ELSEVIER

Spectrochimica Acta Part B 56 (2001) 1133–1142

SPECTROCHIMICA ACTA PART B

www.elsevier.com/locate/sab

Determination of mercury compounds in fish by microwave-assisted extraction and liquid chromatography-vapor generation-inductively coupled plasma mass spectrometry ☆

Chwei-Sheng Chiou, Shiuh-Jen Jiang*, K. Suresh Kumar Danadurai

Department of Chemistry, National Sun Yat-Sen University, Kaohsiung 80424, Taiwan

Received 28 July 2000; accepted 14 January 2001

Abstract

A method employing a vapor generation system and LC combined with inductively coupled plasma mass spectrometry (LC-ICP-MS) is presented for the determination of mercury in biological tissues. An open vessel microwave digestion system was used to extract the mercury compounds from the sample matrix. The efficiency of the mobile phase, a mixture of L-cysteine and 2-mercaptoethanol, was evaluated for LC separation of inorganic mercury [Hg(II)], methylmercury (methyl-Hg) and ethylmercury (ethyl-Hg). The sensitivity, detection limits and repeatability of the liquid chromatography (LC) ICP-MS system with a vapor generator were comparable to, or better than, that of an LC-ICP-MS system with conventional pneumatic nebulization, or other sample introduction techniques. The experimental detection limits for various mercury species were in the range of 0.05–0.09 ng ml^{-1} Hg, based on peak height. The proposed method was successfully applied to the determination of mercury compounds in a swordfish sample purchased from the local market. The accuracy of the method was evaluated by analyzing a marine biological certified reference material (DORM-2, NRCC).

Keywords: Inductively coupled plasma mass spectrometry; Liquid chromatography; Mercury speciation; Vapor generation; Fish samples; Microwave-assisted extraction

☆ This paper is published in the Special Issue of *Spectrochimica Acta Part B* dedicated to the late Professor Velmer A. Fassel.

* Corresponding author. Fax: +886-7-5253908.
E-mail address: sjjiang@mail.nsysu.edu.tw (S. Jiang).

0584-8547/01/$ - see front matter
PII: S0584-8547(01)00180-X

1. Introduction

Since the introduction in 1980 [1], inductively coupled plasma mass spectrometry (ICP-MS) has become a widely used analytical technique. The major applications of ICP-MS have involved elemental analysis. The analytical capabilities of ICP-MS for elemental analysis, particularly the excellent detection limits, make it attractive as an element-selective detector for chromatography. Combining a chromatographic separation with ICP-MS could provide a technique capable of distinguishing between different chemical forms of elements, i.e. 'chemical speciation.' Furthermore, the chromatographic removal of interfering matrix elements would extend the range of application of ICP-MS and simplify or hasten procedures for sample preparation.

Mercury is of considerable interest, as it is widely used in industry in the production of: chemicals; pesticides; electrical apparatus; paints; amalgam tooth fillings, etc. and, therefore, it is found throughout the ecosystem in trace amounts in air, water, soil, and living organisms. The most toxic species of mercury found in environmental and biological samples is of particular concern as it passes through the food chain. It is well known that the toxicity of Hg is highly dependent on its chemical form. Several studies [2,3] indicated that organic mercury can disrupt the blood brain barrier, and can easily cross the placenta and affect the fetus. A rapid and sensitive technique for the determination of mercury species is therefore necessary.

Several methods of liquid chromatography (LC) and gas chromatography (GC) coupled with element-specific detection for mercury speciation have appeared including: electrochemical detection (EC) [4]; cold vapor atomic absorption spectrometry (CVAAS) [5–8]; atomic emission spectrometry (AES) [9–11]; atomic fluorescence spectrometry (AFS) [12]; and inductively coupled plasma mass spectrometry (ICP-MS) [13–18]. The vapor generation (CV) sample introduction technique has been applied in several LC-atomic spectroscopy applications for mercury speciation [5–8,12,13]. The vapor generation technique increases the signal of mercury significantly. In the present work, a simple in situ nebulizer/vapor generator system was employed as a sample introduction device of LC-ICP-MS for mercury speciation determination [19–22].

The ionic compounds containing mercury were separated by reversed-phase liquid chromatography with 0.05% m/v L-cysteine [6,23] and 0.05% v/v 2-mercaptoethanol [7,13,24] as the ion pairing reagent and the mobile phase. The various mercury species studied include inorganic mercury [Hg(II)], methylmercury (methyl-Hg), and ethylmercury (ethyl-Hg). Effluent from the LC column was delivered to the vapor generation system and ICP-MS for mercury determination. The optimization of the vapor generation LC-ICP-MS technique and its analytical figures of merit, as well as its application to the determination of mercury compounds in NRCC DORM-2 dogfish muscle reference material and a swordfish sample purchased from the local market, are described in this paper.

Microwave-assisted digestion has gained wide acceptance as a rapid method for sample decomposition in inorganic analysis. Recently, it has also been verified as an appropriate tool for rapid preparation of solid samples for organometallic speciation analysis [25–28]. A simple and rapid microwave-
assisted extraction method was used for the extraction of mercury compounds in fish samples. The analyte species were quantitatively leached with L-cysteine and 2-mercaptoethanol, the same compounds as the LC mobile phase, in a focused microwave field during a period of 2 min.

2. Experimental

2.1. ICP-MS device and conditions

An ELAN 5000 ICP-MS instrument (Perkin–Elmer SCIEX, Thornhill, ON, Canada) was used. Samples were introduced with an in-situ nebulizer/vapor generation sample introduction system. ICP conditions were selected that maximized the mercury ion signal while a solution containing 5 ng ml^{-1} of Hg(II) in the mobile phase (to be used for subsequent chromato-

graphic separations) was continuously introduced into the vapor generation system. The vapor generated was then transported to the ICP-MS for mercury determination. Sensitivity of the instrument can vary slightly from day to day. The operating conditions of ICP-MS and data acquisition parameters are listed in Table 1. The chromatograms were recorded in real time and stored on the hard disk with the 'graphic' software. The dwell time, sweeps per reading, and points per spectral peak parameters were set so that each data point could be obtained in less than 1 s.

Table 1
ICP-MS equipment and operating conditions

ICP-MS instrument	Perkin–Elmer SCIEX ELAN 5000
Plasma conditions	
rf power	1100 W
Plasma gas flow	15 l min^{-1}
Intermediate gas flow	0.7 l min^{-1}
Aerosol gas flow	1.0 l min^{-1}
Mass spectrometer settings	
Resolution	Normal
Dwell time	100 ms
Sweeps/reading	5
Points/spectral peak	1
Readings/replicate	400
Isotope monitored	^{202}Hg

2.2. Chromatographic apparatus and conditions

A Hitachi Model L-7100 LC pump, injector (Rheodyne 7225i) and reversed-phase column (Alltech Macrosphere C8, 5-μm diameter particles, 2.1-mm i.d. × 250-mm length) comprised the LC system. Samples were loaded with a syringe into a 100-μl sample loop. All separations were performed at room temperature under isocratic conditions. Separations were attempted with several combinations of: column, organic modifier concentration; L-cysteine concentration; 2-mercaptoethanol concentration; and pH. The optimal experimental conditions are given in Table 2. The column outlet was connected to the vapor generation device with Teflon tubing (Fig. 1).

2.3. Vapor generation system and conditions

In this study, a simple in-situ nebulizer/vapor generation sample introduction system was coupled with LC-ICP-MS for the mercury speciation determination [19–22]. The vapor generator system has been described in detail elsewhere [22]. With this sample introduction system, the injected sample was nebulized. The nebulization process, in which the liquid is shattered into fine droplets in an Ar stream, is a very effective way to purge Hg vapor from the liquid. Vapor generated from the vapor generation system was delivered to the ICP-MS for mercury determination.

Table 2
Liquid chromatography and vapor generation conditions

LC conditions	
Pump	Hitachi, Model L-7100
Column	Alltech Macrosphere C8, 5-μm diam., 2.1-mm i.d. × 250-mm length
Mobile phase	0.05% v/v 2-mercaptoethanol and 0.05% m/v L-cysteine (pH 6.6)
Mobile phase flow rate	0.6 ml min^{-1}
Sample loop	100 μl
VG conditions	
$NaBH_4$	0.02% m/v in 0.01 mol l^{-1} NaOH
$NaBH_4$ solution flow rate	0.6 ml min^{-1}
Auxiliary solution	0.05% v/v HNO_3 and 0.5% m/v L-cysteine
Auxiliary solution flow rate	0.6 ml min^{-1}

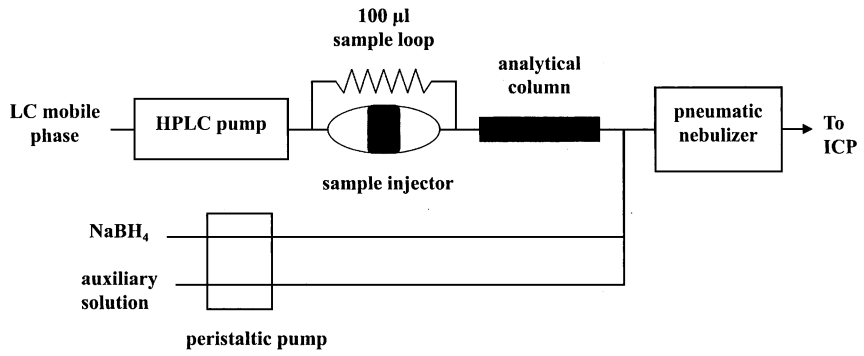

Fig. 1. Schematic diagram of LC-CV system.

The operating conditions for vapor generation were optimized using a flow injection method. The LC pump and column were removed from the system during these studies. A simple FI system was used for all the FI work. It was assembled from a six-port injection valve (Rheodyne Type 50) with a 200-µl sample loop. Stock solutions of various mercury species at 5 ng ml^{-1} of Hg(II), methyl-Hg and ethyl-Hg in the LC mobile phase, were prepared. These stock solutions were then loaded into the injection loop and injected into the vapor generation system. Several operation parameters affected the efficiency of vapor formation. The concentration of $NaBH_4$, HNO_3 and L-cysteine in the auxiliary solution and the volume of mixing coil were studied to get the optimized conditions.

2.4. Reagents

Analytical-reagent grade chemicals were used without further purification. Sodium tetrahydroborate and L-cysteine were obtained from Merck (Darmstadt, Germany). 2-mercaptoethanol was obtained from TCI Chemical (Tokyo, Japan). Methanol and trace metal grade HNO_3 were obtained from Fisher (Fair Lawn, NJ, USA). Mercury nitrate and methylmercury chloride were obtained from Merck. Ethylmercury chloride was obtained from TCI Chemical. Standards containing 200 mg l^{-1} (as element) of each individual species in 2% v/v H_2SO_4 were prepared. These standards were combined and diluted in the LC mobile phase and analyzed by CV – ICP-MS. A suitable amount of L-cysteine and 2-mercaptoethanol were dissolved in pure water to serve as a mobile phase.

2.5. Sample preparation

Mercury compounds were extracted using a Star System 2 microwave digester (CEM, Matthews, USA). A 250-ml standard round-bottom open vessel made of Teflon (CEM) was used. Three weighed 0.025-g portions of DORM-2 dogfish muscle (National Research Council of Canada, Ottawa, Canada) and another three 0.25-g portions of swordfish samples were transferred into Teflon digestion vessels. Extracting solution (25 ml) was added to the sample. The extracting solution contained 0.05% m/v L-cysteine and 0.05% v/v 2-mercaptoethanol. Then, the samples were placed in the microwave digester and exposed to microwave at 60°C for 2 min. The ramp time was set at 1 min. After the samples were cooled to room temperature, the samples were centrifuged for 5 min. Then the clear solution was collected for the subsequent chromatographic separation. For analysis, an aliquot of this extract (100 µl) was injected into the LC-CV-ICP-MS system.

3. Results and discussion

3.1. Selection of LC operating conditions

In order to reduce the amounts of the reagents used for separation, a microbore column (Alltech

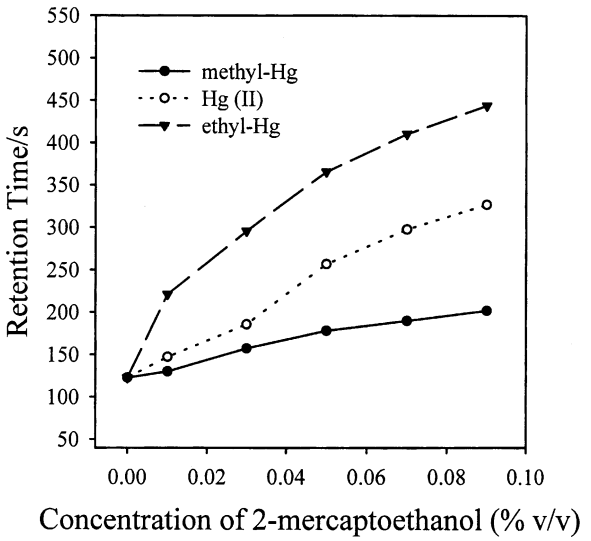

Fig. 2. Effect of 2-mercaptoethanol concentration on LC chromatogram. The concentration of L-cysteine was 0.05% m/v. The mobile phase flow rate was 0.6 ml min^{-1}. Each mercury species present at 50 ng ml^{-1}.

Macrosphere C8 column, 2.1 mm i.d.) was used in this study. Two common reagents, L-cysteine [6,23] and 2-mercaptoethanol [7,13,24], were used as the complexing agents for Hg speciation carried out by reversed phase LC column. However, the mercury species studied could still not be completely separated when the L-cysteine was used alone with the Alltech Macrosphere C8 column. Meanwhile, the retention time was too long when 2-mercaptoethanol was used individually. We found that a mixture of L-cysteine and 2-mercaptoethanol used as the mobile phase gave the best separation in this study, and so the effect of these reagents was investigated in more detail. Fig. 2 illustrates the effect of 2-mercaptoethanol concentration in the mobile phase solution on the LC chromatogram. Each mercury species was present at 50 ng ml^{-1}. As shown in Fig. 2, the retention times of each mercury species increased with an increase of the 2-mercaptoethanol concentration in the mobile phase. For the better LC chromatogram and less separation time in the following experiments, a 2-mercaptoethanol concentration of 0.05% v/v was adopted.

The effect of the concentration of L-cysteine in the mobile phase on the LC chromatogram is shown in Fig. 3. As can be seen, the retention times of each mercury species decreased significantly with an increase of the L-cysteine concentration in the mobile phase. It could be due to the higher hydrophilic character of Hg(L-cysteine)$_2$ complex. For the best LC resolution, a solution containing 0.05% m/v L-cysteine was added in the mobile phase solution in the following experiments.

The effect of the concentration of methanol in the mobile phase on the LC separation was also studied in this work. From our experiment result, we found that the retention times of each mercury species decreased with an increase of the methanol concentration in the mobile phase. For the best LC resolution and to avoid the problems caused by organic solvents [29], no methanol was added in the mobile phase solution in the following experiments. In other experiments, we found that the pH of the mobile phase did not affect the retention times of the mercury species significantly in the range studied (pH 6–7).

In summary, in the following experiments a solution of 0.05% m/v L-cysteine and 0.05% v/v

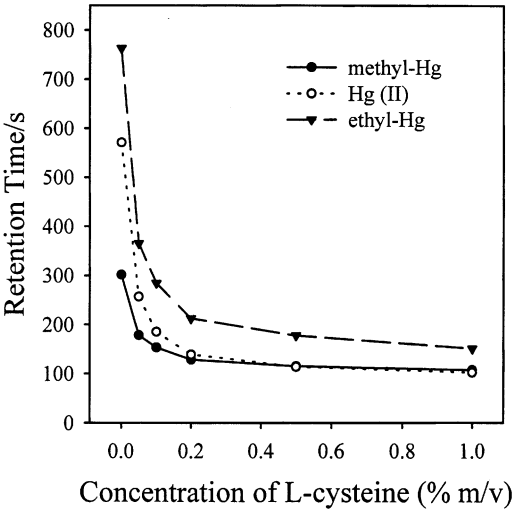

Fig. 3. Effect of L-cysteine concentration in the mobile phase on LC chromatogram. The concentration of 2-mercaptoethanol was 0.05% v/v.

2-mercaptoethanol (pH 6.6), at a flow rate of 0.6 ml min^{-1}, was used as the mobile phase of the LC separation to get the best LC separation. It should be mentioned that the sample was introduced by conventional pneumatic nebulization during these experiments. No vapor generation was used.

3.2. Selection of vapor generation conditions

Since Hg(II), methyl-Hg and ethyl-Hg show different behavior and different sensitivities in the vapor generation process [6,7,22,24], the different mercury species were studied successively to get the compromise operating conditions of the vapor generation system. The concentration of $NaBH_4$, HNO_3 and L-cysteine in the auxiliary solution, and the volume of mixing coil, were studied to get the optimized conditions. The optimized vapor generating conditions are presented in Table 2. The optimized conditions were slightly different from a previous study [22], perhaps due to the 2-mercaptoethanol used in the current study.

3.3. Mercury speciation

A typical chromatogram (ICP-MS detection) for a solution containing 5 ng ml^{-1} of Hg(II), methyl-Hg and ethyl-Hg is shown in Fig. 4. As shown, all three species studied were fully resolved and the separation was complete in less than 6 min. Peak area measurements indicated that the response for mercury was slightly different for these three mercury species. This may be attributed to variation of vapor generation efficiency of the various mercury species mentioned earlier. A similar trend was observed when the analyte was determined in the FI mode. Repeatability was determined using seven injections of a test mixture containing 5 ng ml^{-1} of Hg(II), methyl-Hg and ethyl-Hg. As shown in Table 3, the relative standard deviation of the peak heights was less than 2% for all the species, which is similar to the precision obtained in previous ICP-MS experiments with LC separations using other sample introduction devices [14,20,29–32]. Calibration curves based on peak heights were linear for each mercury compound in the range tested. The detection limits were estimated from these calibration curves and based on the amount (or concentration) necessary to yield a net signal equal to three times the standard deviation of the background. The absolute detection limits were 5–9 pg which corresponds to relative values of 0.05–0.09 ng ml^{-1} (see Table 4). The detection limits achieved by this method are comparable to or better than previously reported results with similar techniques [13,14,16,18,22]. The background of mercury was increased when vapor generation sample introduction was used. This could be due to the trace mercury contaminant in the reagents used for mobile phase, and due to the better analyte transport efficiency with vapor generation sample introduction, or the memory of mercury from the vapor generation system. The use of purer reagent should reduce the detection limit to a lower value.

Table 3
Repeatability of retention time and peak height of the LC elution peaks[a]

Compound	Retention time ± S.D.[b] (s)	Repeatability of peak height (%)[c]
Hg(II)	262 ± 2	1.8
Methyl-Hg	179 ± 1	0.7
Ethyl-Hg	371 ± 2	1.7

[a] $n = 7$.
[b] S.D. = standard deviation.
[c] Relative S.D.

Table 4
Calibration parameters (0.2–20 ng ml^{-1}) of various mercury species

Compound	Sensitivity (counts s^{-1} ng^{-1} ml)	Correlation coefficient	Detection limit (ng ml^{-1})
Hg(II)	1300	0.9997	0.06
Methyl-Hg	1530	0.9997	0.05
Ethyl-Hg	780	0.9997	0.09

3.4. Determination of mercury in fish samples

In order to validate the LC-CV-ICP-MS method, mercury compounds were determined in

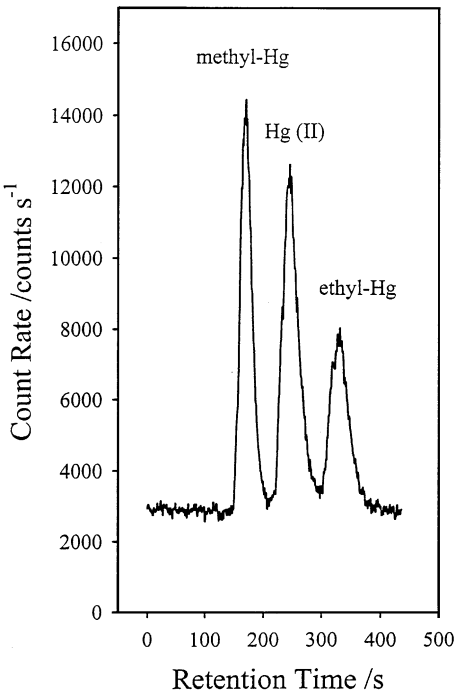

Fig. 4. Typical Hg-selective chromatogram for Hg(II), methyl-Hg and ethyl-Hg. Various mercury species are present at 5 ng ml^{-1} (as element) each. LC and CV conditions see Table 2.

the DORM-2 dogfish muscle reference sample and a swordfish sample purchased from the local market. The sample was prepared by microwave-assisted extraction of the L-cysteine and/or 2-mercaptoethanol complexes. The extracting solution contained 0.05% m/v L-cysteine and 0.05% v/v 2-mercaptoethanol, which was selected to serve as the mobile phase in the current study. From our experiment result, we found that a mixture of L-cysteine and 2-mercaptoethanol was an effective extracting reagent for mercury compounds from the fish sample. It could be due to the formation of stable complexes between mercury compounds and L-cysteine and/or 2-mercaptoethanol. The effects of microwave digester temperature and exposure time were studied in the range of 50–80°C and 1–5 min. After many trials, for the best extraction efficiency and recovery of mercury species in this study, the temperature of the microwave digester was set at 60°C for 2 min. A 100-μl injection of the final extract was analyzed for mercury using the LC vapor generation system. Peak areas of each chromatographic peak were used for quantitation work.

A typical mercury chromatogram of the DORM-2 dogfish sample is shown in Fig. 5a. As can be seen, methyl-Hg and Hg(II) were present in this sample. The concentrations of mercury compounds in the extract were determined by an external calibration method. The results are shown in Table 5. The concentrations of methyl-Hg and Hg(II) in the injected solution are approximately 4.3 and 0.3 ng ml^{-1}, respectively, which

Table 5
Concentrations of mercury in fish samples as measured by LC-CV-ICP-MS[a]

Sample and compound	Concentration found ($\mu g\ g^{-1}$)	Reference value ($\mu g\ g^{-1}$)	Total mercury concentration ($\mu g\ g^{-1}$)
DORM-2			4.64 ± 0.26[b]
Hg(II)	0.22 ± 0.04		
Methyl-Hg	4.39 ± 0.24	4.47 ± 0.32[b]	
Ethyl-Hg	ND[c]		
Swordfish			0.503 ± 0.014[d]
Hg(II)	0.089 ± 0.025		
Methyl-Hg	0.412 ± 0.018		
Ethyl-Hg	ND		

[a] Values are means ± S.D. of three determinations ($n = 3$).
[b] NRCC reference value.
[c] ND = not detectable.
[d] Determined by ICP-MS after digested by microwave digestion system.

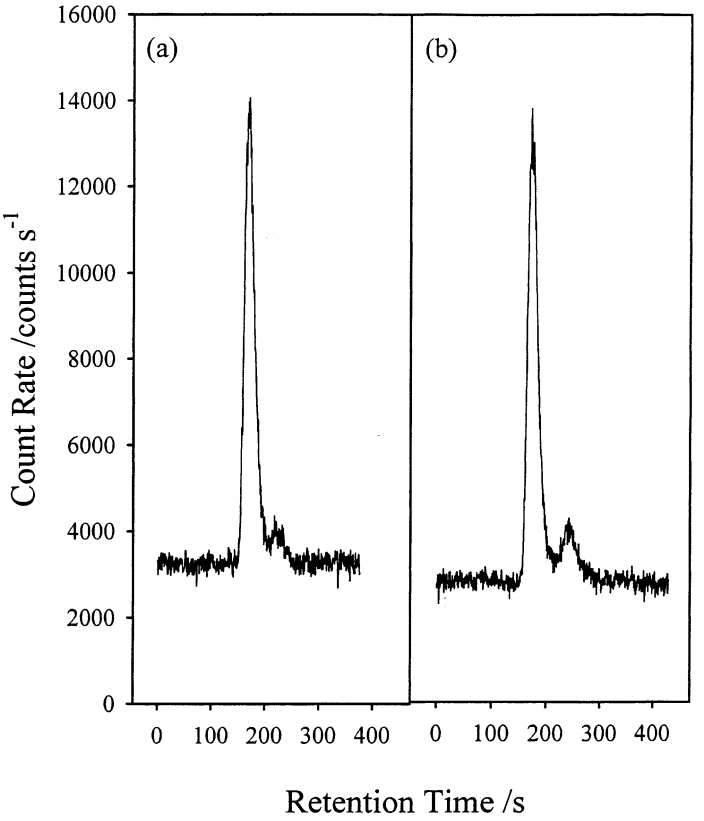

Fig. 5. (a) Typical Hg-selective chromatogram of dogfish muscle reference sample DORM-2. The concentrations of Hg(II) and methyl-Hg in the injected solution are 0.3 and 4.3 ng ml^{-1}, respectively. (b) Hg-selective chromatogram of swordfish sample. The concentrations of Hg(II) and methyl-Hg in the injected solution are 0.8 and 4.2 ng ml^{-1}, respectively.

corresponds to 4.39 ± 0.24 $\mu g\ g^{-1}$ and 0.22 ± 0.04 $\mu g\ g^{-1}$ in the original sample. As shown, the determined methylmercury concentration agreed favorably with the certified value. Compared to the certified value, the error was less than 2%, and the precision between sample replicates was better than 18% for the determinations. The recoveries of methylmercury were $98.2 \pm 5.5\%$ with this extraction method.

Under this extracting condition, there was no detectable decomposition of methylmercury to inorganic mercury. This experiment was carried out by spiking the fish sample with a suitable amount of mercury mixture. The Hg species were extracted and then determined by LC-CV-ICP-MS. The variations of recoveries of methylmercury and inorganic mercury were within the standard deviations for each of these species. Compared to the extraction method used in our previous work [14], the current method has the advantages of: using fewer reagents; reducing reagent blank; saving experiment time and labor work; and better recovery.

A swordfish sample was purchased from the local market and analyzed by LC-CV-ICP-MS. A typical chromatogram of the fish sample is shown in Fig. 5b. As shown, methyl-Hg and Hg(II) were present in this sample. The concentrations of methyl-Hg and Hg(II) in the final extract were approximately 4.2 ng ml^{-1} and 0.8 ng ml^{-1}, respectively, which corresponds to 0.412 ± 0.018 $\mu g\ g^{-1}$ and 0.089 ± 0.025 $\mu g\ g^{-1}$ in the original sample as listed in Table 5. These results agreed with the total mercury concentration of 0.503 ± 0.014 $\mu g\ g^{-1}$ as listed in Table 5. For the determination of total mercury in swordfish sample,

the sample was digested completely by a microwave digestion system (CEM MDS 2000) [33].

4. Conclusion

This work has demonstrated the ability to determine mercury species with vapor generation technique in combination with LC and ICP-MS. In this study, a simple and rapid microwave-assisted extraction method was developed for the extraction of mercury compounds in fish samples. With this extracting method, the reagents, experiment time and labor work used were reduced; and the recoveries of various mercury compounds were improved compared to the extracting method used in our previous work [14]. Detection limits of various mercury species obtained with this system are low enough for the mercury speciation of many real samples without complicated sample pre-treatment. The use of purer reagents should reduce the detection limit to an even lower value.

Acknowledgements

This research was supported by a grant from the National Science Council of the Republic of China under Contract No. NSC 89-2113-M-110-018.

References

[1] R.S. Houk, V.A. Fassel, G.D. Flesch, H.J. Svec, A.L. Gray, C.E. Taylor, Inductively coupled argon plasma as an ion source for mass spectrometric determination of trace elements, Anal. Chem. 52 (1980) 2283.

[2] M. Silva da Rocha, A.B. Soldando, E. Blanco-Gonzaelz, A. Sanz-Medel, Speciation of mercury compounds by capillary electrophoresis coupled on-line with quadrupole and double-focusing inductively coupled plasma mass spectrometry, J. Anal. At. Spectrom. 15 (2000) 513.

[3] O.F.X. Donard, J.A. Caruso, Trace metal and metalloid species determination: evolution and trends, Spectrochim. Acta Part B 53 (1998) 157.

[4] O. Evans, G.D. McKee, Determination of mercury (II) and organomercury compounds by reversed-phase liquid chromatography with reductive electrochemical detection, Analyst 113 (1988) 243.

[5] S. Riosegade, C. Bendicho, Online high performance liquid chromatographic separation and vapor atomic absorption spectrometric determination of methylmercury and inorganic mercury, Talanta 48 (1999) 477.

[6] M. Fujita, E. Takabatake, Continuous flow reducing vessel in determination of mercuric compounds by liquid chromatography/vapor atomic absorption spectrometry, Anal. Chem. 55 (1983) 454.

[7] B. Aizpun, M.L. Fernandez, E. Blanco, A. Sanz-Medel, Speciation of inorganic mercury(II) and methylmercury by vesicle-mediated high performance liquid chromatography coupled to vapor atomic absorption spectrometry, J. Anal. At. Spectrom. 9 (1994) 1279.

[8] C. Schickling, J.A.C. Broekaert, Determination of mercury species in gas-condensates by online coupled high performance liquid chromatography and cold-vapor atomic absorption spectrometry, Appl. Organomet. Chem. 9 (1995) 29.

[9] J.P. Snell, W. Frech, Y. Thomassen, Performance improvements in the determination of mercury species in natural-gas condensate using an online amalgamation trap or solid phase micro-extraction with capillary gas chromatography microwave induced plasma atomic emission spectrometry, Analyst 121 (1996) 1055.

[10] N.G. Orellanavelado, A. Sanz-Medel, R. Pereiro, Glow-discharge atomic emission spectrometry as a detector in chromatography for mercury speciation, J. Anal. At. Spectrom. 13 (1998) 905.

[11] N.G. Orellanavelado, A. Sanz-Medel, R. Pereiro, Mercury speciation by capillary gas chromatography with radio frequency hollow-cathode glow discharge atomic emission detection, J. Anal. At. Spectrom. 15 (1999) 49.

[12] L. Liang, M. Horvat, E. Cernichiari, B. Gelein, S. Balogh, Simple solvent extraction technique for elimination of matrix interferences in the determination of methylmercury in environmental and biological samples by ethylation gas chromatography vapor atomic fluorescence spectrometry, Talanta 43 (1996) 1883.

[13] D.S. Bushee, Speciation of mercury using liquid chromatography with detection by inductively coupled plasma mass spectrometry, Analyst 113 (1988) 1167.

[14] C.-W. Huang, S.-J. Jiang, Speciation of mercury by reversed-phase liquid chromatography with inductively coupled plasma mass spectrometric detection, J. Anal. At. Spectrom. 8 (1993) 681.

[15] H. Tao, T. Murakami, M. Tominaga, A. Miyazaki, Mercury speciation in natural-gas condensate by gas chromatography inductively coupled plasma mass spectrometry, J. Anal. At. Spectrom. 13 (1998) 1085.

[16] S.C.K. Shum, H.-M. Pang, R.S. Houk, Speciation of mercury and lead compounds by microbore column liquid chromatography inductively coupled plasma mass spectrometry with direct injection nebulization, Anal. Chem. 64 (1992) 2444.

[17] S. Slaets, F. Adams, I.R. Pereiro, R. Lobinski, Optimization of the coupling of multicapilllary GC with ICP-MS for mercury speciation analysis in biological materials, J. Anal. At. Spectrom. 14 (1999) 851.

[18] M.J. Bloxham, A. Gachanja, S.J. Hill, P.J. Worsfold, Determination of mercury species in seawater by liquid chromatography with inductively coupled plasma mass spectrometric detection, J. Anal. At. Spectrom. 11 (1996) 145.
[19] J.D. Hwang, H.P. Huxley, J.P. Diomiguardi, W.J. Vaughn, The determination of arsenic in environmental-samples by inductively coupled plasma-atomic emission spectrometry with an in situ nebulizer hydride generator, Appl. Spectrosc. 44 (1990) 491.
[20] C.-J. Hwang, S.-J. Jiang, Determination of arsenic compounds in water samples by liquid chromatography-inductively coupled plasma mass spectrometry with an in situ nebulizer-hydride generator, Anal. Chim. Acta 289 (1994) 205.
[21] M.-F. Huang, S.-J. Jiang, C.-J. Hwang, Determination of arsenic in environmental and biological samples by flow injection inductively coupled plasma mass spectrometry, J. Anal. At. Spectrom. 10 (1995) 31.
[22] C.-C. Wan, C.-S. Chen, S.-J. Jiang, Determination of mercury compounds in water samples by liquid chromatography inductively coupled plasma mass spectrometry with an in situ nebulizer/vapor generator, J. Anal. At. Spectrom. 12 (1997) 683.
[23] E. Munaf, H. Haraguchi, D. Ishii, T. Takeuchi, M. Goto, Speciation of mercury compounds in waste water by microcolumn liquid chromatography using a preconcentration column with cold-vapour atomic absorption spectrometric detection, Anal. Chim. Acta 235 (1990) 399.
[24] J.M. Costa-Fernandez, F. Lunzer, R. Pereiro-Garcia, A. Sanz-Medel, N. Bordel-Garcia, Direct coupling of high performance liquid chromatography to microwave-induced plasma-atomic emission spectrometry via volatile-species generation and its application to mercury and arsenic speciation, J. Anal. At. Spectrom. 10 (1995) 1019.
[25] O.F.X. Donard, B. Lalere, F. Martin, R. Lobinski, Microwave-assisted leaching of organotin compounds from sediments for speciation analysis, Anal. Chem. 67 (1995) 4250.
[26] M.J. Vazquez, A.M. Carro, R.A. Lorenzo, R. Cela, Optimization of methylmercury microwave-assisted extraction from aquatic sediments, Anal. Chem. 69 (1997) 221.
[27] C.M. Tseng, A. De Diego, F.M. Martin, O.F.X. Donard, Rapid and quantitative microwave-assisted recovery of methylmercury from standard reference sediments, J. Anal. At. Spectrom. 12 (1997) 629.
[28] C.M. Tseng, A. De Diego, F.M. Martin, D. Amouroux, O.F.X. Donard, Rapid determination of inorganic mercury and methylmercury in biological reference materials by hydride generation, cryofocusing, atomic absorption spectrometry after open focused microwave-assisted alkaline digestion, J. Anal. At. Spectrom. 12 (1997) 743.
[29] E.H. Evans, L. Ebdon, Effect of organic solvents and molecular gases on polyatomic ion interferences in inductively coupled plasma mass spectrometry, J. Anal. At. Spectrom. 5 (1990) 425.
[30] S.-J. Jiang, R.S. Houk, Inductively coupled plasma mass spectrometric detection for phosphorus and sulfur-compounds separated by liquid chromatography, Spectrochim. Acta Part B 43 (1988) 405.
[31] H.-J. Yang, S.-J. Jiang, Y.-J. Yang, C.-J. Hwang, Speciation of tin by reversed phase liquid chromatography with inductively coupled plasma mass spectrometric detection, Anal. Chim. Acta 312 (1995) 141.
[32] H.-J. Yang, S.-J. Jiang, Hydride generation inductively coupled plasma mass spectrometric detection of lead compounds separated by liquid chromatography, J. Anal. At. Spectrom. 10 (1995) 963.
[33] T.-J. Hwang, S.-J. Jiang, Determination of Cu, Cd and Pb in biological samples by isotope dilution inductively coupled plasma mass spectrometry after on-line pretreatment by anodic stripping voltammetry, J. Anal. At. Spectrom. 11 (1996) 353.