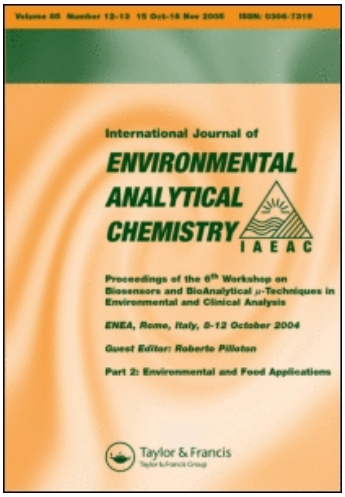

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Microcolumn Field Sampling and Flow Injection-Atomic Fluorescence Spectrometry for Speciation of Mercury in Surface Waters

Wei Jian[a]; M. L. Mena[a]; C. W. McLeod[a]; J. Rollins[b]
[a] Environmental Research Centre, Division of Chemistry, School of Science, Sheffield Hallam University, Sheffield, UK [b] National Rivers Authority (North West Region), Warrington, UK

To cite this Article Jian, Wei , Mena, M. L. , McLeod, C. W. and Rollins, J.(1994) 'Microcolumn Field Sampling and Flow Injection-Atomic Fluorescence Spectrometry for Speciation of Mercury in Surface Waters', International Journal of Environmental Analytical Chemistry, 57: 2, 99 — 106
To link to this Article: DOI: 10.1080/03067319408027416
URL: http://dx.doi.org/10.1080/03067319408027416

Intern. J. Environ. Anal. Chem., Vol. 57, pp. 99-106
Reprints available directly from the publisher
Photocopying permitted by license only

MICROCOLUMN FIELD SAMPLING AND FLOW INJECTION-ATOMIC FLUORESCENCE SPECTROMETRY FOR SPECIATION OF MERCURY IN SURFACE WATERS

WEI JIAN, M. L. MENA and C. W. McLEOD

Environmental Research Centre, Division of Chemistry, School of Science, Sheffield Hallam University, Sheffield S1 1WB, UK.

J. ROLLINS

National Rivers Authority (North West Region), Knutsford Road, Warrington WA4 1HG, UK.

(Received, 3 March 1994; in final form, 28 March 1994)

A novel approach to mercury speciation in waters based on microcolumn field sampling and flow injection-atomic fluorescence spectrometry is described. Microcolumns of sulphydryl cotton are used as a new sampling tool in order to collect, enrich and immobilise organic mercury species. On return to the laboratory the microcolumns are inserted into the flow injection system for elution/quantitative analysis. The technique, applied to survey analyses of the Manchester Ship Canal, revealed relatively high concentrations of organomercury (0.006–0.058 μg Hg l^{-1}) and inorganic mercury (0.0038–0.530 μg Hg l^{-1}). The distribution profiles for the inorganic and organic fractions did not correlate well.

KEY WORDS: Mercury speciation, microcolumn field sampling, flow injection, atomic fluorescence, waters.

INTRODUCTION

There is a continuing need to improve our understanding of mercury transport and cycling in the biosphere on account of the toxicity of mercury. As is well known, organomercury compounds and particularly methylmercury are highly toxic relative to inorganic forms and hence analytical methodology capable of differentiating between the various species is essential. Many approaches have been reported for the determination and speciation of mercury and include: cold vapour atomic absorption/atomic fluorescence with selective chemical reductants/pretreatments[1-3], chromatographic methods based on gas chromatography[4-8] and high performance liquid chromatography[9], solvent extraction and inductively coupled plasma mass spectrometry[10] and electrochemical separation and atomic absorption

spectrometry[11]. Recently, flow injection atomic fluorescence (FI-AFS) with microcolumn separation has been proposed as a novel speciation technique[12]. In this latter approach, a microcolumn of sulphydryl cotton fibre (SCF) is incorporated in the FI system to effect on-line separation of organomercury and inorganic mercury species. The SCF microcolumn is essentially a scaled-down version of that utilised by Lee[6] for gas chromatographic separation/enrichment of organomercury compounds.

With reference to mercury concentrations in natural waters, reliable speciation data are scarce. This is partly because of the extremely low concentrations of individual species (ng l^{-1}) but also is a reflection of the difficulty after sampling of maintaining the natural speciation state until analysis is performed. As is often practised in official monitoring programmes for mercury, chemical species are actually destroyed at the time of sampling (addition of powerful oxidants to the sample) and only total mercury data are reported. A notable exception to the above are the monitoring studies of Lee and Hultberg[6,13] where methylmercury concentration in Swedish surface waters were reported to be in the sub ppt range (0.16–0.41 ng l^{-1}). More recently Frech *et al.*[8] utilised microcolumns of dithiocarbamate resin for trace enrichment of methyl-, ethyl-, and inorganic mercury in freshwater and seawater prior to determination by GC-MIP-AES and observed methylmercury concentrations of 0.08–1.15 ng l^{-1} and inorganic mercury concentrations of 0.31–1.98 ng l^{-1}.

In the present work a new speciation approach based on the combination of microcolumn field sampling and FI-AFS has been developed. Instead of implementing microcolumn enrichment/separation in the laboratory, water samples are processed at the sampling site by passage through microcolumns of sulphydryl cotton in order to immobilise and stabilise organomercury species. The microcolumns with retained analyte are then returned to the laboratory and incorporated into a FI-AFS system for elution/quantitative analysis. In this way it is hoped to preserve and maintain the original organomercury species until analysis is performed as already demonstrated in the case of chromium speciation studies[16]. In addition to determination of organomercury concentrations the measurement scheme also allows for determinations of inorganic mercury. As a trial study the new methodology is applied to the Manchester Ship Canal, a water course known to be contaminated by mercury.

EXPERIMENTAL

Reagents

Tin chloride solution (3% m/V) in hydrochloric acid (15% v/V) was freshly prepared on a daily basis from tin chloride 2-hydrate salt (Spectrosol, Merck, Poole, UK), hydrochloric acid (36% m/m, Aristar, Merck) and high purity water. A potassium bromide/potassium bromate solution (0.5% +0.14% m/V) was made by dissolving respective reagents (Analytical grade, Fisons, Loughborough, UK) in water. Hydrochloric acid solution (0.01 M) was prepared from hydrochloric acid (36% m/m, Aristar, Merck). Hydrochloric acid solution (3 M) was freshly prepared by diluting 50 ml of hydrochloric acid (36% m/m) in a 200 ml pre-cleaned flask prior to analysis.

Preparation of sulphydryl cotton fibre and microcolumn field sampling kit

Sulphydryl cotton fibre was prepared according to the procedure of Lee[6] as follows: thioglycollic acid (50 ml, General Purpose Reagent, UK, 97% m/m, Merck), acetic anhydryde (30 ml, 36% m/m, General Purpose Reagent, Merck), acetic acid (20 ml, 30% m/m, Merck) and sulphuric acid (0.15 ml, 96% m/m, General Purpose Reagent, Merck) were measured into a wide-neck flask and then mixed thoroughly (care exothermic reaction). The mixture was cooled to room temperature and absorbent cotton (15 g) was added and left to soak. The stoppered flask was then placed into an oven at 40°C and left for 4 days. Thereafter the cotton fibre was washed with Millipore water until washings were between pH 6–7 and the material dried at a low temperature (40°C). The dried cotton was next transferred to a sealed light-free container for storage.

Sulphydryl cotton microcolumns were made by inserting the cotton fibre (0.015–0018 g) into PTFE tubing (60 mm × 1.5 mm ID), the absorbent being packed evenly along a 50 mm length of column. Two further PTFE tubes (20 mm × 0.8 mm) were fitted at both ends of the column to allow connection of the microcolumn to the field sampling kit and the flow injection system. The field sampling kit, consisting of an on-line filter (0.45 μm, Anachem, Luton, UK), a syringe (60 ml of capacity) and a sulphydryl cotton microcolumn (60 mm × 1.5 mm), was conditioned by passing through, twice, 2 ml of hydrochloric acid solution (3 M, Aristar, Merck) followed by 2 ml of Millipore water.

Equipment

The determination of organomercury was performed with a 3-line FI system illustrated in Figure 1. Main components were a peristaltic pump (Ismatec, London, UK), rotary injection valve (OmniFit, Cambridge, UK) and an atomic fluorescence detector incorporating gas liquid separator (Merlin, P.S. Analytical, Sevenoaks, UK). Transient signals derived from elution of organomercury from the sulphydryl cotton microcolumn were recorded on a strip

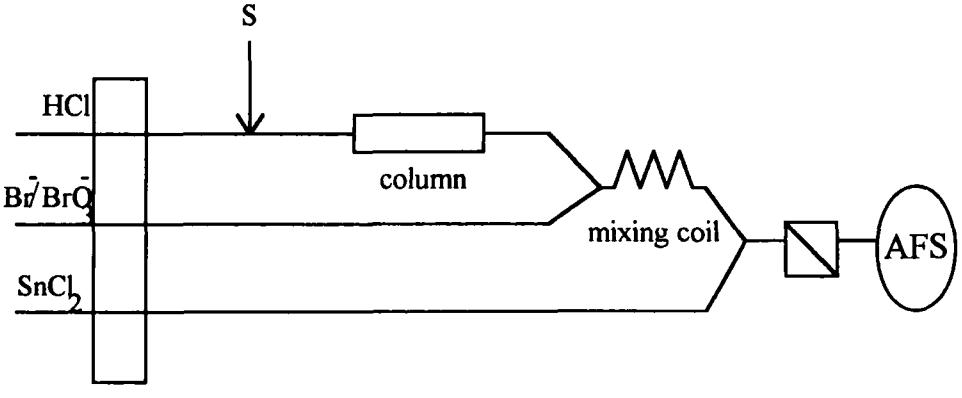

Figure 1. Flow injection system incorporating microcolumn of sulphydryl cotton for determination of organomercury species (see text for operating parameters).

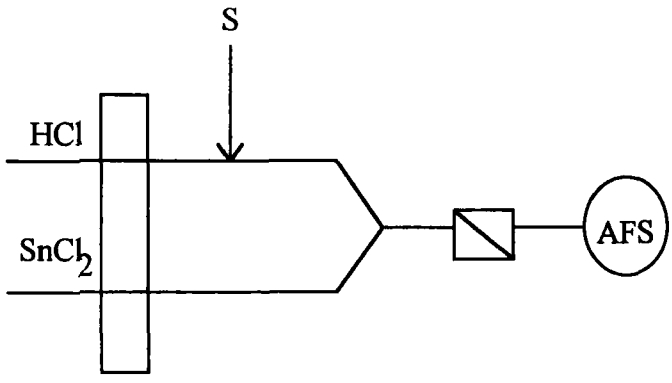

Figure 2. Flow injection system for determination of inorganic mercury (see text for operating parameters).

chart recorder (Hitachi 056) and quantitative measurements were based on evaluation of peak area using standard software routines (Merlin, P.S. Analytical). Key FI parameters were: eluent, hydrochloric acid (0.5 ml, 3 M); mixing coil length 4 m; carrier/reagent stream flow rates, 1.5 ml min^{-1}. Full details concerning the operation and performance of the FI system are detailed elsewhere[11].

The determination of dissolved inorganic mercury was performed using a 2-line FI system (on-line oxidation omitted) as shown in Figure 2. Flow injection operating parameters were as above.

Sampling and pretreatment procedures

The sampling procedure was designed in order to allow determination of dissolved organomercury (corresponding to fraction retained on the microcolumn) and dissolved inorganic mercury (corresponding to fraction in effluent after microcolumn processing).

Sample solutions (1 l), on collection, were adjusted to pH 3.0–3.5 by dropwise addition of concentrated nitric acid. A plastic syringe (60 ml capacity) was filled and rinsed with acidified sample before assembly of the field sampling kit. An aliquot of sample solution (30 ml) was then processed by passage through the filter and microcolumn. At the same time column effluent was collected in a pre-cleaned 50 ml flask, which contained nitric acid (0.5 ml) (for determination of dissolved inorganic mercury). On completion of sampling, microcolumns, stored in a light tight box, and flasks were returned to the laboratory for analysis. For each sample collected 3 replicate analyses (corresponding to processing of microcolumns in triplicate) were performed. The FI-AFS measurements were performed within 48 h of sample collection.

Water samples (sub-surface) were collected at 10 sampling stations throughout a 20 km stretch of the Manchester Ship Canal.

Measurement procedure

The determination of organomercury was based on the elution of organomercury from the sulphydryl cotton microcolumn. Prior to use the FI system (Figure 1) was cleaned and rinsed by pumping hydrochloric acid solution (5 M) for 25 min and Millipore water for 10 min. Then reductant ($SnCl_2$), oxidant ($Br^-/BrO3^-$ and carrier (0.01 M HCl) streams were continuously pumped, each at a low flow rate of 1.5 ml min^{-1}. When a smooth baseline was observed the FI system was ready for calibration and sample analysis.

Standard solutions of methylmercury chloride (0.00, 0.010 and 0.020 μg Hg l^{-1}) were processed as for water samples and fluorescence signal responses for respective columns were used to generate a calibration graph. The peristaltic pump was then switched off to allow insertion of microcolumns (see Figure 1). The pump was then reactivated and when a smooth baseline occurred hydrochloric acid (0.5 ml, 3M) was injected to effect elution of retained mercury species.

Determination of dissolved inorganic mercury was based on direct injections of samples (0.5 ml) into the FI system (Figure 2) and calibration utilised inorganic mercury standard solutions (0.00, 0.10, 0.25 μg Hg l^{-1}).

RESULTS AND DISCUSSION

Prior to survey analysis, reliability of the measurement procedure was checked by analysing synthetic standard solutions of methylmercury chloride and spiked waters of the Manchester Ship Canal. The transient signals for processing the afore mentioned waters are shown in

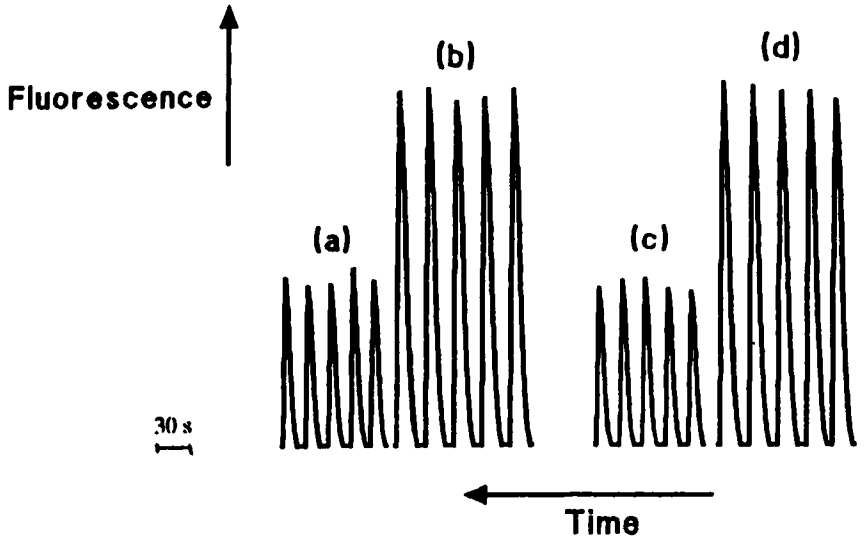

Figure 3. Typical transient signals for standard solutions and spiked waters: (a) 50 ng l–1 MeHgCl, (b) 100 ng l–1 MeHgCl, (c) 50 ng l–1 spike canal water and (d) 100 ng l–1 spike to canal water. Each transient signal correspond to elution of methylmercury from a separate microcolumn.

Table 1. Analytical data for standard solutions of methylmercury chloride using field sampling technique and FI-AFS.

Standard solutions, μg Hg l^{-1}	*Analysed Value, μg Hgl^{-1}*	*% RSD**
0.010	0.007	8.6
0.030	0.026	6.9
0.060	0.058	2.8

* No. of replicates, 10 (10 different microcolumns). Sample volume processed, 30 ml

Table 2. Recovery data for analysis of water of Manchester Ship Canal.

Sample	*Analysed Value, ng Hg l^{-1}*	*Recovery (%)*
Sample (unspiked), ng Hg l^{-1}	<0.002	—
Spiked sample (50 ng Hg l^{-1}	47.43±6.2	94.8±6.2
Spiked sample (100ng Hg l^{-1}	102.6±5.1	102.6±5.1

* No. of replicates, 5 (5 different microcolumns). Sample volume processed, 10 ml. Methylmercury chloride as spike.

Figure 3 and the corresponding analytical data are given in Tables 1 and 2. It is clear that the proposed sampling/FI-AFS measurement scheme is rapid, precise and sensitive and may offer a new and effective approach for determination of methylmercury in waters.

In the case of the Manchester Ship Canal the data of Table 3 reveal significant concentrations of mercury at all sampling stations, confirming the extensive contamination of the water course throughout the 20 km stretch examined. As one might expect, inorganic mercury constituted the major mercury fraction. Concentrations for organomercury were at the low ppt level except for stations 2, 3 and 4, where relatively high values (22–58 ng l^{-1}) were observed (a second survey confirmed elevated concentrations of organomercury at stations 2, 3 and 4). The fact that organomercury data did not correlate well with inorganic mercury data may have significance with respect to biogeochemical cycling/production pathways.

Table 3. Speciation data for mercury in Manchester Ship Canal.

Station	*Organomercury*, μg Hg l^{-1}*	*Inorganic mercury#, μg Hg l^{-1}*
1.	0.009±0.001	0.325±0.006
2.	0.022±0.003	0.320±0.019
3.	0.058±0.003	0.530±0.008
4.	0.035±0.003	0.250±0.017
5.	0.005±0.001	0.140±0.011
6.	0.004±0.001	0.495±0.001
7.	0.005±0.001	0.270±0.025
8.	0.006±0.001	0.265±0.160
9.	<0.002	0.245±0.020
10.	<0.002	0.045±0.004

*Data are mean values for 3 replicate analyses. # Data are mean values for 4 measurements derived from 2 separate column effluents. Uncertainty limits ± σ

It is generally accepted that a principle source of inorganic mercury contamination in the canal is derived from the operation of chloroalkali plants either through direct discharge of effluent containing mercury or from mobilisation of mercury from the bottom sediments. The latter is a known route for formation of methylmercury and the fact that organomercury data do not correlate well with inorganic mercury data does suggest an alternative production pathway may be operative. Apart from direct input from a point source, one possibility is an in-situ alkylation reaction. The surface waters in question (stations 2, 3, 4) are known to contain relatively high concentrations of alkyllead compounds and their distribution profiles [15] (stations 1, 2, 3, 4, 5) were noted to be similar to that obtained for organomercury in this study. This similarity implies that an in-situ alkylation reaction of the type:

$$Hg^{2+} + Me_3Pb^{+} \text{———} MeHg^{+} + Me_2Pb^{2+}$$

might be operating whereby there is a transfer of alkyl groups from alkyl lead to inorganic mercury. Such a possibility although demonstrated in the laboratory [13], and confirmed by ourselves, has to our knowledge, not been reported for environmental waters.

CONCLUSIONS

It is clear that the combination of microcolumn field sampling and flow injection-atomic fluorescence spectrometry provides an elegant yet powerful solution to the determination and speciation of mercury in environmental waters. The approach is extremely efficient both at the sampling and the measurement stages by virtue of the continuous flow/flow injection procedures. The microcolumn field sampling technique is being developed for use with other FI-based detection systems (eg. FI-IC-MS) and hyphenated techniques such as GC-atomic emission spectrometry[17], the latter allowing determination of individual organomercury species unlike the present methodology. Work is in progress to assess long term stability of the immobilised mercury species.

References

1. C. E. Oda and J. D. Ingle, *Anal. Chem.*, **53,** 2305–2309 (1981).
2. S. E. Birnie, *J. Autom. Chem.*, **10,** 140–143 (1988).
3. Wei Jian and C. W. McLeod, *Mikrochim. Acta*, **109,** 117–120 (1992).
4. Y. Talmi, *Anal. Chim. Acta*, **74,** 107–117 (1975).
5. K. Chiba, K. Yoshida, K. Tanabe, H. Haraguchi and K. Fuwa, *Anal. Chem.*, **55,** 450–453 (1983).
6. Y. H. Lee, *Intern J. Environ. Anal. Chem.*, **29,** 263–276 (1987).
7. *AOAC Official Methods of Analysis*, Arlington, USA, (1984) 146–152.
8. H. Emteborg, D. C. Baxter and W. Frech, *Analyst*, **118,** 1007–1013 (1993).
9. I. S. Krull, D. S. Bushee, R. G. Schleicher and S. B. Smith, *Analyst*, **111,** 345–349 (1986).
10. D. Beauchemin, K. W. M. Siu and S. S. Berman, *Anal. Chem.*, **60,** 2587–2590 (1988).
11. M. Filippelli, *Anal. Chem.*, **59,** 116–118 (1987).
12. Wei Jian and C. W. McLeod, *Talanta*, **39,** 1537–1542 (1992).
13. Y. H. Lee and H. Hultberg, *Environ. Toxicol. Chem.*, **9,** 833–841 (1990).
14. C. A. McAuliffe, *The Chemistry of Mercury* (William Clowes, London, 1987), 264 pp.

15. Unpublished Data, The National Rivers Authority, Warrington, UK.
16. A. G. Cox and C. W. McLeod, *Mikrochim. Acta*, **109**, 161–164 (1992).
17. M. L. Mena, C. W. McLeod, P. Jones, A. Withers., V. Minganti, R. Capelli and Ph. Quevauviller, *Microcolumn Field Sampling and GC-Atomic Emission Spectrometry for Mercury Speciation in Waters*, (Winter Conference on Plasma Spectromchemistry, San Diego, California, January 10–15, 1994) paper No. TP 40.