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An accurate and sensitive method for the determination of methylmercury in biological specimens using GC-ICP-MS with solid phase microextraction†

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A highly sensitive and selective method has been developed for the determination of methylmercury in biological specimens and NIST Standard Reference Materials (SRMs). The procedure involves microwave extraction with acetic acid, followed by derivatization and headspace solid-phase microextraction (SPME) with a polydimethylsiloxane (PDMS)-coated silica fiber. Optimization of conditions including gas chromatograph injection temperature, microwave extraction power and microwave extraction time are presented. The identification and quantification (*via* the method of standard additions) of the extracted compounds is carried out by capillary gas chromatography with inductively coupled plasma mass spectrometric detection (GC-ICP-MS) using a unique heated interface that was designed for this work. The SPME-GC-ICP-MS method was validated for the determination of methylmercury (MeHg) concentrations in a variety of biological Standard Reference Materials (SRMs), ranging from 13.2 ng g^{-1} in SRM 1566b Oyster Tissue, to 397 ng g^{-1} in SRM 1946 Lake Superior Fish Tissue. Additionally, this method was applied to the determination of MeHg in seabird eggs (common murres, *Uria aalge* and thick-billed murres, *Uria lomvia*) collected from colonies on Little Diomede and Bogoslof islands in the Bering Sea and Saint Lazaria Island in the Gulf of Alaska and cryogenically banked in the Marine Environmental Specimen Bank. The results obtained demonstrate that SPME-GC-ICP-MS is a sensitive technique for the determination of methylmercury at trace and ultra-trace levels in a variety of natural matrices with high reproducibility and accuracy. In all instances, the sample-to-sample variability was typically 2% relative standard deviation (RSD) and the method detection limit for methylmercury was 4.2 pg g^{-1} (as Hg), based on a 0.5 g tissue sample of SRM 1566b Oyster Tissue.

Introduction

Various levels of information are required for proper assessment of trace element species, including total elemental composition, oxidation states, and bound ligand/molecule identification. While chromatographic methods exist for separating the various ''species'' of a trace metal present in an environmental or biological matrix, many times the analyte of interest is present in such a low concentration that instrumental sensitivity becomes the limiting factor in the analysis. Compared with other detection methods, inductively coupled plasma mass spectrometry (ICP-MS) has the unique advantages of element-specific detection, wide dynamic range, low limits of detection, and the ability to perform isotope dilution analysis. The aforementioned advantages make ICP-MS a powerful instrumental technique for the determination of trace element species in chromatographic effluents.

The widespread presence of methylmercury (MeHg) contamination in the environment and its potential toxicity has produced a demand for sensitive and accurate speciation methods for the determination of MeHg at trace levels in water, sediments, fish and other biological samples. Mercury is a widely distributed and persistent pollutant in the environment and is a highly bioaccumulated trace metal in the human food chain. Mercury has been historically used in numerous products and is naturally present in coal. Its emission from coal combustion and other processes including medical/municipal waste incineration, industrial boilers and chlor-alkali production has resulted in widespread reports concerning its ecotoxicological importance. The methylmercury form of mercury is far more toxic than elemental mercury. Inorganic mercury compounds can undergo methylation in an aquatic environment by biotic-bacteria and algae (both abiotic and biotic pathways exist) in the water column and in sediment and can then bioaccumulate through the food chain. Elemental Hg and organomercury compounds can cross the placental and blood–brain barrier and can be oxidized and accumulated in central nervous system tissue, excreted as Hg(II) (kidney), or sequestered as inorganic and organic mercury (liver), and can potentially result in neurodevelopmental effects to humans (*e.g.*, Minamata disease) if consumed in sufficient quantities.

Mercury's toxic effects on the central nervous system and organs have been known for a long time but immune system effects are less understood. Mercury-related immunological effects will depend on the dose and biologically-active form it assumes. The sensitivity of various animal species (including humans) to low levels of Hg is an important area of research because sub-lethal immunotoxicological effects usually occur at very low doses,[1] so the immune system can be impacted well

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before toxic effects are observed in other organs and tissues. The ability to detect and quantify low levels of Hg species that play a role in the health of physiological and environmental systems is an example of an analytical problem that depends on the coupling of sensitive, hyphenated analytical tools like GC-ICP-MS and the development of accurate methods for the quantification of organometallic species.

To determine the environmental impact and toxicity of organometallic compounds, it is necessary to determine both the species and concentrations that are present in samples, as it is often the species concentration, rather than total concentration, which determines toxicity. To that end, chromatographic separation techniques are powerful tools in the determination of organometallic contaminants. Some recent speciation methods for organometallic compounds based on gas chromatographic (GC) separations include detection with atomic spectroscopies, including fluorescence[2–5] (AFS), absorption[6,7] (AAS), emission[8–14] (AES), and inductively coupled plasma (ICP) atomic emission.[15] However, there is an ever-increasing coupling of GC separations to ICP mass spectrometry[16–22] for speciation analysis of organometallic compounds due to several key advantages. As mentioned previously, ICP-MS has the unique advantages of element specific detection, wide dynamic range, low limits of detection, and the ability to perform isotope dilution analysis. Additionally, the sample is introduced in an already vaporized form, leading to more efficient ionization in the plasma as well as higher transport efficiencies than are seen with liquid chromatography.[16,23]

The technique of solid-phase microextraction (SPME) was developed by Pawliszyn *et al.*[24] for the extraction of organic compounds from aqueous media. The partitioning of the analyte occurs directly from the aqueous solution or headspace to the polymer-coated fiber stationary phase. The analytes can then be thermally desorbed from the fiber in the injector of a GC. SPME offers numerous advantages for sample preparation when analyte speciation is desired because it is simple, rapid, sensitive, and solvent-free. Recently, SPME has found use in speciation analysis including specific applications for organotin[10,25–28] and organomercury[10,11,16,29–31] compounds. Utilizing SPME with GC-ICP-MS offers an additional advantage in that the technique avoids the introduction (injection) of organic GC solvents into the ICP, thus eliminating the need for the addition of oxygen into the plasma.

This paper describes the development of an analytical method for the extraction and quantification of methylmercury from marine biota by SPME-GC-ICP-MS. Specifically, acid-assisted microwave extraction was used for the development of a speciation sample preparation method for a suite of biological reference materials. SRM 1566b Oyster Tissue, SRM 2977 Mussel Tissue, and SRM 1946 Lake Superior Fish Tissue were analyzed to validate the performance and accuracy of an in-house built GC-ICP-MS interface designed for the quantification of methylmercury and then applied to the determination of MeHg content in the eggs of Alaskan murres (*Uria* sp.). Currently, NIST utilizes SPME followed by GC atomic emission detection (GC-AED) or GC-MS (depending on concentration levels in the material) as in-house methods for the certification of methylmercury. The methods described within the text are complementary to those currently employed at NIST, which will allow future certification efforts to be based on two independent analytical methods.

Experimental

Instrumentation

A Varian Model 3500 (Walnut Creek, CA, USA) gas chromatograph equipped with a 30 m 280 μm id MXT-1 stainless steel capillary column coated with a 50 μm film of dimethyl polysiloxane (Restek, State College, PA, USA) was used throughout the study. The column temperature was ramped at 25 °C min^{-1} from an initial temperature of 40 °C to the final temperature of 270 °C. A split/splitless injector maintained at 210 °C was used in the splitless mode. Helium was used as a carrier gas and SPME was performed manually, using fibers coated with 100 μm PDMS (Supelco, Bellefonte, PA, USA). The GC was coupled to a quadrupole ICP-MS (PQ3, VG Elemental, Winsford, Cheshire, UK). Fig. 1 details the configuration of an in-house designed heated interface for coupling the GC with the ICP-MS. It consists of a 1 m MXT stainless steel capillary transfer line (Restek) and MXT low-dead-volume connector (Restek) which connects the transfer capillary to the MXT analytical column. The transfer capillary is housed within 1.6 mm od silcosteel tubing (Restek) and terminates 1.9 mm before the end of the transfer line. The ICP-MS nebulizer output is heated by the GC and plumbed into the 1.6 mm tubing *via* a Silcosteel tee fitting (Restek), which allows for the analyte vapor to be mixed with the heated nebulizer gas and swept into the ICP torch injector, eliminating the need for the heating of the transfer capillary to the terminus of the injector tip. Humidified Ar makeup gas was mixed with the analyte/heated nebulizer gas stream by plumbing the gas output of a gas–liquid separator into the system. A mass flow controller (Aalborg Model GFC 171, Greenwich, CT, USA), controlled with LabView software and National Instruments (Austin, TX, USA) data acquisition hardware, regulated gas flow through the gas–liquid separator. The complete operating conditions for the GC-ICP-MS coupling system are listed in Table 1. Transient signal data for the different species were further processed using both PlasmaLab software (Thermo Elemental, Winsford, Cheshire, UK) and Microsoft Excel.

Reagents and chemicals

Stock solutions of mercury compounds were prepared gravimetrically from reagent-grade methylmercury chloride (Sigma–Aldrich, St. Louis, MO, USA), ethylmercury chloride (Sigma–Aldrich), and propylmercury chloride (Pfaltz & Bauer, Waterbury, CT, USA) in Milli-Q 18 MΩ cm water (Millipore, Bedford, MA, USA). Both sodium tetraethylborate (Sigma–Aldrich) and sodium tetraphenylborate were used as derivatization reagents. Acid digests consisted of either Omni-Trace Ultra acetic acid (EMD Chemicals, Gibbstown, NJ, USA), or Suprapur formic acid (EMD Chemicals). Buffer solution was made from reagent-grade sodium acetate (Sigma–Aldrich) using the same water source. For validation of MeHg measurements, the following biological SRMs were analyzed: SRM 1566b Oyster Tissue, SRM 2977 Mussel Tissue (Organic Contaminants and Trace Elements), and SRM 1946 Lake Superior Fish Tissue from the Standard Reference Materials

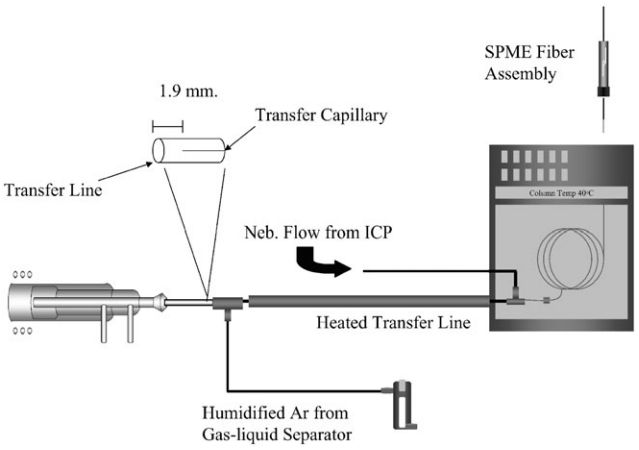

Fig. 1 Diagrammatic representation of the basic components of the SPME-GC-ICP-MS interface.

Table 1 GC-ICP-MS parameters

GC parameters	
Column	MXT Silcosteel 30 m, id 0.28 mm
Inlet pressure	12 psi
Injection port	Splitless
Injection port temperature	210 °C
Makeup gas flow	Ar 400 ml min^{-1}
Oven program	
Initial temperature	40 °C (1 min)
Ramp rate	25 °C min^{-1}
Final temperature	270 °C (3 min)
Transfer line	
Outer	Length 1 m Silcosteel, id 1.0 mm, od 1.6 mm
Inner	Silcosteel, id 0.28 mm, od 0.53 mm
Temperature	230 °C
ICP-MS parameters	
rf power	1350 W
Gas flow	
Plasma	13.50 L min^{-1}
Auxiliary	0.86 L min^{-1}
Nebulizer	0.90 L min^{-1}
Isotopes/dwell times	118, 120, 200, 201, 202; 30 ms

Program at the National Institute of Standards and Technology (NIST, Gaithersburg, MD).

WARNING: Methylmercury and derivatized forms of organomercury compounds are highly toxic and must be handled with appropriate personal protection. This requires the use of silver-lined gloves, use of a fume hood, and approved breathing apparatus.

Sample preparation

The sample dissolution procedure used multiple iterations of microwave digestion. Approximately 0.5 g samples (exact mass known) were placed in quartz digestion vessels and the species of interest were extracted for 10 min in 5 ml of glacial acetic acid, in a PerkinElmer (Shelton, CT, USA) Multiwave microwave oven. The contents were allowed to cool to room temperature, vented, quantitatively transferred to 50 ml centrifuge tubes, and buffered with 10 ml of 2 mol L^{-1} sodium acetate solution, weighed, and finally centrifuged at 2000 rpm for 5 min. Two aliquots of supernatant $\approx$5 ml volume each (exact mass known) were transferred into 20 ml glass amber vials and spiked with either a known concentration of methylmercury (spike solution) or a dummy spike of makeup water (unspiked solution).

GC analysis of organometallic compounds requires derivatization to form volatile species. The most common derivatization methods for methylmercury analysis by GC-ICP-MS include ethylation, propylation and phenylation by the appropriate sodium tetraorganoborate solutions. A known mass ($\approx$1 g) of either 2% (w/v in water) of sodium tetraethylborate or tetraphenylborate solution was used to derivatize the species to their volatile forms. Vials were capped with a PTFE-coated silicon rubber septum. The SPME needle was inserted through the septum, and the solution was vigorously stirred with a Teflon coated magnetic stir bar while headspace sampling was performed for 10 min at 65 °C. The SPME extraction temperature was optimized between room temperature and 100 °C to yield the highest MeHg signal at a set extraction time of 10 min. At temperatures near 100 °C, a significant decrease in the response of MeHg was noted and therefore 65 °C was used throughout the study.

The collected analyte was then desorbed from the SPME fiber onto a GC column. A 3 min desorption time at an injector temperature of 210 °C ensured complete desorption from the fiber, initiating the analysis. Quantification was achieved by employing the method of standard additions. Instrumental responses (integrated peak areas) for the unspiked and spiked samples were obtained by monitoring transient signals for Hg isotopes at m/z 200, 201, and 202. Separate sample aliquots ($n = 3$) of the freeze-dried SRMs (1566b and 2977) were freeze dried again at the time of analysis to produce a moisture correction value for the analysis.

Results and discussion

Optimization of GC-ICP interface

GC separations of MeHg and Hg^{2+} with detection by ICP-MS result in the generation of transient signals of relatively short duration. To optimize the ICP-MS instrument for ion transmission at the selected mercury isotopes, a continuous Hg vapor generation system employing a gas–liquid separator was inserted into the system between the heated transfer line and the ICP torch. Mercury vapor was introduced into the ICP-MS instrument by reduction of a solution of Hg^{2+} with tin(II) chloride. Following optimization of the instrument, it was noted that the analytical signals for the GC-separated mercury species were significantly lower than those obtained for continuous vapor generation when compared on a unit-mass basis. It was further found that the transient mercury signals could be substantially increased by introducing water vapor into the system, which was achieved by pumping high-purity de-ionized water through the gas–liquid separator. The influence of water on plasma excitation characteristics and ion/atom ratios has been extensively studied,[32–36] principally with respect to plasma sources for atomic emission spectrometry. The introduction of water vapor has been shown generally to increase the electron density in the central channel of the plasma. In a system where electron collisional excitation is an important mechanism, this would have an impact on signal intensities for analytes with relatively high excitation and ionization energies,[36] such as mercury (first ionization energy 10.4 eV). The presence of hydrogen in the central channel from dissociation of water vapor also appears to improve[35,36] the plasma to analyte energy transfer as a consequence of the higher thermal conductivity of hydrogen relative to argon (approximately a factor of ten). For example, Mermet and co-workers[35] recorded significant improvements in Mg ion-to-atom ratios by adding hydrogen (equivalent to 30 mg min^{-1} of water) to a plasma operating with a desolvating ultrasonic nebulizer. Fig. 2 demonstrates the typical chromatograms from quantitative extractions of $MeHg^{+}$ from SRM 2977 Mussel Tissue with and without the addition of humidified argon into the plasma. A dramatic increase in the analyte intensity for both mercury species can be seen with the introduction of the humidified argon.

Influence of injector temperature

The temperature of the GC injector is a critical factor because elevated temperatures lead to thermal decomposition of the derivatized mercury compounds while lower injection temperatures can lead to inefficient desorption of the analyte, causing sample carry-over. A temperature of 210 °C for 3 min assured sufficient desorption of the mercury species while minimizing any decomposition of the organomercury derivatives to yield elemental Hg^0. This falls within the operating temperature range of 200–280 °C for the 100 μm PDMS fibers. As previously reported,[30] the source of this elemental mercury peak was further verified to be thermal decomposition of the derivatized Hg species, as indicated by the fact that a linear relationship was observed between the intensity of Hg^0 from methyl-Hg, ethyl-Hg, and propyl-Hg as a function of increasing injector temperature.

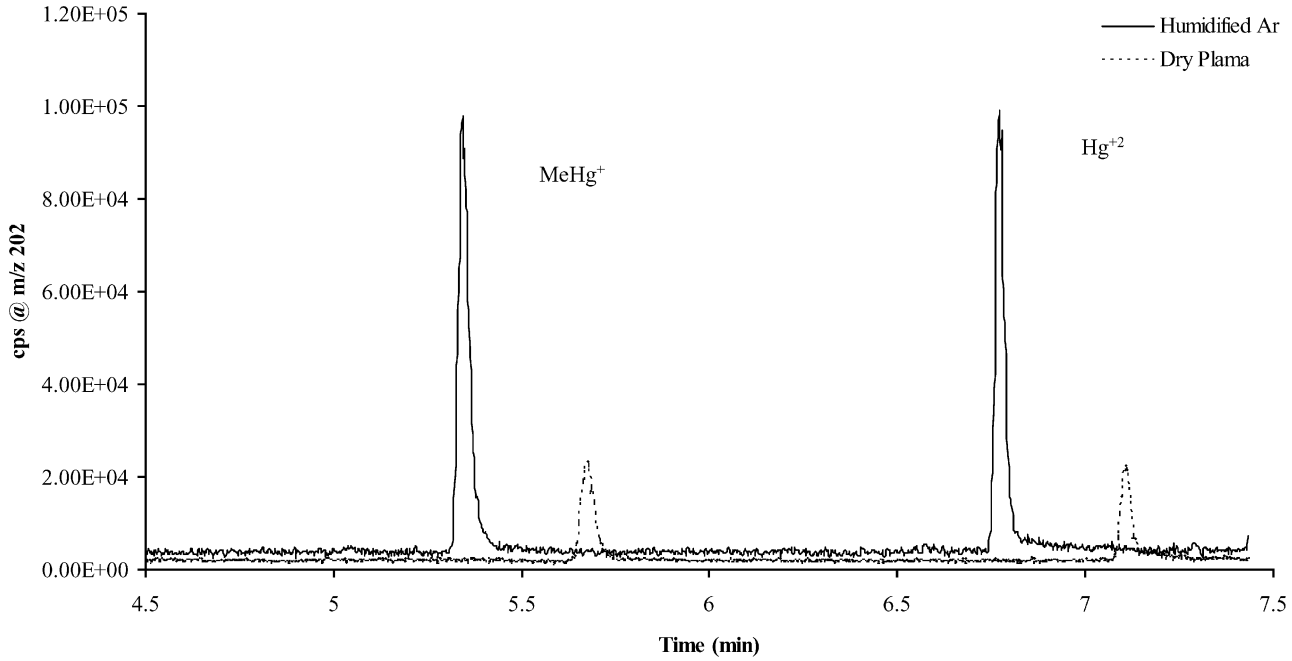

Fig. 2 Chromatogram of ethylated mercury species from unspiked SRM 2977 extract obtained by SPME-GC-ICP-MS for both the humidified argon and dry plasma modes of operation (traces shifted for clarity).

Application and validation of the acid-assisted microwave extraction method

Before the actual determination by the SPME-GC-ICP-MS method, the analytes need to be isolated from the matrix. A commonly used approach for removing organometallic species from different types of matrices is microwave-assisted acid extraction. Numerous examples of utilizing microwave fields for the extraction of organometallic species have been reported for a variety of samples.[10,11,17,19,21,37] Optimization of the extraction conditions is critical when employing this approach to achieve both complete extraction and to minimize decomposition of the analyte of interest. For this investigation, samples of $\approx$0.5 g of the aforementioned SRMs were extracted in 5 ml acetic acid. The power of the microwave field was optimized in the range from 0 W to 1000 W and extraction time of between 1 min and 15 min. Quantitative extractions were accomplished with 1000 W of microwave power for 10 min, which resulted in maximum temperatures ranging from $\approx$150 °C and $\approx$165 °C for the mussel and fish tissue extracts, respectively. While acetic and formic acids demonstrated quantitative extraction from the tissues, acetic acid was chosen because it had the lowest reagent Hg concentration ($<$1 ng g^{-1} from the certificate of analysis) of mercury impurity in the acetic acid as compared with $<$5 ng g^{-1} for the formic acid.

Both methylmercury and inorganic mercury were monitored and quantified during microwave method development in order to determine that species transformation was not occurring during extraction. At the described optimum microwave extraction conditions, the sum of the methyl and inorganic mercury species resulted in concentrations of total mercury certified in each reference material within the stated uncertainty, demonstrating no occurrence of species transformation. However, the inorganic mercury species is not certified for any of the reference materials and thus the inorganic fraction of mercury was not considered for this study.

Quantification and components of uncertainty

Both one-point and two-point standard additions provided similar results for standard solutions. Quantitative results for SRM 1566b with both one-point and two-point standard additions also gave similar results, including slope and intercept. All quantitative results presented in this paper are the result of single-point standard additions based on the peak areas resulting from the MeHg chromatographic traces. In all instances, the sample-to-sample variability ($n = 6$) was $<$6% RSD, with the values being typically 2% RSD. For a single measurement of SRM 1566b, this would translate into an uncertainty of $\approx$14% or 1.8 ng g^{-1} absolute.

The individual components of uncertainty for MeHg in each sample were determined according to ISO guidelines.[38] The major Type A uncertainty components include the standard deviation of the mean of the sample measurement (replication) and moisture correction of the freeze-dried SRMs, while Type B uncertainty contributions include weighing measurements on a balance possessing 0.001 g readability and the purity of the methylmercury chloride salt used as the working standard.

The Type A uncertainty contributions for each sample were first compiled in relative terms before conversion into absolute terms. RSDs ranged from between 2% and 5% ($n = 6$ measurements) for the SRMs and between 2% and 6% ($n = 3$ measurements) for the seabird eggs.

The Type B uncertainty contributions for each sample were also compiled in relative terms before conversion into absolute terms. The variability in the weighing measurements (0.2% RSD) was based on weighing approximately 0.5 g of sample into each microwave vessel, on a balance with a resolution of 0.001 g. The uncertainty due to the purity of the methylmercury chloride salt is derived from manufacturer's data reported purity of 98%, assuming a rectangular distribution.

Determination of methylmercury in biological SRMs

Three different biological SRMs with certified values for methylmercury were analyzed to demonstrate the accuracy of the SPME-GC-ICP-MS method. Samples of SRM 2977 Mussel Tissues (Organic Contaminants and Trace Elements),[39] SRM 1566b Oyster Tissue,[39] and SRM 1946 Lake Superior Fish Tissue[10] were analyzed. The certified concentrations of methylmercury in the SRMs range from SRM 1566b Oyster Tissue at (13.2 $\pm$ 0.7) ng g^{-1} to SRM 1946 Lake Superior Fish Tissue at (397 $\pm$ 15) ng g^{-1}. Fig. 3 show the chromatograms for the extraction of methylmercury from SRM 1566b. SRM

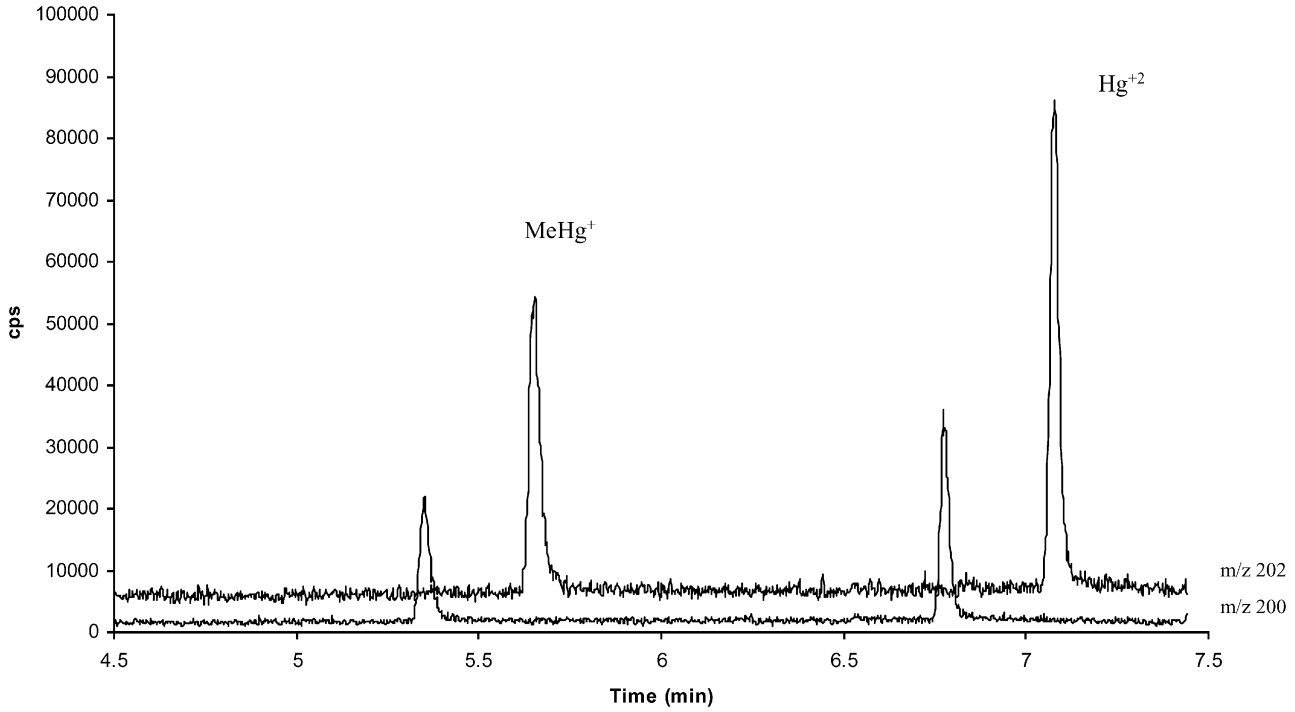

Fig. 3 Chromatogram of ethylated mercury species for unspiked SRM 1566b extract obtained by SPME-GC-ICP-MS (traces shifted for clarity).

1556b contains the lowest certified value for methylmercury (13.2 ng g^{-1}) and is easily detected by GC-ICP-MS. Both the ethyl and phenyl derivatives provided quantitative results, but the ethylation of methylmercury in both the fresh frozen SRM 1946 fish tissue and murre eggs was inefficient; therefore, the phenyl derivatives were analyzed. The results of the analyses of these SRMs were in good agreement with the certified values for methylmercury, as shown in Table 2.

The limit of detection (LOD) was calculated with the method of Long and Winefordner[40] in terms of concentration. Using the standard deviation of three blanks and the average slope ($n = 6$) from the single-addition spikes of SRM 1566b, the LOD of the SPME-GC-ICP-MS method for methylmercury is 4.2 pg g^{-1} (as Hg) from a 0.5 g tissue sample of SRM 1566b. The detection limits for methylmercury presented here compares favorably with other recent SPME-GC-ICP-MS work on the determination of methylmercury in biological tissues where Yang and co-workers reported a method detection limit of 2.1 ng g^{-1} of MeHg in 0.25 g of biological tissue with a PDMS fiber,[31] while Jitaru and co-workers reported a detection limit of 1.3 pg g^{-1} for MeHg based on standard solutions and a PDMS-DVB fiber.[41] This technique offers significant improvement in detection limits over the current GC-AED method ($\approx$1–2 ng g^{-1} based on a 0.5–1 g tissue sample analyzed) used in certification of MeHg at NIST.[10]

Table 2 Results for the determination of methylmercury in selected biological SRMs

	Concentration/ng g^{-1} (as Hg)	
SRM	MeHg (SPME-GC-ICP-MS)	Certified value MeHg
1566b Oyster tissue $n = 6$	12.9 ± 0.7[a]	13.2 ± 0.7[b]
2977 Mussel tissue $n = 6$	35.8 ± 1.8[a]	36.2 ± 1.7[b]
1946 Lake superior fish tissue (wet mass) $n = 6$	388 ± 12[a]	394 ± 15[b]

[a] The uncertainty associated with the measured value is expressed as the expanded uncertainty. [b] The results are expressed as the certified value ± the expanded uncertainty.

Determination of methylmercury in murre egg samples for the seabird tissue archival and monitoring project STAMP

The Seabird Tissue Archival and Monitoring Project (STAMP) is one of several projects providing specimens to the Marine Environmental Specimen Bank (Marine ESB) operated by NIST and located at the Hollings Marine Laboratory (Charleston, SC) and has been described in detail elsewhere.[42] Briefly, STAMP was implemented in 1999 as a long-term collaborative Alaska-wide effort by the US Fish and Wildlife Service's Alaska Maritime National Wildlife Refuge (USFWS/AMNWR), the U.S. Geological Survey's Biological Resources Division (USGS/BRD), and NIST to identify and monitor long-term trends in environmental quality by banking colonial seabird tissues (including eggs) and analyzing them for contaminants.

In this study, a subset of homogenized murre eggs, which were previously analyzed for total Hg (HgT) content[42] by isotope dilution (ID) ICP-MS, were analyzed for methylmercury. The subset consisted of three eggs with high (276.9 ng g^{-1} HgT), medium (109.1 ng g^{-1} HgT), and low (10.5 ng g^{-1} HgT) concentrations chosen from three colonies to determine if the measured HgT concentration could be used as a surrogate measurement for the methylmercury fraction of the samples. Past studies of the mercury content of the eggs of gulls, terns,

Table 3 Results for the determination of methylmercury in Alaskan seabird eggs

	Concentration/ng g^{-1} (as Hg)		
Sample information	MeHg (SPME-GC-ICPMS)	Total Hg (ID-ICP-MS)	MeHg (%)
Little Diomede island (*Uria* sp.) $n = 3$	9.1 ± 1.1[a]	10.1[b]	87.5
St. Lazaria island (*U. aalge*) $n = 3$	243 ± 9.1[a]	276.9[b]	87.8
Bogoslof island (*U. lomvia*) $n = 3$	92.1 ± 4.8[a]	109.1[c]	84.4

[a] The uncertainty associated with the measured value is expressed as the expanded uncertainty. [b] From ref. 42. [c] Unpublished data.

and loons showed that upwards of 75–90% of the total mercury was in the methyl form.[43,44] The results of the murre eggs (Table 3), which yielded 84% to 88% of the total mercury was present as the methylated form compare favorably to the previously reported values for other sea birds. In the future, a larger subset of samples will be analyzed in order to compute a reliable conversion factor for future long-term environmental monitoring studies, where high sample throughput requirements dictate the measurement of HgT for samples.

Conclusions

A sensitive and accurate method for methylmercury determination has been developed that provides very low detection limits (pg g^{-1} levels) required for reliable quantitative mercury speciation in biological tissues by SPME-GC-ICP-MS. The methods described here are complementary to those currently employed at NIST, which will allow for future certification efforts to be based on two independent analytical methods. The method has been applied to the determination of MeHg in murre eggs collected for STAMP, a collaborative seabird contaminants monitoring program. Method reproducibilities for six separate sample aliquots subjected to microwave extraction, derivatization, followed by solid-phase microextraction, GC-separation, and ICP-MS detection at the high and low ends of this range were 2% and 5% RSD, respectively.

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