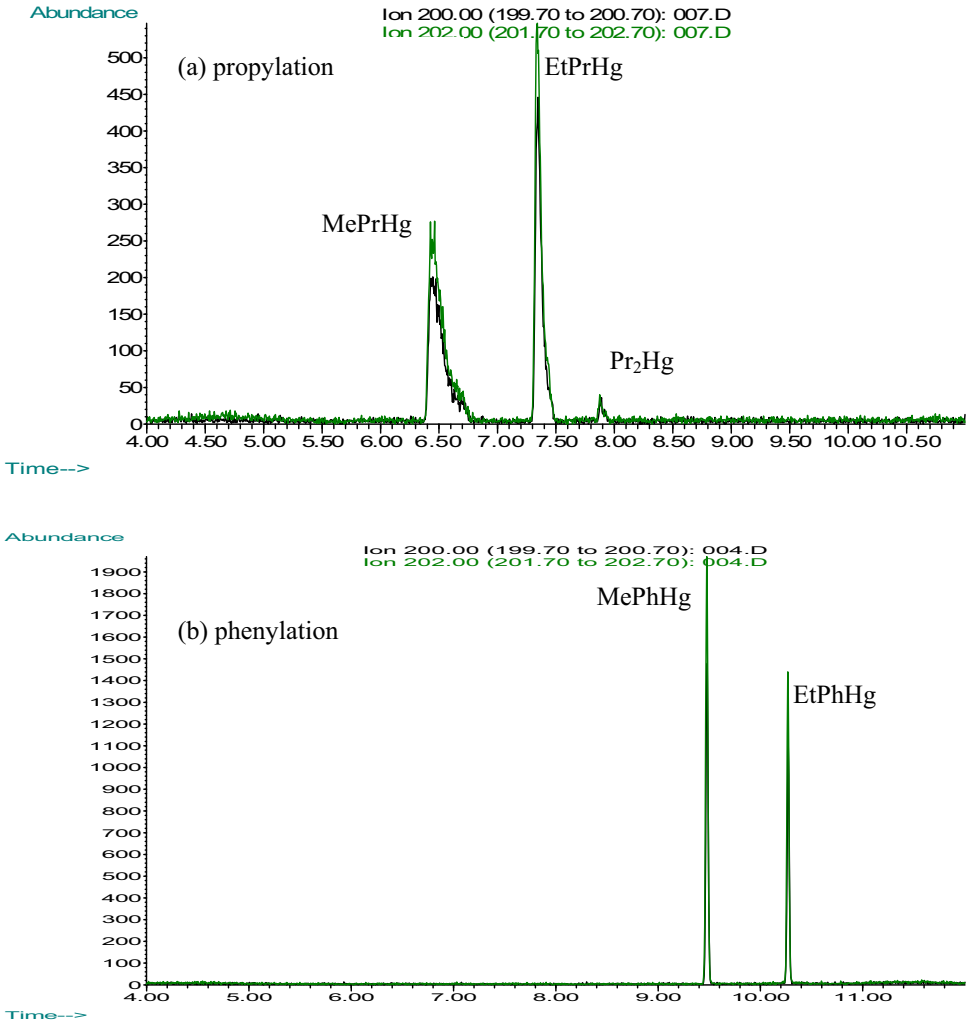

Fig. 1. GC-ICP/MS chromatogram of MeHg and EtHg standard of 10 μg Hg kg^{-1} after derivatized by (a) sodium tetrapropylborate and (b) sodium tetraphenlyborate respectively.

2.4. Derivatization with tetraphenylborate

Transferred quantitatively 8 mL of the supernatant solution to a clean 30 mL vial or a centrifuge tube. Added 8 mL 2 M acetate buffer into the supernatant solution. Placed the tube into the ice water bath and added 10 mL 6 M NaOH solution into the mixture after cooled. The pH value of the mixture should be within 4.1–5.0. Added 2 mL amount of tetraphenylbroate derivatization agent into the mixture. For headspace solid-phase microextraction (HS-SPME) analysis, the mixture was capped in a 30 mL vial and transferred for analysis. Otherwise, added immediately 2 mL iso-octane into the centrifuge tube. Shook the reaction mixture for 2 h on a reciprocal shaker. Centrifuged at 3000 rpm (or 2000 × *g*) for 20 min. Transferred the iso-octane fraction into a GC autosampler vial for GC-ICP/MS analysis.

3. Results and discussion

3.1. Optimization of leaching/extraction conditions

3.1.1. Optimization of sample digestion

Amongst the various digestion methods, alkaline digestion was the most common leaching method for MeHg from fish tissue. Therefore, methanolic potassium hydroxide (KOH) [6,8,9] digestion was considered during the initial stage of the development work. However, it was observed that excessive amount of potassium in the extract after methanolic KOH digestion precipitated the derivatization agent tetraphenylbroate. Therefore, such approach was considered not suitable as digestion method. Though other derivatization agents could be used to avoid precipitation, the benefit of phenylation over ethylation and propylation would be discuss in the forthcoming section. Furthermore, the low limit of quantification for MeHg cannot be attained easily owing to the dilution effect of the alkaline extraction. In this connection, the acid digestion procedure was adopted.

Emteborg et al. [21] reported a large volume of liquid carbon dioxide was required for complete extract of MeHg in sediment when SFE was used for extraction. Regarding MAE, lost of MeHg could be occurred if the parameters were not optimized, especially for EtHg [30]. Owing to the variety of matrices to be analyzed in the total diet study, both SFE and MAE were not considered as the best extraction means. For acid extraction of MeHg from foods, severe emulsion was formed commonly. As such, the food sample was digested firstly with pancreatin so that the bounded MeHg was transformed to cysteinate, glutathionate or other amino acids adduct of MeHg and EtHg. These MeHg and EtHg adducts were then hydrolyzed by hydrochloric acid to form MeHg and EtHg chloride. By doing so, it was observed that emulsion formation was reduced significantly. Furthermore, good recovery results were obtained for low level spike in different matrices.

Table 2
Optimized test parameters for conducting HS-SPME analysis.

HS:	
Sample/standard volume:	2 mL
2M acetate buffer:	2 mL
6M sodium hydroxide:	2.5 mL
1% sodium tetraphenlyborate:	1
SPME:	
Fiber:	Polydimethylsiloxane (PDMS) 100 μm
Incubation temperature:	65 °C
Incubation time:	50 minutes
Extraction time:	20 minutes
Thermal desorption temperature:	220 °C
Thermal desorption time:	1 minutes

3.1.2. Optimization of derivatization

According to the literature, ethylation [6], propylation [8,11,12] and phenylation [3] with sodium tetraalkyl- or tetraaryl-borate respectively were employed to derivatize MeHg. As EtHg is one of the target analyte and ethylation of both EtHg and inorganic mercury gives diethylmercury, ethylation does not fit for the purpose of detection of MeHg and EtHg simultaneously. In order to assess the performance of different derivatization, a study with standard solution of MeHg and EtHg at 10 μg Hg kg^{-1} was conducted and the results was shown in Fig. 1. It could easily observed that phenylation provided higher peak intensity and better peak shape than propylation. Even if the peak areas were approximately the same, the target analytes after phenylation were eluted much slower when compared with the solvent peak. Hence, early eluting matrix interference peaks could be avoided. Therefore, phenylation was chose as the derivatization method.

3.1.3. Optimization of detection method

Since HS-SPME has been used in organomercury speciation analysis [7,31–33], the feasibility of employing such technique to improve the limit of detection was studied by coupled with a GC/MS. During the study, the essential testing parameters for HS-SPME analysis such as incubation temperature, incubation time, extraction time as well as type of fibre used had been optimized and summarized in Table 2. Though the measured peak area of MeHg and EtHg obtained by HS-SPME were comparable to that of GC-ICP/MS, HS-SPME gets much lower linearity range (0.2–5 μg Hg L^{-1}) and matrix effect has to be overcome by standard addition calibration [33]. Furthermore, the acid digested mixture could not be pre-concentrated easily before conducting HS-SPME analyses, GC-ICP/MS was chosen as the detection method.

3.2. Analytical performance

The calibration curve was found to be linear over the range 0.01–5 μg Hg kg^{-1} with r values > 0.995 when internally standardized. Absolute responses showed some drift with time, necessitating the use of surrogate/internal standard for accurate results. Repeated injections of MeHg standard solution at a concentration equivalent to 1.5 μg Hg kg^{-1} gave an RSD of 23% for the measured peak area while the RSD of the peak area ratio was improved to 4.5%. Although the isotope dilution method was used for MeHg analysis to compensate for any matrix effects, EtHg cannot be quantified simultaneously, PrHgCl was added as surrogate standard as these compounds are chromatographically well resolved.

In order to assess the accuracy and precision of the GC-ICP/MS method, spike recovery of MeHg and EtHg in various food matrices at the level of interest, 1.5 μg Hg kg^{-1}, and its two and 6.7 times were conducted and summarized in Table 3. These results demonstrated good method accuracy at 1.5 μg Hg kg^{-1}, giving mean recoveries of 103 and 104% for MeHg and EtHg respectively with acceptable RSDs. As noted above, internal standardization also makes it possible to allow some variation in the final extract volume so that a method designed for optimal use of an internal standard cannot simply be recalculated by the external standard method.

Besides, MeHg content was determined in the certified reference materials (CRM) Lobster Hepatopancreas Tort-2 of the National Research Council and oyster tissue SRM 1566b and SRM 1947 of the National Institute of Standards and Technology. The CRMs were prepared by extracting MeHg as described in Section 2. A typical GC-ICP/MS chromatogram of the oyster tissue CRM is shown in Fig. 2(a). MeHg was the major mercury species in this chromatogram. Di-substituted species from inorganic mercury was also observed. No matter internal standardization with PrHgCl or IDMS with ^{201}Hg-

Table 3
Recovery (level found as percentage of level spiked) and relative standard deviation for determination of MeHg and EtHg in various sample matrices (n = 3).

Food matrix	Recovery, % (RSD, %)					
	MeHg			EtHg		
	1.5	3	10	1.5	3	10
Chicken meat	104 (5.3)	105 (0.2)	103 (4.3)	113 (3.7)	96 (0.8)	105 (3.2)
Chicken egg	96 (2.8)	98 (1.0)	101 (0.2)	88 (6.2)	98 (4.3)	104 (0.9)
Glutinous rice dumpling	107 (0.8)	105 (0.2)	104 (1.6)	103 (2.6)	101 (3.2)	103 (1.0)
Oyster sauce	105 (13)	99 (3.1)	98 (2.2)	112 (6.7)	116 (0.8)	98 (4.5)
Grass crap	*	105 (1.0)	99 (0.6)	106 (1.3)	106 (0.6)	102 (1.3)
Grey mullet	*	*	103 (0.9)	101 (1.6)	99 (5.0)	105 (1.1)
Oyster	*	*	97 (0.5)	107 (4.0)	117 (3.1)	97 (1.0)

* Since these samples were found to contain MeHg in the range of 5–15 μg kg^{-1}, the spike recovery analysis at low level(s) were not performed.

Table 4
Recoveries and relative standard deviations of MeHg as Hg in different certified reference materials.

Sample	Certified Value (μg Hg kg^{-1})	Surrogate standard		IDMS	
		Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
Lake superior fish NIST SRM 1947	233 ± 10	108.9 (n = 3)	2.0	103.3 (n = 3)	1.5
Oyster tissue NIST SRM 1566b	13.2 ± 0.7	104.1 (n = 3)	5.0	105.4 (n = 3)	1.2
Lobster hepatopancreas NRC CRM Tort-2	152 ± 13	106.8 (n = 3)	3.8	105.6 (n = 3)	0.83

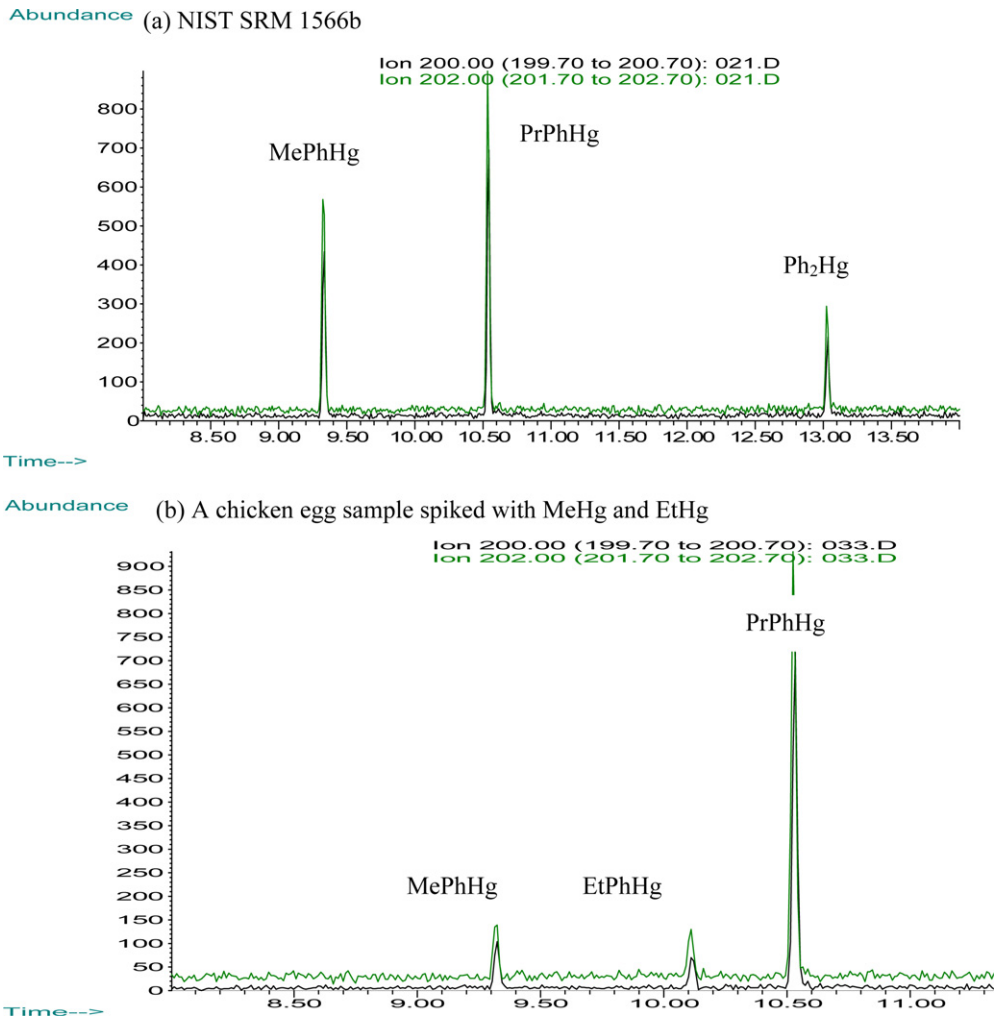

Fig. 2. GC-ICP/MS chromatograms of the extract of (a) a certified reference material – oyster tissue (NIST SRM 1566b) and (b) a chicken egg sample spiked with MeHg and EtHg at 1.5 μg Hg kg^{-1} added with PrHgCl as surrogate standard.

enriched MeHg, the value obtained for MeHg was agreed well with the certified or reference values (Table 4).

Other method performance in terms of precision and limit of detection (LOD) were evaluated by analyzing spiked blank food sample with MeHg and EtHg in the range of interest. A typical chromatogram of spiked recovery study at 1.5 μg Hg kg^{-1} is shown in Fig. 2(b). Relative standard deviation values between 1 and 5% were obtained from the analysis of CRMs. The LODs of the method was worked out based on the approach of the Code of Federal Regulations [34].

4. Conclusions

A method that is reliable and accurate for the determination of organomercury species in foods was developed and validated. This method involved the combination of the highly sensitive and selective inductively coupled plasma mass spectrometry with gas chromatography that permits simultaneous detection of MeHg and EtHg down to the level of 0.3 μg Hg kg^{-1} in foods. Each organomercury compound is baseline separated from other species. Although an additional enzyme digestion step was conducted prior to acid extraction and derivatization with tetraphenylborate, less emulsion was observed and provided good recovery at low parts-per-billion level. The method was also validated by analyzing certified reference materials and spiked recoveries in various food matrices.

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