

Method Development and Sample Processing of Water, Soil, and Tissue for the Analysis of Total and Organic Mercury by Cold Vapor Atomic Fluorescence Spectrometry

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Abstract. Atomic Fluorescence-based methods have been developed for measuring ultratrace levels of mercury (Hg) in environmental (water, soil) and biological (fish tissue) samples. In addition, methods for preparation of water, soil, and tissue samples have been developed. For the analysis of total Hg in soil, sediment and fish the samples are digested with concentrated nitric acid in sealed glass ampules, and subsequently autoclaved. Water samples are digested using standard brominating procedures. A Merlin Plus, PS Analytical atomic fluorescence spectrometer (AFS) system equipped with an autosampler, vapor generator, fluorescence detector and a PC based integrator package is used in the determination of total Hg. The determination of Hg mercury species in water, without pre-derivatization, involves adsorbent pre-concentration of the organomercurials onto sulfhydryl-cotton fibers. The organic Hg compounds are eluted with a small volume of acidic KBr and CuSO₄ and extracted into dichloromethane. Sediment, soil and tissue samples are homogenized and the organomercurials first released from the sample by the combined action of acidic KBr and CuSO₄ and extracted into dichloromethane. The initial extracts are subjected to thiosulfate clean-up and the organomercury species are isolated as their chloride derivatives by cupric chloride addition and subsequent extraction into a small volume of dichloromethane. Analysis of organic Hg compounds is accomplished by capillary column chromatography coupled with atomic fluorescence detection.

1. Introduction

Mercury is a widely distributed pollutant in the environment and has gained considerable toxicological concern in recent years. In some cases, the desired quantitation levels of this metal challenge the detection limits of the instrumentation and methods in current use (Swift and Campbell, 1993; Kammin and Knox, 1992). This has certainly encouraged the development of sensitive, reliable and precise methods for the analysis of Hg. Further, the organic forms of Hg, particularly methylmercury (CH₃Hg⁺), are far more toxic than the inorganic forms (Hg²⁺, Hg⁰) of the pollutant (Rubi *et al.*, 1992; Bryan and Langston, 1992). In efforts to project long-term health risks and the ecological impact associated with trace amounts of Hg in the environment, reliable quantitation and accurate speciation at increasing lower levels are necessary.

The open-vessel digestion procedures and detection methods for total Hg analysis in water samples that are commonly used are based on acid leaching and permanganate/persulfate oxidation followed by cold vapor atomic absorption (CVAAS), (Szakács *et al.*, 1980; Van Delft and Vos, 1988). One of the most commonly used analytical technique for the determination of organomercurials is gas chromatography with electron capture detection (GC-ECD), (Rubi *et al.*, 1992; O'Reilly, 1982) with or without pre-derivatization of the organic mercury compounds. The instrumentation and sample preparation

of the existing methods strongly limit the ultimate sensitivity and efforts to lower the detection limits have not been entirely successful (Swift and Campbell, 1993). In addition, the ECD is an unselective detector and the column has to be tediously conditioned with large injections of Hg (II) chloride to alleviate poor chromatographic response to organomercurials (Hight and Capar, 1984; Rubi *et al.*, 1992; Uthe *et al.*, 1972; Bryan and Langston, 1992; Bulska *et al.*, 1992). These disadvantages demonstrate the need for the development of new methods in this field.

This paper describes atomic fluorescence-based methods for analyzing total Hg and organic Hg compounds at low part-per-trillion levels in environmental and biological samples. The atomic fluorescence (AFS) method (Bloom, 1989; Alli *et al.*, 1994) has become increasingly important compared to CVAAS, since the instrumental detection limit of this method is about 1 picogram or less and at least one order of magnitude better than for CVAAS (Lindqvist, 1993). Total Hg analysis involves three stages: sample digestion, cold vapor generation and atomic fluorescence detection.

In water samples, the difficulty in measuring MeHg and other organomercurials lies in concentrating these compounds from solution. This work employs a sulfhydryl cotton fibre medium (Lee and Mowrer, 1989) which effectively adsorbs and preconcentrates trace levels of organomercurials. The organic Hg compounds are eluted with acidic potassium bromide and extracted into dichloromethane and subjected to GC analysis with AFS detection. Soil, sediment and tissue samples are treated with acidic potassium bromide and copper sulfate, and extracted with dichloromethane. The initial extracts are subjected to sodium thiosulfate clean-up subsequent to capillary gas chromatography with atomic fluorescence detection (Alli *et al.*, 1994).

2. Materials and Methods

2.1 SAMPLE COLLECTION AND PREPARATION

Surface water samples are collected in 2 L Teflon (Nalgene) bottles using a vacuum system. Samples are screened (105 μm Nytex netting) to prevent the collection of large particles with the water samples. All tubings and fittings used in the sampling system are constructed of teflon (SERP, internal SOP, 1994). The samples are collected by a "clean person" using double gloves (short vinyl gloves under shoulder length polyethylene gloves, OakTech) and a double bagging technique. All samples are placed in zip-lock polyethylene bags (Fisher Scientific), then in an additional plastic sample bag and placed in an icechest/cooler. In the clean room, concentrated hydrochloric acid, (trace metal grade, Fisher Scientific) is added to the water samples for preservation.

Surface, soil and sediment samples are collected using either a stainless steel spade, trowel or Eckman dredge. These samples are placed into wide mouth polyethylene specimen cups (125 ml, Fisher Scientific). Subsurface soil or sediment samples are collected in polycarbonate core tubes. Upon arrival to the laboratory the samples are immediately frozen to preserve their chemical integrity.

Fish samples are collected using a dip net, with the sampler wearing two pairs of gloves. The fish are placed in zip-lock sample bags, labelled, and stored in a cooler with ice for transport to the laboratory. Fish samples remain frozen until ready for analysis.

2.2 SAMPLE DIGESTION FOR TOTAL MERCURY DETERMINATION

Water Samples. Water samples are digested in a 125 mL teflon bottle with 1 mL HCl and 2.5 mL potassium bromate (KBrO_3)/potassium bromide (KBrO) mixture overnight (Szakács *et al.*, 1980; Bloom and Fitzgerald, 1988). These

samples are prepared and remain (in capped bottles) in the Hg-clean room. Prior to analysis, 500 μL hydroxylamine hydrochloride is added to destroy excess bromine and the samples thoroughly shaken.

Soil and Sediment Samples. Soils (such as peat, marls and marly peat) are first homogenized by adding 30 to 50 mL of deionized water and blended for 3 minutes to a uniform consistency with a blender (Osterizer). From the homogenized slurry 5 mL is diluted into 45 mL of 0.6N HCl to neutralize any carbonates, in a clean specimen cup. Of this mixture 1 mL is placed in a 10 mL ampule with 2 mL of concentrated nitric acid (HNO_3), (trace metal grade, Fisher Scientific). Digested soil and sediment samples are left to stand under a fume hood for 20 minutes. The ampules are subsequently sealed and autoclaved for 1 h at 151°C. Before analysis the digestates are diluted with 0.12N HCl solution in a 20 mL polyethylene vial.

Fish Samples. To quantify total Hg in small fish (< 0.4 g, < 30 mm in length) the entire fish is weighed and placed in 10 mL ampules and digested using 1 mL deionized water and 2 mL concentrated HNO_3 . After standing 20 minutes under a fume hood, the ampules are sealed and autoclaved as described above. For the analysis of larger fish (approximately 30 cm or longer), 3 tissue plugs (stainless steel core tube, 4 mm in diameter) are taken from the left side (using only muscle tissue), and combined to obtain a representative sample (approximately 0.4 g). The samples are then processed as indicated above for soil and sediment.

These digestion procedures result in the conversion of organic forms of Hg to inorganic mercury (Hg^{2+}). The digested samples are introduced to the cold vapor generator, at which point tin (II) chloride is used to effectively reduce inorganic mercury (Hg^{2+}) to its elemental gaseous form (Hg^0), prior to detection by atomic fluorescence.

2.3 INSTRUMENTATION AND ANALYSIS

A PS Analytical Merlin Mercury Fluorescence Detector System used in this study was supplied by P.S. Analytical Ltd. (UK). This system incorporates an Autosampler, Vapor Generator, Fluorescence Monitor and an IBM compatible Computer System. Instrument operating conditions for ultratrace and high levels of Hg concentrations are given in Table I.

Table I. Optimized operating conditions of the AFS System for total-Hg concentrations.

<i>Ultratrace levels</i>		<i>High levels</i>	
Carrier gas mL/min	125	Carrier gas mL/min	200
Sheath gas mL/min	150	Sheath gas mL/min	350
Calibration range	1000	Calibration range	100
Fine grain	4.0	Fine grain	2.5
Damping Switch	On	Damping Switch	On

Cold Vapor Generation. In the continuous flow vapor generator system, Hg(II) is reduced to Hg⁰ following the addition of tin(II) chloride. The volatile Hg is stripped from the solution (in the gas liquid separator) by a carrier gas (argon). The rate of argon flow depends on whether the analysis is for ultratrace or high levels of Hg determination (P.S. Analytical, 1991).

Atomic Fluorescence Detection. A sheath gas (also argon) is used to channel the Hg vapor through a chimney past a light source and a photomultiplier tube that are at right angles to each other. With a specific high intensity Hg lamp source (Cathodeon Ltd., Cambridge) and a fixed 254 nm filter, efficient isolation of the required excitation and emission wavelengths is achieved (P.S. Analytical, 1992).

Reagents. All reagents used in total Hg analysis are of certified ACS grade and obtained commercially from Fisher Scientific, unless otherwise stated. A Barnstead B-pure system (located in the Hg-clean room) produces all deionized water used in making up reagents, sample digestates, calibration solutions, stock solution and quality control standards. This water is first filtered through a Culligan system consisting of activated charcoal and two mixed bed ion exchange cartridges before being piped to the Hg-clean room. 0.1 N KBrO₃, 0.2 N KBrO and 1.7 M hydroxylamine hydrochloride solutions are made up by dissolving the appropriate amounts of the salts in deionized water. The KBrO₃ and KBrO salts are heated overnight in a glass vial at 250°C to remove adsorbed Hg. The digesting solution is made up daily by mixing equal volumes (100 mL) of 0.1N KBrO₃ and 0.2N KBrO solutions. All solutions are prepared weekly and stored in borosilicate bottles with teflon lined caps.

Standards. Working standards are prepared daily from a Hg stock solution (100 ng/mL) and diluted to the desired concentration. The stock solution is also made up daily from a commercially available mercury standard (1000 µg/mL, SPEX Industries, Edison, NJ). Calibration solutions are made up in 500 mL teflon bottles and stabilized by adding 5 mL concentrated HCl. No certified material exists for quality control of Hg in water near ultratrace levels. Soil (NIST sediment nominal value 60 ng/g, 8406) and tissue (NBS 1566a Oyster Tissue, 64 ng/g) quality control standards are obtained from the National Institute of Standards and Technology (Gaithersburg, MD).

2.4 ORGANIC MERCURY DETERMINATION

Sediment, Soil and Tissue Samples. A 1.0-5.0 g portion of the homogenized sample (as prepared above) is placed in a 20 mL borosilicate glass scintillation vial (Kimble, #74511). To the vial 5 mL distilled water, 3.0 mL of 1.0 M copper sulfate and 3.0 mL of acidic potassium bromide solution are added. The mixture is shaken for 1 hr at 330 rpm (Gyrotory Shaker Model G2). Dichloromethane (5 mL) is added and the mixture is shaken for 24 h at 330 rpm and then centrifuged for 10 min at 5000 x g in a Sorvall Model RC-5 refrigerated centrifuge (Dupont). An exactly known volume of the dichloromethane layer (3.5-4.0 mL) is transferred to a 7.0 mL borosilicate glass scintillation vial (Kimble, #0333726) and 1.0 mL of 0.01 M sodium thiosulfate is added. The mixture is shaken for 20 min at 330 rpm and centrifuged at high speed in a IEC clinical centrifuge. The aqueous layer (0.9 mL) is placed in a 2.0 mL microcentrifuge tube (Fisherbrand, Fisher Scientific), and 0.3 mL of 0.5 M copper chloride and 0.3 mL dichloromethane are added. The contents are mixed for 1 min on a Vortex Genie mixer and centrifuged for 2 min at high speed (16,749 x g) in a Hermle centrifuge. The dichloromethane is transferred to a 2.0 mL glass sampling vial containing a few crystals of anhydrous sodium sulphate and subjected to GC analysis. Injections of 5.0 µL are used. Samples spiked with known concentrations of methyl - and ethylmercury chloride are

extracted to evaluate the recovery factor used for quantification.

Water Samples. The sulfydryl-cotton (SFC) fibre columns are made of 1 mL disposable pipette tips containing 0.1 g of SFC fibre, packed loosely and as evenly as possible. Two SFC columns are connected in series and the water sample is passed through these by vacuum. One mL of acidic potassium bromide and 0.5 mL of 1.0 M copper sulfate are then pipetted on the surface of the adsorbent and the eluate is collected in a 2 mL micro-centrifuge tube (Fisher Scientific). This is extracted with 0.2 mL dichloromethane on a Vortex Genie mixer for 1.5 min and centrifuged as described above. The dichloromethane layer is then transferred to a 2 mL glass sampling vial containing a few crystals of anhydrous sodium sulfate and subjected to GC analysis.

2.5 INSTRUMENTATION AND ANALYSIS

A schematic diagram of the GC-AFS system used in this work is shown in Figure I and the optimum operating conditions are summarized in Table II. A

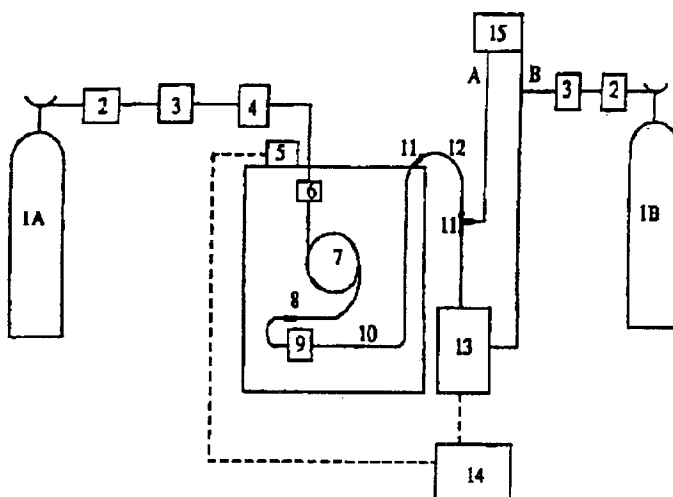


Figure I. Gas Chromatographic-Atomic Fluorescence Spectrometric System. 1A: Helium, 1B: Argon, 2: Oxygen trap, 3: Mercury trap, 4: Moisture trap, 5: Automatic sampler, 6: Injector, 7: Column, 8: Press-fit union, 9: Pyrolyser, 10: Deactivated fused-silica 0.53mm i.d., 11: Teflon unions, 12: Teflon transfer line 0.5mm i.d., 13: Atomic Fluorescence detector, 14: E-Lab chromatographic control and data acquisition system, 15: Mass flow controller-Channel A make-up, Channel B sheath gas.

Hewlett-Packard (Model 5890 Series II) gas chromatograph coupled with an HP (Model 7673) automatic sampler is used. A fused-silica, bonded phase megabore column (15 m x 0.53 mm i.d., 1 μ m non-polar DB-1 coating, J & W Scientific) and the splitless injection mode is employed. The effluent from the

column is led through a pyrolyser (P.S. Analytical Ltd., UK), positioned inside the GC oven *via* a piece of 65 cm length of deactivated fused-silica (0.53 mm i.d., J & W Scientific), which is connected to the column with a glass "press fit" union (J & W Scientific). The Hg atoms formed in the pyrolysis unit are transferred from the outlet end of the deactivated fused-silica tubing to the fluorescence detector (teflon transfer line, 0.5 mm i.d., Alltech Associates). The transfer line is passed through a small hole on the top of the GC oven to a Merlin Mercury Fluorescence Detector, and the connections are made *via* teflon unions.

Table II. Optimized operating conditions of GC-AFS.

<i>Gas chromatograph.</i>	
Injector temperature	250°C
Temperature program	1 min at 40°C, 60°C/min to 140°C, 3 min at 140°C, 50°C/min to 200°C, 10 min at 200°C.
Pyrolyser temperature	800°C
Column flow	4.0 mL/min
Make-up flow	60 mL/min
<i>Atomic fluorescence system</i>	
Sheath gas flow	300 mL/min
Integrate time	0.25s
Calibration range	1000 (most sensitive)
Fine gain	10 (maximum)
Recorder output voltage	1V
Damping switch	On
(for signal smoothing)	

A real time chromatographic control and data acquisition system (E-Lab, Version 4.10R, OMS TECH, INC.) is interfaced with the GC and AFS detector system. In this work, the detection limit is defined as the amount of Hg necessary to give a peak area equal to three times the standard deviation of the background signal.

Gases. All gases are supplied by Liquid Carbonic Speciality Gases and are of zero grade quality. Helium (99.995%) is used as the carrier gas (GC), passed first through an oxygen trap, then through a Hg trap (gold-activated carbon) and a moisture trap prior to the GC. Argon (99.998%) is employed as the make-up gas and the sheath gas for the GC-AFS system and is also passed through moisture and Hg traps before use. Its flow is regulated by a mass flow controller (Omega) equipped with two channels, channel A (make-up flow) and channel B (sheath gas flow, see Figure 1).

Reagents. Double deionized water produced by a Barnstead B-Pure system is used in all solutions. Certified ACS grade potassium bromide, copper(II) sulfate, copper(II) chloride and sodium thiosulfate (Fisher Scientific) are used throughout this work. The acidic potassium bromide solution is prepared by dissolving 180 g in 200 mL water. Trace metal grade concentrated sulphuric acid (50 mL, Fisher Scientific) is added to 100 mL of water. After cooling to room temperature the solutions are mixed and made up to 1 L with water. Copper sulfate (1.0 M), copper chloride (0.5 M) and sodium thiosulfate (0.01 M) solutions are prepared by dissolving appropriate amounts of the salts in water. All solutions are extracted with dichloromethane prior to use.

Standards. All Hg standards are purchased from Ultra Scientific. Stock standard solutions of methyl- and ethylmercury chloride are prepared by dissolving appropriate amounts of the standards in optima grade methanol (Fisher

Scientific). These solutions are stored in dark brown bottles and diluted with dichloromethane to give working standards of the desired concentrations when required.

Synthesis of Sulfydryl-cotton (SHC) fiber adsorbent. This synthesis follows the procedure used by Lee and Mowrer (1989). A mixture is first prepared by adding the following reagents in sequence to round bottom flask: 100 mL thioglycolic acid, 60 mL acetic anhydride, 40 mL acetic acid (36%) and 0.30 mL concentrated sulfuric acid. The mixture is allowed to cool to 45°C, then 30 g of cotton wool are added and allowed to soak thoroughly in the mixture. The reaction bottle is placed in an oven for 3 to 4 days at 40°C, then the product is placed in a filter-funnel with suction filtration and washed thoroughly with deionized water to remove traces of thioglycolic acid. The SHC fiber obtained is dried at 40°C for 24 h and stored in the refrigerator.

3. Results and Discussion

Internal standard operating procedures (SERP, Internal SOP, 1994) for quality assurance purposes have been developed for ultratrace levels of Hg determination. The method detection limit (MDL, ppt), accuracy (%R) and precision (%RSD) for the various matrices and analytes considered in this study are shown in Table III. An MDL of 0.3 ng/L is achieved which is based on the US EPA method used for the calculation of this parameter. This number can also be viewed as the instrument detection limit, since the matrix of determination is a spiked blank that did not undergo the standard Hg digestion procedure. The method detection limit obtained is based on the analysis of seven replicate samples of spiked reagent blank water stabilized with concentrated HCl conducted on 3 nonconsecutive days. The standard deviation for each set of analyses is multiplied by the students' t value for a 99% confidence level and a standard deviation estimate with $n-1$ degrees of freedom is, $t = 3.14$ for seven replicates (US EPA, 1993). As shown in Table III, the MDL for water samples has a precision of about 5% relative standard deviation (%RSD) and recovery between 90 and 110%. The concentrations of Hg in sediment and tissue samples are significantly higher than water samples and can be determined at better precision (<5 %RSD) and accuracy (95 to 105 %R). The MDL is reevaluated every 6 months (SERP, Internal SOP, 1994).

In total-Hg determination, samples are prepared and analyzed according to the internal SOP established. The optimized operating conditions of the AFS System are listed in Table I, and as indicated, these parameters vary markedly depending on whether ultratrace levels or high levels of Hg are to be measured. In addition, the calibration levels used in the generation of daily calibration curves also depend on the level of Hg to be monitored in the sample. For ultratrace levels of Hg determination, calibration levels are 0, 10, 20 and 30 ng/L. Calibration levels for soil, sediment and fish samples are 0, 100, 250 and 500 ng/L. The linear correlation coefficient met EPA Contract Laboratory Program requirements of ≤ 0.995 (Inorganic USEPA CLP SOW 3/90). Quality control checks are performed on NIST soil and tissue standards that are digested and autoclaved. Subsequent analysis of the digestates (1:20 dilution) yielded recovery values of 90 to 110% (58 to 70 ng/g) for the tissue standard and 95 to 105 % (57 to 63 ng/g) for soil standard. These values are within the acceptance criteria window for soil and tissue standards of $\pm 10\%$.

Table III. Precision, recovery and method detection limits for inorganic, total and organic Hg.

Analyte	Matrix	Precision (%RSD)	Recovery (%R)	MDL
Inorganic Hg	Water	~5	90 - 110	0.3 ng/L
Total Hg	Water	~5	90 - 110	0.3 ng/L
Total Hg	Tissue (NBS oyster tissue 1566a 64 ng/g)	<5	90 - 110	—
Total Hg	Soils, sediments (NIST sediment 8406 60 ng/g)	<5	95 - 105	—
Organic Hg (MeHg ⁺ , EtHg ⁺)	Water	<5	98 - 110	0.02 ng/L
Organic Hg (MeHg ⁺ , EtHg ⁺)	Soils, sediments, tissue	<5	67 - 80	0.2 pg

In the analysis of organomercurials, the mercuric chloride conditioning of the GC column is associated with many drawbacks (Rubi *et al.*, 1992) and this procedure is a major limitation of the analytical technique. The aqueous phase ethylation technique derivatizes both inorganic mercury (Hg²⁺) and ethylmercury (C₂H₅Hg⁺) to diethylmercury [(C₂H₅)₂Hg] and thus the quantification of these species inherent in the sample can become difficult. These disadvantages indicate the need for the development of more straightforward methods in the analysis of organic Hg compounds.

This work employed a capillary column for higher efficiency separation and a mercury fluorescence detector which affords better selectivity and sensitivity compared to the ECD. The configuration of the GC-AFS System is outlined in Figure I and the optimized operating conditions is shown in Table II. The extraction of soil, sediment and tissue samples involve a thiosulfate clean-up step and with this procedure, no mercuric chloride conditioning is necessary (Alli *et al.*, 1994). In addition, the thiosulfate back-extraction step effectively removes sample matrix interferences (high-molecular-weight compounds, possibly containing sulfur), which cause rapid stationary phase deterioration (Alli *et al.*, 1994; Lansens *et al.*, 1991; O'Reilly, 1982). A typical chromatogram of a sediment sample is shown in Figure II. Note that both methyl- and ethylmercury are efficiently separated.

In natural waters, organomercurials are present in very low concentrations and this is one of the major limitations in analyzing these compounds. The SHC fiber lends efficiently to solid phase extraction (SPE) and

allows for the analysis of trace levels of organomercurials. Further, since the SHC fiber has a high selectivity for organic mercury compounds, it avoids the extraction of extraneous compounds which causes severe column problems.

Quantitative data are obtained using the calibration curves generated daily. The chlorides of methyl- and ethylmercury are used to create the standard calibration curves expressed in terms of peak area vs organomercury chloride concentration (pg Hg/5 μ L injection). The relative standard deviation of the signal for a 2 pg Hg/5 μ L standard was 1.5% for peak area measurements ($n=3$). The linear range used for the generation of calibration

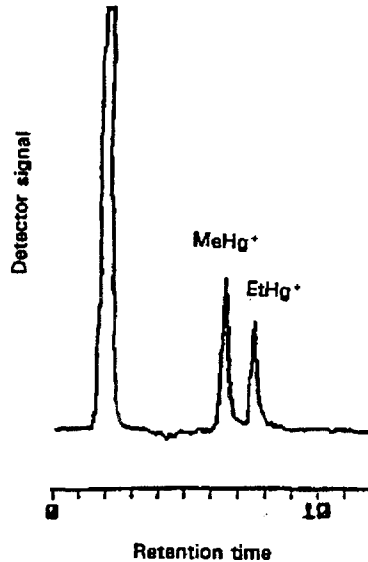


Figure II. Chromatogram of sediment sample after thiosulfate clean-up (MM: 1945 pg Hg/g, EM: 1236 pg Hg/g)

curves is 0 and 4 pg Hg/ μ L and the linear correlation coefficients are typically 0.998 and 0.999 for methylmercury chloride and ethylmercury chloride respectively.

Quality control is maintained by determination of % recoveries for each sample. The recovery factor (%R) varies between 67 and 80% for soil, sediment and tissue samples, compared to 98 and 110% for water samples (Table III). This establishes the importance for determining a recovery factor for each sample since this value is influenced by differences in sample matrices which affect the partitioning of organic Hg compounds. Further support for this determination (%R) is not possible due to the lack of official standard materials (for organic Hg analysis) and also demonstrates the current need for internal standard(s).

4. Conclusion

Sealed ampule digestion of environmental and biological samples for total Hg determination described in this article is a relatively new method which provides accuracy of 95 - 105% recovery of Hg⁰. Digestion of soil, sediment and fish samples in sealed 10 mL ampules is a clean and straightforward method for Hg determination. When these samples are autoclaved they liquify which makes it very easy to dilute samples suitable for AFS detection. Closed vessel digestion followed by cold vapor generation and atomic fluorescence detection has yielded detection limits that allow the quantification of ultratrace levels of Hg in water samples. The preparation techniques and use of an Hg-clean room have made it possible to reduce significantly contamination of samples.

In the speciation of organic Hg by GC, sample matrix interferences become adsorbed or bound to the stationary phase of the column after various injections, exerting a negative effect on the efficiency of the analysis. With a thiosulfate back-extraction step, these interferences can be effectively removed, allowing efficient analysis of the organomercurials. In water samples, the organic Hg compounds can be efficiently preconcentrated onto the SHC fiber, which also provide a sample clean-up. The column life becomes considerably longer with the clean-up step and can be used routinely for the analysis of organomercurials with no apparent loss in efficiency.

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References

- Alli, A., Jaffe, R. and Jones R.: 1994, (in press) *J. High Res. Chrom.*
- Bloom, N.S.: 1989 *Can. J. Fish. Aquat. Sci.* 46, 1131-1140.
- Bloom, N. S. and Fitzgerald W. F.: 1988 *Anal. Chim. Acta* 208, 151-161.
- Bryan, G. W. and Langston, W. J.: 1992, *Environ. Pollut.* 76, 89-131.
- Bulska, E., Emteborg, H. and Baxter, D. C. *et al.*: 1992, *Analyst* 117, 657-663
- Hight, S. C. and Capar, S. G.: 1984, *J. Off. Anal. Chem.* 67, 715-717
- Kammin, W. R. and Knox, R.: 1992, *Environ. Lab. Aug/Sept.* 32-34
- Lansens, P., Casais, C. and Meuleman, C., *et al.*: 1991, *J. Chromatogr.* 586, 329-340.
- Lee, Y. H. and Mowrer, J.: 1989, *Anal. Chim. Acta* 221, 259-268.
- Lindqvist O.,: 1993, *Water, Air and Soil Pollution* (Ed.), Kluwer Academic Publishers, Netherlands.
- O'Reilly, J.: 1982, *J. Chromatogr.* 239, 433-444.
- P S Analytical, Merlin Plus Manual, 1991. P S Analytical Ltd., Arthur House, B4 Chaucer Business Park, Watery Lane, Kemsing, Sevenoaks, Kent TN156QY, UK.
- Rubi, E., Lorenzo, R.A. and Casais, C., *et al.*: 1992, *J. Chromatogr.* 605, 69-80.
- SERP, Internal Standard Operating Procedures (SOP) 1994. F.I.U., University Park, Miami, FL. 33199
- Swift, R. P. and Campbell, J. E.: 1993, *Spectroscopy* 8(2), 38-47.
- Szakács, O., Lásztity, A. and Horváth, ZS.: 1980, *Anal. Chim. Acta* 209, 147-156.
- US EPA. 40 CFR Ch. 1, Part 136, Appendix B, revision 1.11. 1993, Office of Water Regulations and Standards, Washington. 569-570.
- Uthe, J. F., Solomon, J. and Grift, B.: 1972, *J. Off. Anal. Chem.* 55, 83-589.
- Van Delft, W. and Vos, G.: 1988, *Anal. Chim. Acta* 209, 147-156.