Speciation of Mercury by Reversed-phase Liquid Chromatography With Inductively Coupled Plasma Mass Spectrometric Detection

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An inductively coupled plasma mass spectrometer coupled with ultrasonic nebulization was used as a detector for the liquid chromatographic determination of mercury compounds. The detection limits were in the range 70–160 pg of Hg. The method was applied to the determination of methylmercury in a National Research Council of Canada Reference Material DORM-1 Dogfish Muscle, of thimerosal in contact lens solutions and of inorganic mercury in waste water reference solution. Good agreement was observed between the literature or expected values and the experimentally determined values. The precision was better than 8% for all determinations.

Keywords: *Mercury speciation; reversed-phase liquid chromatography; ultrasonic nebulization; inductively coupled plasma mass spectrometric detection*

The environmental and toxicological effects of a metal often depend on the form or species of the metal in the original sample.[1] The determination of the total metal content by most spectrometric detectors does not provide this often vital information. However, interfacing chromatography with metal-specific detectors can provide discrimination of the various species.

Mercury is used in a variety of products and industrial processes. The determination and monitoring of mercury in environmental samples are extremely important because of the high toxicity of mercury and its derivatives.

Gas chromatography (GC) and liquid chromatography (LC) have been interfaced with element-specific detection methods such as inductively coupled plasma atomic emission spectrometry (ICP-AES), d.c. plasma atomic emission spectrometry (DCP-AES) and atomic absorption spectrometry (AAS)[2–10] for metal speciation studies. The most commonly employed method for the determination of low concentrations of mercury in environmental samples is cold vapour AAS (CVAAS).[11–15]

Inductively coupled plasma mass spectrometry (ICP-MS) is a trace metal detection method with unique analytical capabilities,[10,16–18] offering both exceptional sensitivity and multi-element capability compared with flame AAS and ICP-AES.

Although some speciation applications can be addressed by chromatographic separations with ICP-MS detection in its present state,[16–19] there is still substantial room for improvement. Most LC–ICP-MS studies have employed conventional nebulizers, which introduce only 1–3% of the sample into the plasma and have large dead volumes, which can cause band broadening. In fact, the nebulizer is generally recognized to be one of the weakest components of the entire ICP-MS apparatus. The ultrasonic nebulizer has been satisfactorily coupled with LC–ICP-MS. Thompson and Houk[19] employed an ultrasonic nebulizer as the sample introduction device for the metal speciation of compounds containing As, Se and Cr with ICP-MS detection.

Results obtained for the determintion of mercury species by LC–ICP-MS with ultrasonic nebulization sample introduction are presented in this paper. The method was applied to the determination of mercury species in several reference samples. A brief comparison of this method with other sample introduction devices for LC is also given.

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Experimental

ICP-MS Device and Conditions

An Elan 5000 ICP-MS system (Perkin-Elmer SCIEX, Thornhill, Ontario, Canada) with a Model U-5000 ultrasonic nebulizer (Cetac, Omaha, NE, USA) was used. These components are described in Table 1. Under these conditions, one data point could be obtained every 1 s. The ICP conditions were selected to maximize the signal-to-background for mercury with a solution of 40 ppb of Hg in the mobile phase to be continuously aspirated and used for the subsequent chromatographic separations. The operating conditions for the ultrasonic nebulizer were optimized by flow injection (FI) techniques. A simple FI system was used for all of the FI performed in this work. It was assembled from a six-port injection valve (Rheodyne Type 50) with a 200 μl sample loop. A stock solution of mercury at 40 ppb in the mobile phase was prepared and then loaded in the injection loop and nebulized. The pump and transfer line to the nebulizer were flushed with LC mobile-phase solution after each injection. Baseline signals were determined using about 20 points prior to the injection of the sample

Table 1 LC–ultrasonic nebulization-ICP-MS operating conditions

Plasma conditions	
R.f. power/W	1200
Plasma gas flow rate/l min^{-1}	14
Intermediate gas flow rate/l min^{-1}	0.9
Aerosol gas flow rate/l min^{-1}	0.75
Mass spectrometer settings	
Bessel box lens/V	12.04
Bessel box plate lens/V	−63.26
Photon stop lens/V	−5.04
Einzel lenses 1 and 3/V	0.36
Dwell time/ms	100
Sweeps per replicate	10
Replicate time/ms	1000
Ultrasonic nebulizer conditions	
Condenser temperature/°C	0
Desolvation tube temperature/°C	100
LC conditions	
Column	C_{18} (reversed phase)
Mobile phase flow rate/ml min^{-1}	1.5
Mobile phase	3% v/v methanol–1.5% v/v acetonitrile–0.1% v/v 2-mercaptoethanol containing 0.06 mol l^{-1} ammonium acetate

solution. The optimization process was repeated each day for each mobile phase used. The optimum conditions varied slightly with time.

Chromatographic Apparatus and Conditions

A dual-piston HPLC pump (Hitachi L-6000), injector (Rheodyne Model 7125) and reversed-phase column (Vydac 201 TP, C_{18} stationary phase, 10 μm diameter particles, 250×4.6 mm i.d.) comprised the LC system. Samples were loaded with a syringe onto a 200 μl sample loop.

All separations were performed at room temperature under isocratic conditions. Each separation was attempted under several different combinations of column, organic modifier concentration, type and concentration of counter ion, pH, *etc.* The conditions listed in Table 1 are those which yielded the best chromatographic resolution of the various sets of conditions tested. The column outlet was connected to the nebulizer of the ICP-MS device through Teflon tubing (110×0.16 mm i.d.), which has a dead volume of approximately 2.8 μl.

For the determination of total mercury in fish tissue samples by FI-ICP-MS,[19,20] the LC column was removed. The mobile phase solution used for the LC separation was used as the carrier, at a flow rate of 1.5 ml min^{-1}, to reduce memory effects. A 200 μl sample loop was used in this experiment.

Reagents

Analytical-reagent grade chemicals were used as received. Methylmercury chloride (Merck) and ethylmercury chloride (TCI Chemical) standards containing about 500 ppm of Hg (as the element) were prepared by dissolving each individual species in 1% H_2SO_4. These standards were then stored in Teflon vessels.[21–24] Inorganic mercury was obtained from Spex as a 1000 ppm Hg solution. These standards were combined and diluted in 1% H_2SO_4 for these experiments. The mobile phases were prepared by dissolving acetonitrile (Fisher), methanol (Fisher), 2-mercaptoethanol (TCI Chemical) and ammonium acetate in de-ionized, distilled water to the desired concentration. The solution was adjusted to pH 6.8.

Sample Preparation

Three weighed 0.5 g portions of DORM-1 Dogfish Muscle (National Research Council of Canada, Ottawa) were transferred into 10 ml centrifuge tubes. Each sample was washed with 3 ml of acetone to remove fat from the tissue, centrifuged and the supernatant was decanted. A solution of 4 ml of 3% KBr in 3 mol l^{-1} HBr and 1 ml of saturated $CuSO_4$ solution was then added to the samples. After shaking for 20 min, 2 ml of toluene were added. After shaking for 20 min more, the sample was centrifuged for 5 min. Two further extractions with 1 ml aliquots of toluene were carried out and the toluene layers were combined. A 3 ml volume of mobile phase was added to the toluene fractions. This mixture was shaken for 10 min and then centrifuged until both layers were clear. The toluene layer was evaporated by drawing nitrogen over the top of the solution. A 2 ml aliquot of the remaining aqueous layer was then diluted to 10 ml and injected onto the chromatographic column.[5,16,20]

The recovery of organic mercury was measured using the above procedure. Three portions of fish tissue sample were spiked with 4 μg of Hg as methylmercury. These samples and a blank were carried through the extraction procedure, as outlined above. The recovery of methylmercury was 65 ± 5%, which is similar to previous results with a similar extraction procedure.[16] This factor was used to determine the methylmercury content in fish tissue samples.

For the determination of total mercury in fish samples, the samples were digested by a microwave digestion system (CEM MDS 2000). A 0.25 g fish sample, 3 ml of concentrated HNO_3 and 2 ml of Milli-Q water were placed in Teflon vessels. The heating programme was a three-step process: 30% power for 5 min, 45% power for 8 min and 30% power for 20 min. After cooling, 0.25 ml of 2-mercaptoethanol was added to the solution and the solutions were diluted to 25 ml with de-ionized, distilled water.[25]

Two thimerosal [sodium 2-ethylmercuriomercapto)benzoate] solutions for contact lens cleaning (Alcon and Wu-Fu Brand) and WasteWatR, waste water quality control standard solution (Environmental Resource Associates, Arvada, CO, USA) were diluted with LC mobile phase to suitable concentrations. Mercury species were determined by LC–ICP-MS.

Effect of Organic Solvent on Ion Signal

Flow injection techniques were employed for this study. Stock standard solutions of Hg, Cd, Rh and Pb at 40 ppb at various concentrations in methanol and acetonitrile were prepared and introduced successively into the nebulizer. An inorganic stock solution was introduced after each injection to correct for signal drifting. The sample volume injected was 1.0 ml. The pump and transfer line to the nebulizer were flushed with 1% HNO_3 after each change of solvent composition. The carrier solution flow rate was maintained at 1.5 ml min^{-1}. The ICP-MS operating conditions were optimized to provide the maximum Hg^+ signal from 40 ppb of Hg in de-ionized, distilled water using continuous introduction.

Results and Discussion

Effect of Organic Solvent on Ion Signal

In LC–ICP-MS, increasing the organic content of the mobile phase generally causes problems such as a decrease in analyte sensitivity, an increase in the abundance of polyatomic ions containing carbon and deposition of solid carbon on the sampling orifice. Nebulization of volatile solvents such as methanol can extinguish the plasma or cause it to be unstable.[10,26–32] For these reasons, most LC experiments with ICP detection have been isocratic with aqueous eluents containing only modest amounts of organic modifiers (*e.g.*, 30% methanol or less). In this section, the effects of the solvent composition on the analyte signal with ultrasonic nebulization are described.

In order to show the different behaviour between mercury and other elements when the sample contained organic solvent, and was introduced with an ultrasonic nebulizer, four elements were selected at random. Figs. 1 and 2 show the effect of solvent composition on ion signal for Hg, Rh, Cd and Pb. The signals shown are blank corrected. The mercury ion signal increased gradually whereas other ion signals decreased gradually as the organic solvent concentration increased.[33] Results from repeated experiments showed the same trend of variation of ion signal with solvent composition. The cause of the increasing Hg signal could be the formation of some volatile mercury compounds during the nebulization process, which increased the transport efficiency of mercury to the plasma. The organic concentration could enhance the mercury signal and the plasma stayed on and remained stable even when 20% methanol was nebulized; however, carbon deposition from the solvent on the sampling cone caused substantial signal drift. Therefore, the LC conditions were designed to use as little organic solvent as possible.

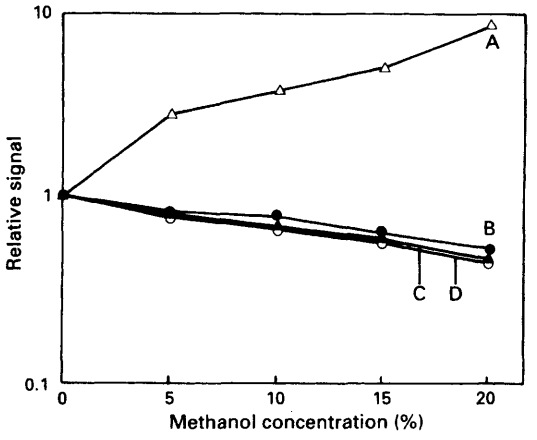

Fig. 1 Effect of methanol concentration on ion signals (normalized to that at 0% methanol): A, ^{202}Hg (40 ppb); B, ^{114}Cd(40 ppb); C, ^{207}Pb (40 ppb); and D, ^{103}Rh (40 ppb)

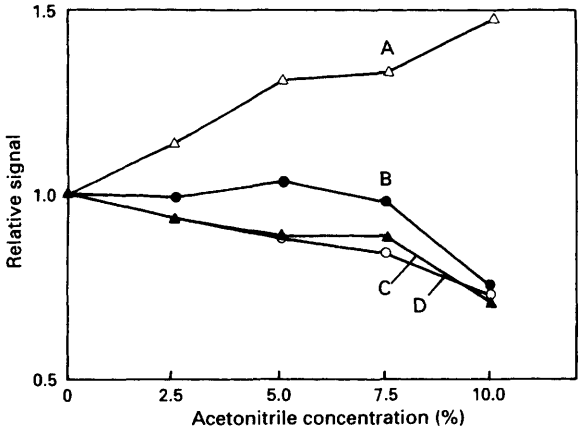

Fig. 2 Effect of acetonitrile concentration on ion signals (normalized to that at 0% acetonitrile): A, B, C and D as for Fig. 1.

Selection of ICP Operating Conditions

The performance of an ICP-MS device depends strongly on the operating conditions. The two key parameters are the aerosol gas flow rate and the plasma forward power. The dependence of the ion signals on the aerosol gas flow rate for mercury is depicted in Fig. 3. The dependence of ion signals on the plasma forward power shows the same general behaviour as the aerosol gas flow rate and is shown in Fig. 4. These two results are similar to those reported by others.[34] A lower aerosol gas flow rate and higher forward power were needed when organic solvent was introduced compared with the conditions that yielded the maximum signal when aqueous solutions were used.[35]

Effect of Ultrasonic Nebulization Conditions

The desolvation tube temperature and condenser temperature are two important operating parameters for the ultrasonic nebulizer.[36] The dependence of the ion signal on the desolvation tube temperature is shown in Fig. 5. When the desolvation tube temperature was too high, some mercury evaporated and then condensed in the condenser. However, when the desolvation tube temperature was too low, too much water and organic vapour was introduced, which cooled the plasma. Therefore, the desolvation tube temperature was adjusted to 100 °C, which is slightly above the boiling-point of the mobile phase used. The effect of the condenser temperature on ion signal is shown in Fig. 6. Except for CH_3HgCl, the condenser temperature did not affect the ion signal very much. The condenser temperature was set at 0 °C, as indicated in Table 1.

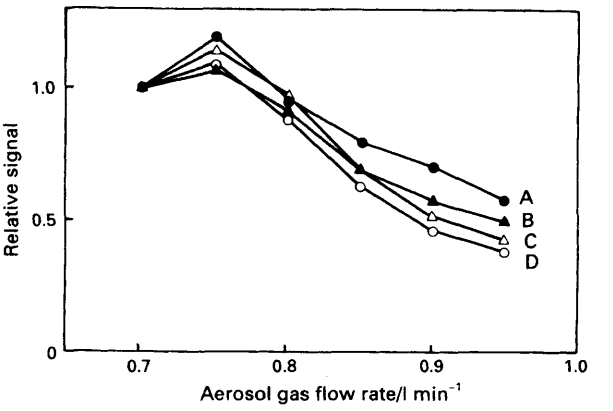

Fig. 3 Effect of aerosol gas flow rate on ion signals (relative to first point): Plasma forward power, 1.1 kW. Each species was present at 40 ppb (as element) in the LC mobile phase, 3% methanol, 1.5% acetontrile, 0.1% v/v 2-mercaptoethanol and 0.06 mol l^{-1} ammonium acetate: A, CH_3HgCl; B, Pb; C, C_2H_5HgCl; and D, $HgCl_2$

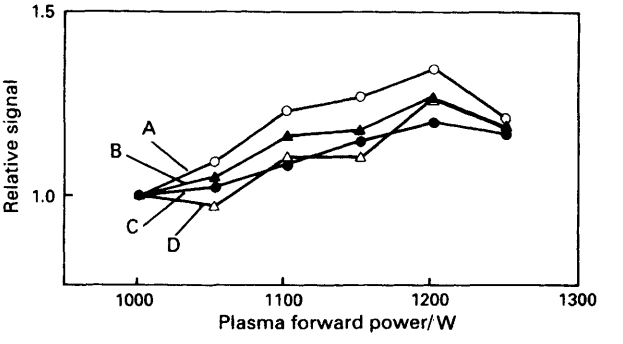

Fig. 4 Effect of plasma forward power on ion signals (relative to first point). Aerosol gas flow rate, 0.75 l min^{-1} and mobile phase as in Fig. 3: A, $HgCl_2$; B, Pb; C, CH_3HgCl; and D, C_2H_5HgCl

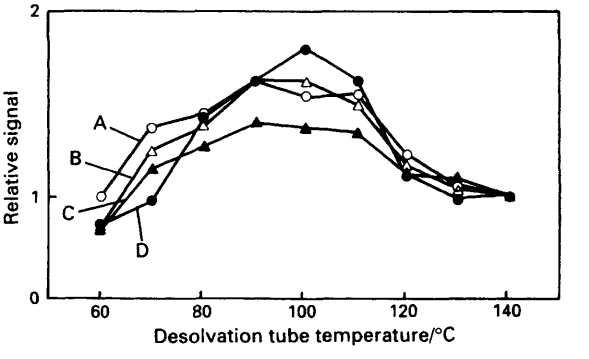

Fig. 5 Effect of desolvation tube temperature on ion signals (relative to first point): A, $HgCl_2$; B, C_2H_5HgCl; C, Pb; and D, CH_3HgCl. Mobile phase as in Fig. 3.

Mercury Speciation

A typical chromatogram of a solution containing methylmercury, ethylmercury and inorganic mercury is shown in Fig. 7. All three of the compounds were fully resolved and the separation was complete in less than 15 min. For these

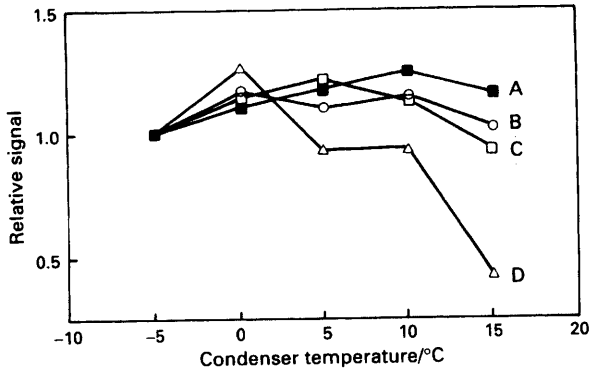

Fig. 6 Effect of condenser temperature on ion signals (relative to first point): A, Pb; B, $HgCl_2$; C, C_2H_5HgCl; and D, CH_3HgCl. Mobile phase as in Fig. 3.

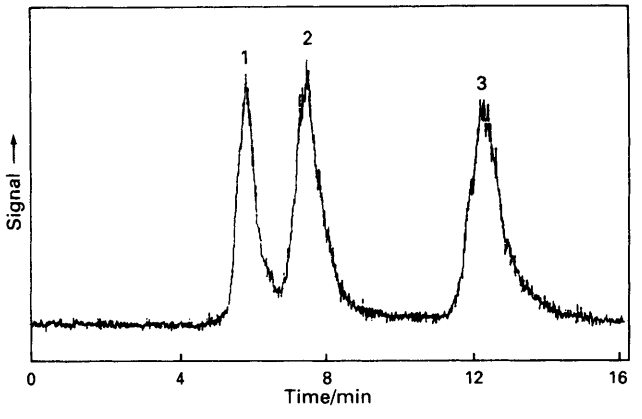

Fig. 7 Mercury-selective chromatogram for: 1, CH_3HgCl (20 ppb); 2, Hg^{2+} (10 ppb); and 3, C_2H_5HgCl (20 ppb). HPLC conditions are given in Table 1. Background 43 ± 6 counts s^{-1}. Peak heights are 680, 720 and 620 counts s^{-1} for $HgCl_2$, CH_3HgCl and C_2H_5HgCl, respectively

200 μl injections, the chromatographic peak heights were approximately 20% of the steady-state signal, *i.e.*, those obtained during continuous introduction of mercury standards. The reasons for this degradation of signal when LC separations are used with ICP-MS detection include injection of a discrete sample, dilution by the eluent, band dispersion and distortion. Peak areas estimated by calculating the areas under the elution peaks indicated that the response for mercury was slightly different for these three mercury species. The variation of the ICP ionization efficiency and the transport efficiency of ultrasonic nebulization, as mentioned above, could be the cause of the variation of the response for the different mercury species. Repeatability was determined by five injections of a 10 ppb (as Hg) $HgCl_2$, 20 ppb CH_3HgCl and 20 ppb C_2H_5HgCl test mixture. Peak heights were determined by averaging the peak maximum and the two data points around the maximum. The relative standard deviations of the peak heights for these five injections were less than 4% for all the species, which is similar to the precision obtained in previous ICP-MS experiments with LC separations.[34] The deviations of the retention time were less than 1%, as indicated in Table 2. Calibration graphs based on peak heights were linear (correlation coefficients better than 0.997) for each mercury compound in the range tested (1 ppb–1 ppm). The detection limits were calculated from these calibration graphs as the amount (or concentration) necessary to yield a net signal equal to three times the

Table 2 Repeatability of peak height and retention time for mercury species by LC–ICP-MS ($n=5$). Each mercury species present at the following mercury concentrations: $HgCl_2$, 10 ppb; CH_3HgCl, 20 ppb; and C_2H_5HgCl, 20 ppb. Sample loop, 200 μl

Parameter	CH_3HgCl	$HgCl_2$	C_2H_5HgCl
RSD of peak height (%)	4.2	3.1	4.9
RSD of rentention time (%)	1	0.9	0.9

Table 3 Mercury detection limits [ppb (ng ml^{-1})]

Method*	CH_3HgCl	$HgCl_2$	C_2H_5HgCl
LC–USN-ICP-MS†	0.7	0.4	0.8
LC–PN-ICP-MS‡	7	16	16
LC–CV-ICP-MS‡	0.6	1.2	1.2
PC–LC-CVAAS§	1	ND	ND
LC–ECD¶	1.9	1.8	1.7
LC–CVAES‖	37	35	62
LC–CVAAS**	0.78	0.78	0.42
LC–DIN-ICP-MS††	4	—	4

* USN=ultrasonic nebulization; PN=pneumatic nebulization; PC=preconcentration; ECD=electron-capture detection; CV=cold vapour; DIN=direct injection nebulization.
† This work, 200 μl sample loop.
‡ Ref. 16, 100 μl sample loop.
§ Ref. 12, 100 μl sample loop and preconcentrated.
¶ Ref. 37, 100 μl sample loop.
‖ Ref. 2, 200 μl sample loop.
** Ref. 11, 5.6 ml sample volume and preconcentrated.
†† Ref. 18, 2 μl sample loop.

Table 4 LC–ICP-MS determination of mercury in contact lens solutions and waste water solution

Solution	Experimental value*	Expected value
WasteWatR (ppb)†	17.7 ± 0.5	18 ± 4
Contact lens solution (Alcon) (ppm)‡	12.0 ± 0.2	10
Contact lens solution (Wu-Fu) (ppm)‡	9.8 ± 0.4	10

* Mean $\pm$ standard deviation for a minimum of three injections of each solution.
† Inorganic mercury only.
‡ Ethylmercury only.

standard deviation of the baseline signal. The absolute detection limits were in the range 70–160 pg of Hg, corresponding to relative values of 0.4–0.8 ppb. These results are given in Table 3 and compared with those for other techniques. Overall, the detection limits obtained by LC–ultrasonic nebulization-ICP-MS are comparable to previous results. These values are ten times better than those obtained with LC–ICP-MS with a conventional nebulizer and are comparable to those for LC–ICP-MS with cold vapour generation.

Determination of Mercury Species in Contact Lens Solutions and Waste Water Solution

Two contact lens cleaning and soaking solutions were analysed by LC–ICP-MS. Mercury-selective chromatograms for these two samples are shown in Fig. 8. The results obtained are in good agreement with the expected values (see Table 4). Fig. 8 indicates that all the mercury was present as ethylmercury. Probably all the thimerosal was dissociated into ethylmercury during handling of the sample or during the LC run. 2-Mercaptoethanol in the LC mobile phase could promote this dissociation.

Fig. 9 shows the mercury-selective chromatogram for a waste water sample. All the mercury was present as inorganic mercury. The results agree well with the reference value as shown in Table 4.

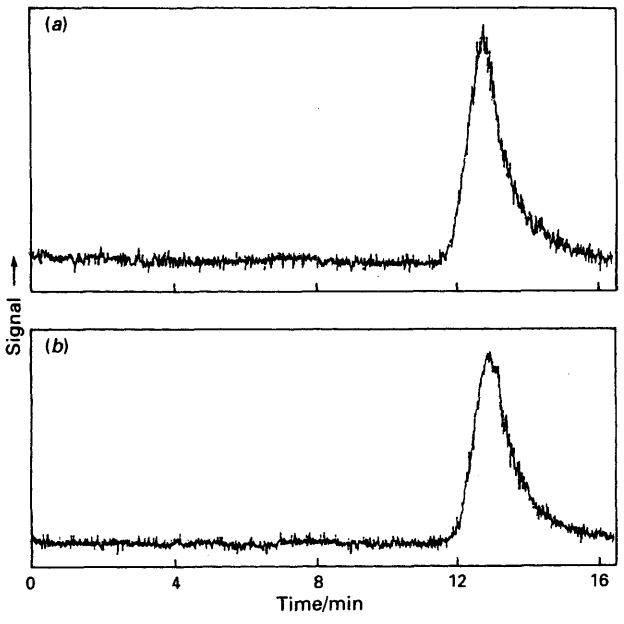

Fig. 8 Mercury chromatogram of contact lens solution: (*a*) Alcon Brand; and (*b*) Wu-Fu Brand. Mercury species present as ethylmercury

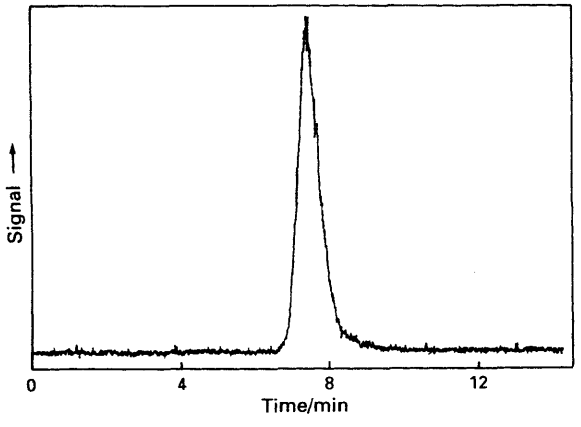

Fig. 9 Mercury chromatogram of waste water solution. Mercury species present as inorganic mercury

Determination of Organic Mercury in Fish

In order to validate the LC–ICP-MS method, methylmercury and ethylmercury were determined in the DORM-1 Dogfish Muscle reference sample. The sample was prepared by toluene extraction of the chloride complexes as described under Experimental.

A typical mercury chromatogram of a fish sample is shown in Fig. 10. The concentration of mercury in the final extract was about 20 ng ml^{-1}. After correction for the recovery (approximately 65%), the value obtained was 819 ± 66 ng g^{-1} of Hg, as methylmercury, in the original sample (Table 5), which agrees favourably with the value reported previously.[16] Fig. 10 indicates that all the organic mercury present in the fish tissue was present as methylmercury.

Table 5 LC–ICP-MS and FI-ICP-MS determination of mercury species in DORM-1 Dogfish Muscle reference material

Mercury species	Experimental value/ ng g^{-1}	Expected value/ ng g^{-1}
Total mercury	841 ± 18*	798 ± 74† 757 ± 25‡
Methylmercury	819 ± 66*	721 ± 33§

* Mean ± standard error (n = 3).
† NRCC certified value.
‡ Ref. 25.
§ Ref. 20.

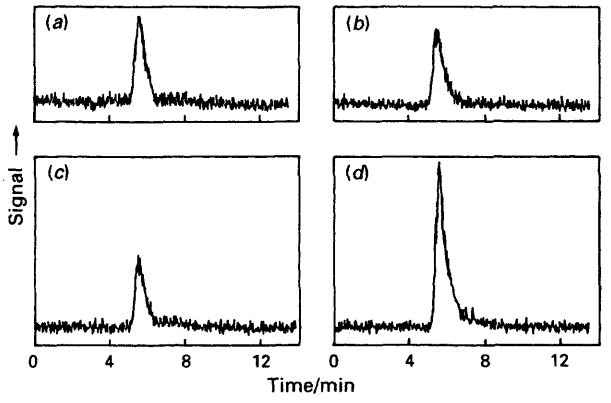

Fig. 10 Mercury-selective chromatogram of three repetitive injections [(*a*), (*b*), (*c*)] of DORM-1 Dogfish Muscle. Mercury species present as methylmercury. A 4 μg amount of methylmercury was spiked in chromatogram (*d*) as described under experimental. HPLC conditions are given in Table 1

The FI method was used to determine the total mercury content in the dogfish sample because of the problems with a mercury memory effect in the direct ICP-MS mode. In this experiment the LC mobile phase was used as a carrier to reduce the mercury memory effect. The value obtained was 841 ± 19 ng g^{-1} in the original sample, which agrees well with certified value as shown in Table 5. The FI-ICP-MS and LC–ICP-MS results illustrate that most of the mercury in this fish tissue was present as methylmercury.

Conclusion

The merits of coupling LC and FI with ICP-MS with ultrasonic nebulization for mercury speciation have been demonstrated. Post-column derivatization is not necessary for the determination of trace amounts of mercury in real samples. Compared with alternative methods of determining organomercury species, such as GC with electron-capture detection, ICP-MS provides sensitive element-selective detection. As a transient sample introduction technique and an LC mobile phase carrier were used in the LC and FI experiments, these techniques proved superior to direct ICP-MS for the determination of mercury because of a large, persistent, mercury memory problem in conventional ICP-MS. The ICP-MS instrument can also be simply and quickly interfaced with the LC system with a minimum of disruption to direct ICP-MS analysis.

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