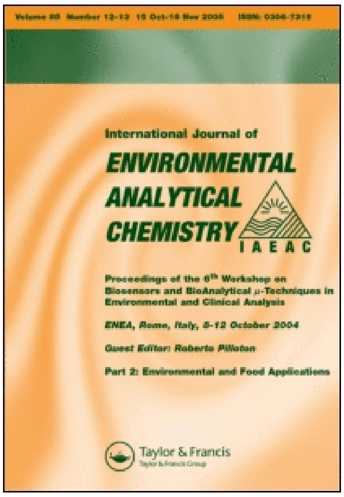

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An Instrumental Analytical Technique for Speciation of Atmospheric Mercury†

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Chemical speciation of toxic elements released into the environment is of fundamental importance in understanding their environmental behaviour and ultimate fate, as well as in assessing their ecotoxicity and associated human health risks. This paper describes the research and development activities culminating in an instrumental analytical methodology for speciating several volatile forms of mercury in the atmosphere: elemental mercury; mercuric chloride; methylmercuric chloride; and dimethyl mercury. The noble metals, silver and gold, as well as numerous chemically impregnated or untreated sorbent materials (including several special chromatographic supports) were evaluated to determine their collection efficiency, release characteristics, and selectivity, with respect to the candidate mercury species. On the basis of these laboratory tests, the materials ultimately selected for sequential collection of the four mercury species were Chromosorb W treated with hydrochloric acid vapour, Tenax GC, Carbosieve B, and gold wire. Pyrolysis was employed to convert the mercury compounds to elemental mercury for the purpose of detection and quantification by resonance atomic fluorescence spectrophotometry.

KEY WORDS: Mercury, atmospheric mercury, speciation, ecotoxicity, pyrolysis, resonance atomic fluorescence spectrophotometry, AAS.

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INTRODUCTION

Several ecologically important metals (lead, mercury, tin) and trace elements (arsenic and selenium) exist in various inorganic as well as organometallic forms, or species, in nature.[1-3] However, most of the instrumental techniques employed in environmental trace metal analysis provide only a total metal value for the element(s) of interest in the sample, be it air, water, soil, sediment or biological tissue. As a result, there is a sparsity of data regarding the specific chemical forms in which toxic trace elements exist in different compartments of the ecosystem. Once released into, or mobilized in, the natural environment their dynamic behaviour, toxicity and ultimate fate are strongly dependent upon the physical, chemical and biological properties of the individual species emitted, mobilized or subsequently formed via chemical transformation processes. This is especially true in the case of mercury, since its environmental behaviour and toxicity to biota are strongly dependent upon the particular chemical form under consideration.[4,5]

Because of the volatility of elemental mercury and many of its chemical compounds, the atmosphere plays a major role in the cycling of this element through the environment.[6] Despite this fact, in comparison with the scientific data base for mercury in aquatic and terrestrial ecosystems, relatively little definitive information exists regarding typical atmospheric concentration ranges, the relative distribution between vapour and particulate phases, and the individual chemical forms of atmospheric mercury in urban, rural and remote locations. Owing to the small amounts of this contaminant generally encountered in ambient air, at least at locations beyond the direct influence of major industrial or natural sources, the determination of mercury in the atmosphere falls into the realm of trace analysis. Such measurements are thus subject to the formidable difficulties, precautions and limitations of this area of analytical chemistry.[7,8] To produce meaningful and valid experimental data from which to derive a better understanding of the atmospheric pathways for mercury, it is necessary to have reliable instrumentation, methodologies and techniques for sampling and analysis of the major forms of atmospheric mercury. This points to a need for a field-portable instrument with speciation capabilities.

The objective of this paper is to describe salient features of the research and development efforts resulting in the design, testing and fabrication of a mercury monitoring system capable of quantitatively collecting and analyzing the principal gaseous species of airborne mercury. Other aspects of this work have been reported previously.[9–11] For this project, two inorganic and two organometallic mercury species were selected: elemental mercury, mercuric chloride, methylmercuric chloride and dimethyl mercury. This selection was based on previous investigations relating to speciation of mercury in ambient air.[12–18] The following operating and performance criteria were established for the vapour-phase mercury sampling system at the outset of this investigation: (a) quantitative collection and retention of the four mercury species during the sampling period; (b) maintenance of sample integrity and stability prior to the analytical determination; (c) efficient separation/resolution of the individual mercury species on the selected substrates; (d) quantitative release (desorption) of mercury species collected on the individual substrates; (e) compatibility of the sampling procedure with the detection system of choice (resonant atomic fluorescence spectrophotometry).

EXPERIMENTAL METHODS AND RESULTS

Selection of specific sorbents

In 1974, Braman and Johnson[13] described a novel technique for collecting four types of mercury species from ambient air. They passed the air through a series of 4 absorption tubes each of which was intended to retain one of the species of interest. The packing materials used by these workers were: (i) Chromosorb-W treated with hydrochloric acid vapour; (ii) Chromosorb-W treated with sodium hydroxide (0.05 M); (iii) glass beads coated with a thin film of silver, and ; (iv) glass beads coated with a thin film of gold. These sorbents were reported to selectively collect inorganic "mercuric chloride-type" compounds, organometallic "methylmercuric chloride-type" compounds, metallic mercury and dimethyl mercury, respectively. Prior to the initiation of the investigations reported here, it had come to our attention[19] that attempts by other scientists to reproduce this work had met with limited success. It was thus decided at the start to evaluate the specificity and collection/release properties of sorbents prepared according to the procedures published by Braman and Johnson.

The experimental set-up used for the evaluation studies described here is illustrated in Figure 1 in the form of a simplified schematic diagram. The apparatus consisted of: a borosilicate glass sample injection port fitted with a gas chromatographic-type septum; the candidate sorbent material contained in a quartz tube (between quartz wool plugs); a pyrolyzer (to release elemental mercury from the combined forms) located downstream of the specific sorber tube; a gold trap (to collect the elemental mercury and subsequently release it as a narrow plug into an inert carrier gas stream); and a cold vapour mercury detector (Laboratory Data Control, Milton Roy Co., Riviera Beach, FL) which measures the absorbance of 253.7 nm radiation by ground-state mercury atoms in the vapour phase. The detector was calibrated before and after each set of experiments using a procedure similar to that previously described by Long *et al.*,[20] Slemr *et al.*,[21] and Schroeder.[22]

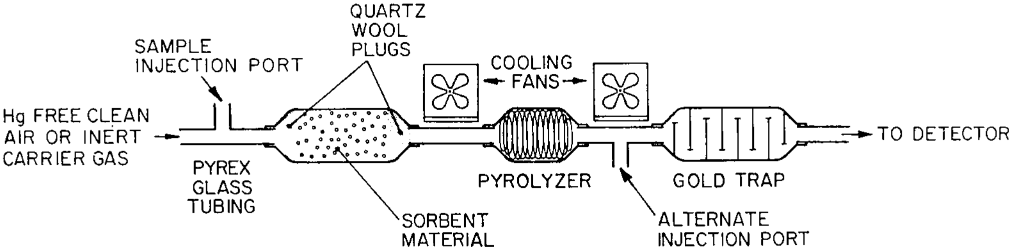

FIGURE 1 Schematic of apparatus for evaluation of candidate sorbent materials.

The selectivity of the sorbent materials towards the mercury species of interest as well as their combined collection and desorption efficiencies were established as follows. Known amounts (in the nanogram range) of the various mercury species in the gaseous state were slowly introduced over periods of 10 to 30 minutes (approximating the length of an ambient air sampling cycle) into a clean, mercury-free air stream flowing at a rate of 500 mL/min through the quartz tube containing the sorbent material being examined. The test substance passing through the sorbent bed was collected on the gold trap downstream of the pyrolyzer assembly. The amount passed was measured at the end of each test by raising the temperature of the gold trap to 450°C, thus releasing the mercury into a stream of inert carrier gas (nitrogen or argon) which entered the sample cell of the detector. Following this step, the material collected by the sorbent under investigation was thermally desorbed into the carrier gas stream (500 mL/min flow rate) for quantitation in the same manner as before.

The experimental results from these tests are summarized in Table I. It can be seen that Chromosorb-W (HCl) and Chromosorb-W (NaOH) passed virtually all of the elemental mercury (Hg°) and dimethyl mercury (DMM) vapour, while both silver-coated and gold-coated glass beads completely retained both species. The findings for Hg° are in agreement with the earlier work,[13] but not those for DMM which was reported to be retained only on the gold-coated glass beads. As anticipated from the work of Braman and Johnson, Chromosorb-W treated with HCl displayed a high collection efficiency (97%) for mercuric chloride (MC) and the other three

TABLE I

Collection of mercury species on sorbents prepared according to Braman and Johnson.[13]

Sorbent	Collection and release efficiency (%) MC	MMC	Hg°	DMM	Observations/ Comments
Chromosorb-W (HCl)	97	5	2	0	High selectivity and sampling efficiency for MC
Chromosorb-W (NaOH)	100	46	0	0	Medium selectivity and poor sampling efficiency for MMC
Silver-coated glass beads	100	100	100	100	No selectivity but high sampling efficiency
Gold-coated glass beads	100	100	100	100	

Diameter of quartz sorber tubes: 15 mm o.d.; 13 mm i.d.
Length of sorbent bed: 8 cm for Chromosorb-W
4 cm for coated glass beads.
Flowrate of air = 500 mL/min; room temp. (20—22°C).

sorbent materials also retained this compound quantitatively. However, with respect to methylmercuric chloride (MMC) they reported that Chromosorb-W (NaOH) quantitatively collected this substance, while our study resulted in a collection efficiency of only 46%.

Based on these investigations, Chromosorb-W (HCl) is satisfactory for separating mercuric chloride from elemental mercury and the two organomercury species.

However, sorbent materials other than Chromosorb-W (NaOH) and silver-coated glass beads should be utilized to effectively separate and collect the latter three mercury species. Table II provides information on tests conducted as part of this study to evaluate other potential sorbents for the selective pre-concentration and quantitative determination of Hg°, MMC and DMM. Of the ten materials screened, two were subsequently selected for further testing on the basis of the experimental results and consideration of other factors such as commercial availability, purity and consistency, useful lifetime, potential for regeneration, thermal stability and suitability for ambient air measurements. The 2 sorbents chosen from this group were: Carbosieve-B (a granulated form of activated charcoal) and Tenax-GC (a porous polymer chromatographic column material based on 2, 6-diphenyl-*p*-phenylene oxide).

Concentration and separation of vapour-phase mercury species.

The experiments described in the previous section led to the selection of four candidate sorbent materials showing the greatest potential for efficiently collecting, and subsequently releasing for detection, the mercury species of interest. Table III describes the sequential collection and separation scheme adopted for the speciation of vapour-phase mercury in ambient air.

Based on this scheme, a prototype atmospheric mercury speciation train was designed and fabricated. Design considerations included: (a) scaling up the size of collector tubes used previously to permit at least a ten-fold increase in the sampling flowrate compared to that used in the initial tests (viz. 500 mL/min); (b) independent temperature control of each of the 4 collector tubes, and; (c) capability of operating the speciation train in either a manual or an automatic

TABLE II

Screening of other potential sorbent materials for speciation of mercury (Hg°, MMC and DMM).

Sorbent material	Collector dimensions I.D. × length (mm)	Collection and release efficiency (%)			References[a]
		Hg°	MMC	DMM	
Silver wool	6 × 60	100	100	100	Long *et al.*[19]
Silver wire	6 × 30	100	5	4	Henriques and Isberg[15]
Silver-coated Chromosorb-P	13 × 40	100	100	100	Trujillo and Campbell[17]
CdS-treated Chromosorb-W	13 × 80	100	61	64	Christie *et al*[18]
Copper wire	6 × 30	100	44	52	Henriques and Isberg[15]
Au-Pt alloy	6 × 30	100	71	—	Henriques and Isberg[15]
Au-Si alloy	6 × 30	44	32	20	Henriques *et al.*[14]
Carbosieve-B	13 × 25	100	100	100	Trujillo and Campbell[17]
MSA charcoal	6 × 60	100	100	100	Barringer Magenta Ltd.[24]
Tenax-GC	13 × 10	0	100	100	Barringer Magenta Ltd.[24]

Test conditions: Air flowrate = 500 mL/min; room temperature (20–22°C).

[a] References to be consulted on source, preparation and/or pre-treatment of sorbent materials.

TABLE III

Vapour-phase mercury collection and separation scheme.

Specie collected	Collecting substrate	Residual specie(s)[a]
Mercuric chloride (MC)	Chromosorb-W (HCl)	Hg°, MMC, DMM
Methylmercuric chloride (MMC)	Tenax-GC	Hg°, DMM
Dimethyl mercury (DMM)	Carbosieve-B	Hg°
Elemental mercury (Hg°)	Gold wire	—

[a] *Specie(s) passing through the specific collector(s) and remaining for subsequent collection.*

fashion. Sampling flowrate and temperature of the sorbent materials during the sampling cycle are crucial parameters influencing the capacity, collection efficiency and selectivity of the collection tubes comprising the speciation train.

Using the prototype unit, tests were conducted to optimize the selectivity and collection as well as release efficiency of each of the four sequential collectors. This was achieved by adjusting the sampling flowrate through the speciation train, the physical dimensions of each collector tube, the temperature of the sorbent bed during the sampling period and the parameters for desorption (temperature and time). As a result of the information derived from these tests, the second collector (Tenax GC) and the fourth collector (gold wire coil) are maintained at room temperature during the sampling sequence, whereas the first collector (acid-treated Chromosorb-W) and the third collector (Carbosieve-B) are maintained at 180°C. For the purpose of efficiently desorbing the mercury species collected on the various sorbent materials employed in this scheme, elevated temperatures ranging from 250°C to 450°C are maintained for either 5 or 10 minutes depending upon the specific collector. The physical dimensions, thermal parameters and operating conditions of the collector tubes in the mercury speciation train, which resulted from the system optimization process at a sampling flowrate of 8 L/min, are displayed in Table IV.

TABLE IV

Physical dimensions, thermal parameters and operating conditions of mercury speciation train collector tubes.

Collector number	Dimensions I.D. × length (mm)	Specie retained	Collection temp. (°C)	Desorption Temp. (°C)	Desorption Time (min.)
1	15 × 40	$HgCl_2$	180	250	10
2	15 × 50	CH_3HgCl	25	300	10
3	15 × 5	CH_3HgCH_3	180	300	5
4	6 × 60	Hg°	25	450	5

Flowrate during sample collection step = 8 L/min.
Flowrate during sample desorption step = 0.3 L/min.

Detection of mercury compounds

The atmospheric mercury speciation train described here is intended for use with either a cold vapour atomic absorption (AA) or atomic fluorescence (AF) spectrophotometer as the detector of choice, although other types of detectors (e.g. plasma emission or mass spectrometric detectors) could conceivably be used also.

Both of the first two detectors make use of the "cold vapour resonance atomic absorption principle" by which elemental mercury vapour strongly absorbs (and re-emits via a resonance phosphorescence process[23]) electromagnetic radiation at a wavelength of 253.7 nm. Compounds of mercury, however, are transparent to ultraviolet light of this wavelength. As a corollary, an atomic fluorescence detector operating at $\lambda = 253.7$ nm will respond to metallic mercury vapour, but not to the other mercury species of interest here.

The key to the analytical determination of all the mercury species of environmental interest by either cold vapour AAS or AFS lies in the application of pyrolysis. Pyrolytic decomposition of mercuric chloride, methylmercuric chloride and dimethyl mercury liberates elemental mercury vapour— the species which can be readily determined by the aforementioned techniques.

Investigations were conducted to establish the experimental conditions required for efficient pyrolysis of the three mercury compounds mentioned previously. For these experiments, crushed quartz chips (10–20 mesh size fraction) were packed into a quartz tube having an inside diameter of 9 mm and a length of 150 mm and fitted with ball and socket joints at the ends. The 7.5 cm long section of inert packing material (quartz chips) was held in place with quartz wool plugs. The pyrolysis tube was first wrapped with asbestos insulation, then 30 turns of nichrome wire (0.4 mm diameter), and finally covered with split pipe insulation (25 mm i.d. and 75 mm o.d.). Using a Variac power supply, this pyrolyzer unit could be heated to greater than 1100°C at a setting of 30 volts. Temperatures were measured with a type K thermocouple inserted between the insulation layers.

Pyrolysis data were obtained by sending the mercury species, contained in an argon stream at a flowrate of 500 mL/min, through the pyrolyzer at various temperatures. The outlet end of the pyrolysis unit was connected directly to the mercury monitor for these tests. The effect of pyrolyzer temperature on the magnitude of the detector signal (and hence the pyrolysis efficiency) was obtained for replicate injections of similar amounts of the test species. Experimental results from these pyrolysis tests are presented graphically in Figures 2–4. From these figures it can be seen that, for the pyrolyzer configuration and conditions employed here, dimethyl mercury is completely dissociated at 500°C, whereas methylmercuric chloride requires a temperature of 700°C and mercuric chloride a temperature of 900°C for complete conversion to elemental mercury. In designing the final pyrolysis unit for incorporation into the atmospheric mercury speciation train, an operating temperature of 900°C was used.

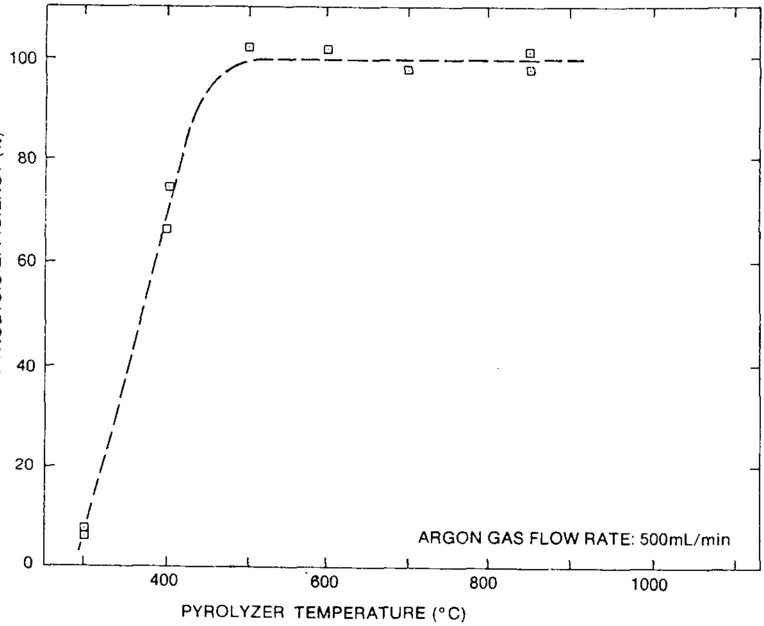

FIGURE 2 Pyrolysis data for dimethyl mercury.

Mercury speciation system

Employing the concepts and experimental results described previously, an atmospheric mercury monitoring system with speciation

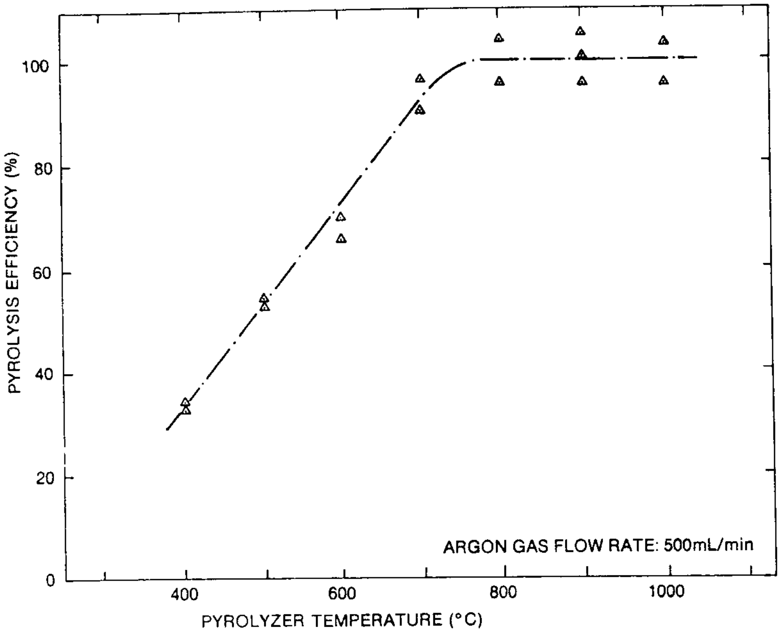

FIGURE 3 Pyrolysis data for methylmercuric chloride.

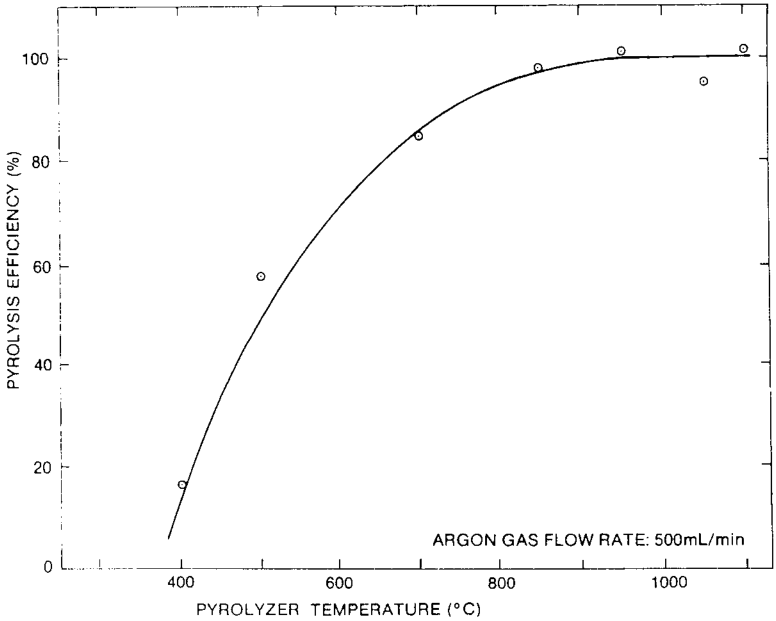

FIGURE 4 Pyrolysis data for mercuric chloride.

capabilities was designed and fabricated. The front end of this modular instrumental system consists of the mercury speciation train. Figure 5 shows a simplified flow schematic for this unit. Ambient air, after passage through a micro-quartz fibre filter to remove suspended particulate matter, flows through the four collector tubes arranged in tandem, subsequently through a flow meter, and is then expelled through an electro-mechanical pump. At the conclusion of the sampling cycle the inflow of ambient air is terminated, each of the collector tubes is isolated by solenoid valves, and purified argon gas is passed through each of the four collectors in turn while the temperature of each one is raised to its pre-selected value. During the desorption cycle, the carrier gas flow is in the opposite direction to that of the sampling flow, thus taking advantage of the elegant chromatographic practice of "back-flushing."

As shown in the flow schematic, a "gold-trap" is situated between the pyrolyzer and detector assemblies. This gold wire serves two functions: (a) it collects and pre-concentrates the elemental mercury vapour coming from the pyrolyzer, and; (b) upon heating, it quickly and reproducibly introduces the analyte to the detector for quantitation.

Both during the development of the prototype unit and prior to fabrication of the final instrumental system, the mercury speciation train and ancillary equipment were subjected to a comprehensive electronic, mechanical and chemical testing and evaluation phase in the laboratory. The results from a series of five replicate experiments conducted on the final speciation train assembly are presented in Table V. For these experiments, gaseous mixtures containing known quantities (a few nanograms each) of elemental mercury, methylmercuric chloride and dimethyl mercury in air were slowly introduced at the inlet of the speciation train which was sampling an otherwise mercury-free clean air stream at a flowrate of 8L/min for a duration of 10 minutes. Mercuric chloride was not one of the constituents of this synthetic test mixture due to problems encountered at that time in reproducibly generating accurately known quantities of mercuric chloride vapour in air. However, our previous experiments as well as the work of Braman and Johnson[13] have established that, of the four mercury species of interest, treated Chromosorb-W (the first collector in the speciation train) retains only mercuric chloride with a high efficiency ($\geq 97\%$) and allows the

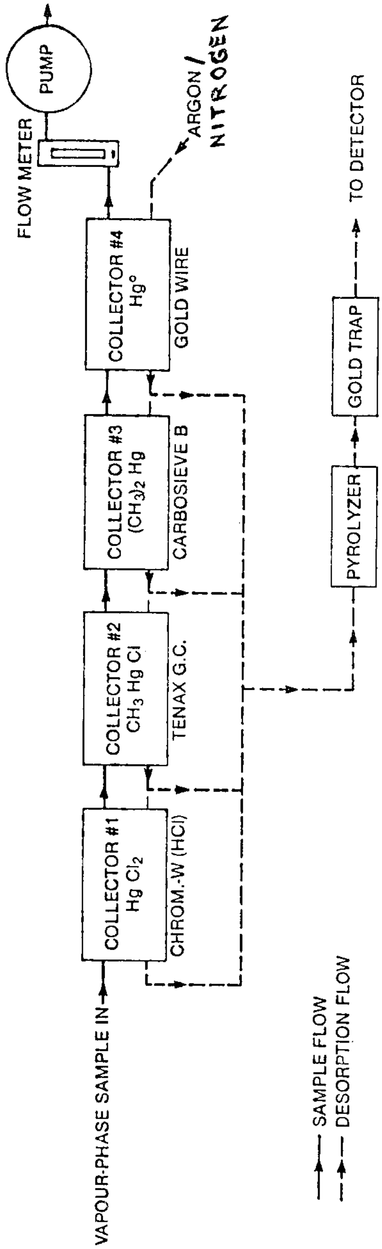

FIGURE 5 Simplified flow diagram for atmospheric mercury speciation train.

TABLE V

Laboratory testing and evaluation of mercury speciation train—experimental results.[a]

Test no.	Amount of mercury measured on each collector (ng Hg)[b] No. 1 MC	No. 2 MMC	No. 3 DMM	No. 4 Hg°	Total amount (ng Hg)
1	0.06	1.9	1.2	2.8	6.0
2	0.04	2.0	1.2	3.2	6.4
3	0.05	1.8	0.9	3.0	5.8
4	0.06	2.0	1.2	2.8	6.1
5	0.07	2.1	1.0	3.2	6.4
Mean value	0.06	2.0	1.1	3.0	6.1
Std. Dev.	0.01	0.1	0.1	0.2	0.3
expected[c]	0	2.1	1.1	3.1	6.3
Recovery (%)	—	95	100	97	97

[a] At a sampling flowrate of 8L/min air for 10 min duration; other conditions as given in Table IV.

[b] Results are corrected for sampling and analytical blank values.

[c] Based on replicate injections ($n=5$) of a synthetic mixture containing known amounts of three mercury species.

[d] (Mean value/expected value) × 100.

other 3 mercury species to pass by for subsequent collection by the other substrates. At the end of the 10-minute sampling cycle, each of the four collectors in the speciation train were heated sequentially (starting with collector number four) to desorb and hence determine the amount of mercury retained on each one.

The information contained in Table V demonstrates the effectiveness of the speciation train with respect to separation and quantitation of the mercury species under investigation. The overall recovery efficiency of this system (a composite parameter including selectivity as well as the efficiencies for the adsorption and the desorption processes) under controlled laboratory conditions lies in the 95% to 100% range for the mercury species tested. The speciation train coupled with an atomic fluorescence detector (Barringer Research Inc., Toronto) has been successfully tested and evaluated under a variety of field conditions in and around metropolitan Toronto. Description of this work and discussion of the results from

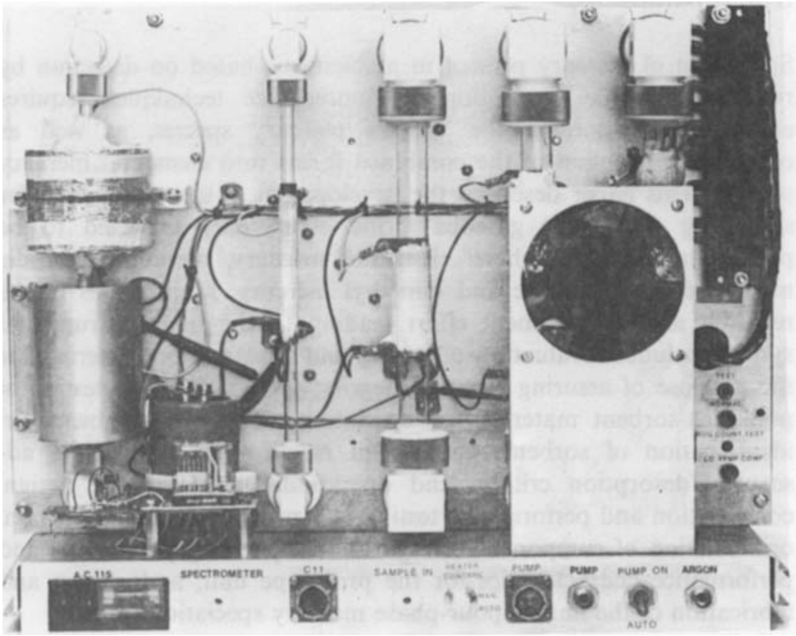

FIGURE 6 Mercury speciation train module (rear view).

these field tests are beyond the scope of this paper. Figure 6 is a view of the speciation train as seen from the rear and Table VI gives the design specifications and operating parameters for this unit.

TABLE VI
Equipment specifications and operating parameters for mercury speciation train.

Collector tubes/materials	— see Tables III and IV
Air sampling flowrate	— $\leqq 8$ L/min
Desorption flowrate	— 0.3 L/min
Pyrolysis temperature	— 900°C
Pyrolysis efficiency (at 0.3 L/min)	— 100% for mercury compounds tested
Pump capacity required	— 8 L/min at 380 mm Hg vacuum
Electrical requirements	— 100 V a.c.; 950 W max.
Physical dimensions (cm)	— 38 H × 51 W × 46 D
Weight (kg)	— 31.5

SUMMARY

Speciation of mercury present in ambient air based on detection by resonance atomic absorption or fluorescence techniques requires efficient separation of the various mercury species, as well as complete conversion of the combined forms into elemental mercury vapour. This paper describes the development of a methodology for speciating the major gaseous forms of mercury expected to be present in the atmosphere: elemental mercury, mercuric chloride, methylmercuric chloride and dimethyl mercury. Major steps in the research and development effort leading to the final instrumental system included: evaluation of tubing and construction materials for the purpose of assuring sample integrity; preparation and testing of potential sorbent materials for speciating mercury in ambient air; identification of sorbents capable of meeting the established adsorption/desorption criteria and operational requirements; design, construction and performance testing of a prototype speciation train; optimization of component configuration, operating parameters and performance characteristics for the prototype unit, and; design and fabrication of the final vapour-phase mercury speciation train.

Laboratory tests were carried out to determine the collection efficiency, release characteristics, and selectivity of the noble metals silver and gold (in different physical forms) as well as numerous chemically treated or untreated sorbent materials (including several special chromatographic supports) towards the four mercury species. Performance characteristics of various candidate sorbent materials were evaluated in detail. The chromatographic-type sorbents ultimately selected were Chromosorb-W, Tenax GC and Carbosieve-B.

Pyrolysis is the method of choice for converting mercuric chloride and the two organomercury compounds to elemental mercury for quantitation by resonance atomic absorption/fluorescence spectrophotometry. Data are presented from tests which were conducted to establish the experimental conditions and pyrolyzer configuration necessary for complete conversion of environmentally pertinent mercury compounds to the elemental form. Also, a description is given of the mercury speciation train and associated equipment which was designed and built as a result of the research and development program described herein.

Acknowledgements

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