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The Capillary Cold Trap as a Suitable Instrument for Mercury Speciation by Volatilization, Cryogenic Trapping, and Gas Chromatography Coupled with Atomic Absorption Spectrometry

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An innovative accessory for speciation analysis has been developed. The system is based on the combination of cryogenic trapping and gas chromatographic separation, carried out within the same capillary. The instrument, hyphenating derivatization, gas-phase extraction, preconcentration, and analyte separation, is semiautomated, and all operational parameters are adjustable via an in-house-developed control unit, which regulates the selected parameters throughout the analysis process. Species detection was carried out by atomic absorption spectrometry. The detection limits achieved were 33, 39, and 71 ng L^{-1} for dimethylmercury, methylmercury, and inorganic mercury, respectively. A complete chromatogram could be obtained within three minutes, resulting in the duration of one whole analysis cycle of about 15 min. The proposed method was applied to mercury speciation in freeze-dried tuna fish powder after microwave-assisted extraction, finding that mercury is present at 80% as methylmercury and about 20% as inorganic mercury, in this kind of biological material.

Mercury is a well-known toxic element from which, yearly, about 10 000 tons[1] are released into the environment by human activities. Since the fatal Minamata bay[2] accident, it is well-known that inorganic mercury can be transformed by microorganisms into the fat soluble and much more toxic methylmercury which again enters the human food chain, especially by accumulation in fish[3] tissue. This explains the rising interest in species-selective determination of mercury since Westöö[4] made the first extraction and separation methods for methylmercury in biological material available. Particular emphasis has been put on analytical techniques which allow the simultaneous determination of inorganic mercury and organic compounds such as $MeHg^+$ or Me_2Hg. A number of methods have been developed, mostly based on derivatization of the analyte by hydride formation or ethylation coupled to gas chromatography and detection with atomic absorption[5−7] (AAS), fluorescence[8−10] (AFS), ion coupled plasma mass spectrometry[11,12] (ICPMS), or microwave induced plasma atomic emission spectroscopy[13−15] (MIP-AES). Besides the conventional GC, preconcentration and separation of the analyte by cryogenic trapping[16−19] became popular. Here, a silanized quartz tube filled with a chromatographic material was immersed into liquid nitrogen, and desorption was carried out by electric heating, thus avoiding the use of a quite voluminous chromatographic oven as well as interferences caused by the need of injecting the sample together with a volatile organic solvent. But even these systems suffer several drawbacks, such as relatively high dead volume, the impossibility of controlling either the trapping temperature or the heating rate during desorption, resulting in peak broadening and unsatisfactory reproducibility. Recently, an accesory for mercury speciation has been described[20] which uses cryofocusing within a capillary as the sample introduction device for a multicapillary column followed by detection with ICPMS.

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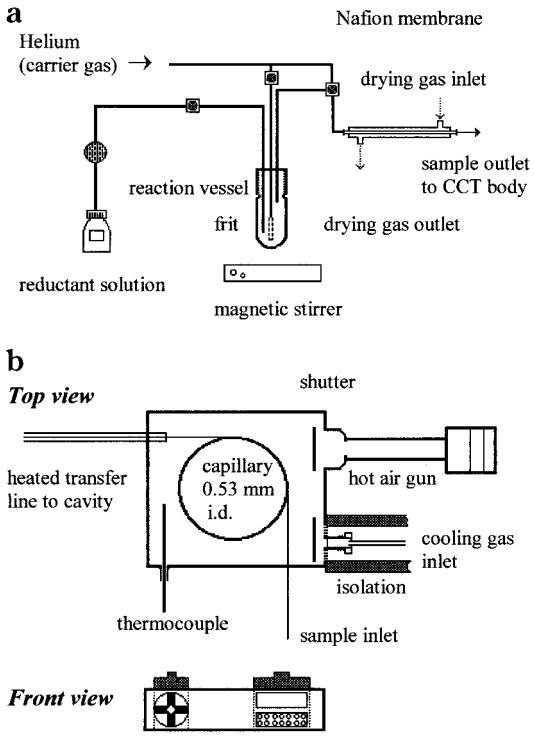

Figure 1. (a) Block scheme of the purge system; (b) schematic diagram of the CCT body.

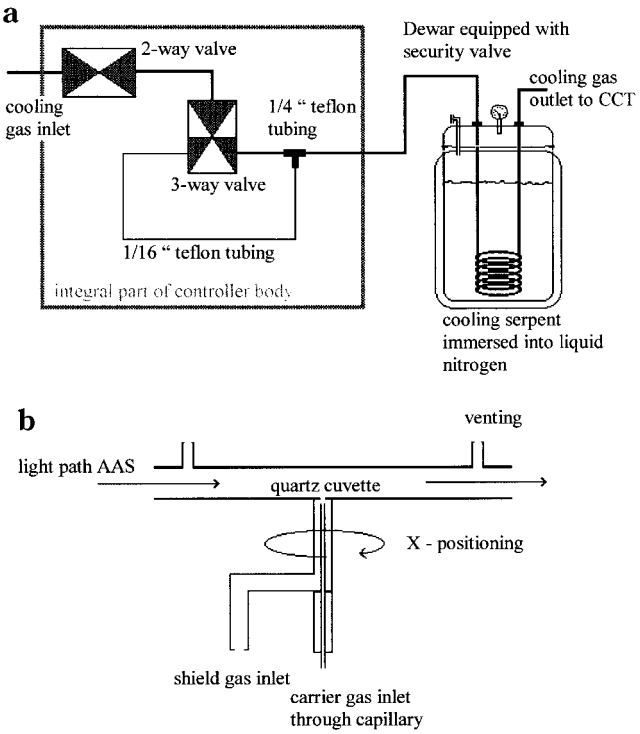

Figure 2. (a) Setup of the nitrogen precooling system; (b) special designed quartz cuvette used for AAS detection.

In this paper, a laboratory-built capillary cold trap system is presented and optimized for mercury speciation using AAS detection. The instrument is based on the idea of performing trapping and separation within the same capillary. The device hyphenates a derivatization and gas-phase extraction step with a cryogenic trap and gas chromatographic separation module from where the analyte is led through a heated transfer line into the quartz cell of the AAS instrument. All instrumental parameters, such as valve positions, trapping and desorption temperature, heating rate, and transfer-line temperature are controlled by an in-house-developed control unit.

EXPERIMENTAL SECTION

Instrumentation. The purge system is schematically shown in Figure 1a. It consists of a 30-mL reaction vessel equipped with a purge head containing reagent and a carrier gas inlet as well as an outlet for the analyte-loaded carrier gas. The carrier gas could be switched off-line by the means of two electromagnetic valves; a third one controls the reagent inlet of $NaBEt_4$ solution. The latter could be added by the means of a peristaltic pump or be added manually by using a syringe. In the on-line mode, carrier gas enters the reaction vessel through a frit and is swept through a Nafion dryer membrane (Permapure, MD-110−12FP) toward the CCT module.

The Capillary Cold Trap (CCT) module is presented in Figure 1 b. It consists of a 10 × 10 × 4 cm brass box, containing a round capillary cage and housed in a stone wool isolated receptacle. For the inlet from the purge side a stainless steel $^1/_{16}$−$^1/_{31}$-in. adapter is soldered to the brass box while the outlet to the transfer line consists of a Teflon piece housing a low dead volume capillary union (Supelco, Madrid, Spain). Temperature control in the CCT is carried out by a K-type thermocouple placed behind the capillary and connected to the controller unit. A manipulated 2000 W hot air gun (PHG 600-2 CE, Bosch, Germany) is placed beside the inlet of the precooled air stream; both inlets are equipped with shutters in order to close the hot-air inlet during the trapping step and the Swagelock connection of the cooling system during desorption. The transfer line, housing the capillary used as interface, consists of a $^1/_8$-in. copper tubing, surrounded by 220 V resistance wires and an attached thermocouple for temperature control.

The precooling system is shown in Figure 2 a. It is based on cooling an air stream by passing it through a cooling serpent placed into a Dewar filled with liquid nitrogen. The Dewar is equipped with a security valve to prevent accidents in case of overpressure; the gaseous nitrogen produced by the precooling process is released into the atmosphere. The trapping temperature is controlled with dedicated electronics by regulating the air stream passing into the Dewar. This is done by switching two electromagnetic valves passing the incoming air either through a $^1/_{16}$-in. Teflon tubing or through a $^1/_4$-in. tubing toward the Dewar, depending on the readout voltage of the thermocouple. The line leaving the Dewar is isolated until the CCT body and the cool air leaving the CCT is led in countercurrent toward the Dewar in order to provide precooling of the line. By this setup, the liquid nitrogen consumption, compared with that for a similar cooling system described elsewhere,[18] could be drastically reduced. The liquid nitrogen consumption is about 0.6 L per cooling cycle (see Table 1). The system allows the CCT to cool down from room temperature to aproximately −160 °C within three minutes.

The controller has one setup mode in which the user can select trapping and desorption temperature by means of a setpoint controller. In the trapping mode, the controller starts actuating cooling the CCT and holding the temperature until switched into

the desorption mode. The air stream of the hot air gun actuating in this mode as well as the potentiometer position affecting the heatup velocity are adjustable. Actual and destination temperatures of trapping and desorption are visualized on a screen, while a second screen shows the transfer-line temperature; the latter can be adjusted by manipulating the output voltage to the resistance wires. The capillaries used for the trapping column and the transfer line were fused silica capillaries with an i.d. of 0.53 mm, purchased from Supelco. Two types were tested, one deactivated and another one with a stationary phase containing 95% dimethylpliysiloxane and 5% diphenylpolysiolxane.

The AAS instrument used in this work was Perkin-Elmer atomic absorption spectrometer 1100 B run in the Scan mode. The light source was a Hg hollow cathode lamp mantained at 5 mA. The analytical response was recorded with an Epson FX850 printer, and data evaluation was carried out manually using the printed chromatograms. The system was equipped with a special quartz cell, presented in Figure 2b, to improve the sensitivity of mercury detection, mainly by providing a considerably more stable baseline. This cell had a venting at each end and a design in which the shield gas was mixed with the analyte loaded carrier gas directly in the part of the cell which is positioned in the light path of the instrument.

The microwave sample preparation system used for extraction of mercury species from tuna fish powder was a CEM Corp. (NC) model MSP 100, working at 2.45 GHz with a nominal maximum power of 1000 W, allowing temperature as well as pressure control during sample preparation.

Standards and Reagents. Sodium tetraethylborate ($NaBEt_4$) was obtained from Strem Chemicals. The reagent was manipulated under an argon atmosphere to prevent degradation; 0.2% (m/v) aqueous solutions were prepared every 8 h and stored at 0 °C until used. The acetate buffer solution was prepared by dissolving 1 M of sodium acetate in water and adjusting the pH to 4 with acetic acid. An aqueous solution of tetramethylammonium hydroxide (TMAH) was purchased from Fluka. A 1000 mg L^{-1} stock solution of inorganic mercury was prepared by dissolving 135.35 mg of $HgCL_2$ (Carlo Erba) in 100 mL of 5% sub-boiling hydrochloric acid. Methylmercurychloride (MeHgCl) was purchased from Alfa, and a 1000 mg L^{-1} stock solution was prepared by dissolving 125.16 mg of the reagent in 50 mL of methanol and 50 mL of 2% nitric acid. Dimethylmercury (Me_2Hg) was obtained from Sigma Aldrich, and a 1000 mg L^{-1} stock solution was prepared by dissolving 115 mg in 100 mL of the solvent used for MeHgCl. All standard solutions were stored at 4 °C. Aliquots of the stock solutions were then diluted to the desired concentration. Deionized water was obtained from a Millipore (Bedford, MA) ZMFQ 23004 Milli-Q water system. Helium, argon, and nitrogen were obtained from Carburos Metalicos. The purity of helium and argon gases was 99.99%.

Safety note: Organic merury compunds are extremely highly toxic. Especially hazardous is dimethylmercury, a flammable and volatile liquid with teratogen properties. Further, it can cause neurological damage as well as kidney malfunction. Direct contact with the skin can lead to death. Precautions and adequate clothing are absolutely necessary when manipulating the reagent. Preparation of the stock solutions has to be carried out in a flow box to avoid inhalation, wearing adequate clothing, gloves, and protective glasses. Working standards should be low-concentration, i.e., 1 μg L^{-1}.

EXPERIMENTAL SECTION

Measurement with the CCT Device. A total sample volume of 25 mL was placed in the purge vessel and the vessel closed. After selecting the trapping and desorption temperature, the cooling process was started by switching the controller into the "Trap" position. Reaching the destination temperature, the system was held at this temperature an additional "precooling time" of one minute. During this time, 0.5 mL of 0.2% $NaBEt_4$ solution was added to the reaction vessel and then the purge process was started by switching two electromagnetic valves from the controller. By this procedure, the helium carrier gas stream was led through the purge vessel, passing the dryer membrane, and the analytes were trapped in the CCT device. After purging for seven minutes, the reaction vessel was switched off-line and could be used for preparing the subsequent sample, in the same moment detection was started. In the following 30 seconds, the carrier gas flow was reduced to the value applied for desorption, the shutter of the cooling gas inlet closed, the one for the hot-air gun opened, and then desorption started by switching the controller into "Desorption" position. Desorption started by heating the trap with an ambient-temperature air stream of 500 L min^{-1} for 30 seconds, then the controller was switched to a 300 L min^{-1} hot air stream with a heating rate dependent on the potentiometer position. A summary of the operating conditions for the CCT-AAS optimized for the current configuration and type of analyte system is given in Table 1. After recording the chromatogram, the conroller was switched into "Reset" position, which allowed a change of theinstrumental parameters and a cooling of the system before it was used for the next cycle. The overall time needed for one cycle, including precooling, purge, separation, recording of the chromatogram, and preparing the system for the following analysis, is about 15 min. An example chromatogram, obtained under optimized conditions, for 5 ng of each of Me_2Hg, MeHg, and Hg, is presented in Figure 3. Note that the chromatographic peaks of methylethylmercury and diethylmercury correspond to methyl- and inorganic mercury, respectively, while dimethylmercury passes the derivatization step unaltered.

Biological Material Extraction. The fish tissue sample used in this study was dried tuna fish powder (Aquacon Sub-Project 2, no. 9/97, T30). For extraction and separation of the mercury species, open-focused microwave-assisted digestion has been chosen, as this technique provides several advantages compared with conventional methods such as the use of potassium bromide and sulfuric acid saturated with copper(II) sulfate or steam distillation, especially in terms of time consumption and possible losses of methylmercury. A comparative study[17] using different media for the extraction of mercury species from biological tissue demonstrated that, using microwave extraction, alkaline solutions such as TMAH result in high accuracy, good recoveries, fast reaction kinetics, and thus, short analysis time, good reproducibility, and low cost. About 0.1−0.2 g of the sample was weighed into Teflon extraction containers, and 5 mL of TMAH was added. The mixture was exposed for 2.5 min to 45 W microwave power in closed reaction vessels and, after digestion, the resulting solution was diluted to 15 mL by adding Milli-Q water. Three hundred microliters of this sample was buffered in 25 mL of 0.08

Table 1. Optimized Operating Conditions for the CCT-AAS Device

AAS	
wavelength:	253.6 nm
spectral band-pass:	0.7 nm
Hg-HCL:	5 mA
gain:	62
quartz cell temperature:	900 °C
shield gas (Ar):	200 mL min^{-1}

Reagent Concentration	
$NaBEt_4$ (0.2%):	0.5 mL
buffer, NaAc/HAc (1 M):	2 mL
total sample volume:	25 mL
resulting pH:	4.7

CCT and Purge Operating Conditions			
trapping temperature:	**−100 °C**		
desorption temperature:	**250 °C**	**heating rate potentiometer:**	**half power**
t_1 (precooling time):	1 min		
t_2 (purge time):	7 min	carrier gas flow purge (He)	30 mL min^{-1}
t_3 (desorption cold):[a]	**30 s at 500 L min^{-1}**	carrier gas flow desorption (He)	12 mL min^{-1}
t_4 (desorption hot):	**4 min at 300 L min^{-1}**		
transfer line temperature:	100 °C	drying gas (N_2)	300 mL min^{-1}

[a] Boldface parameters affecting temperature profile given in Figure 5.

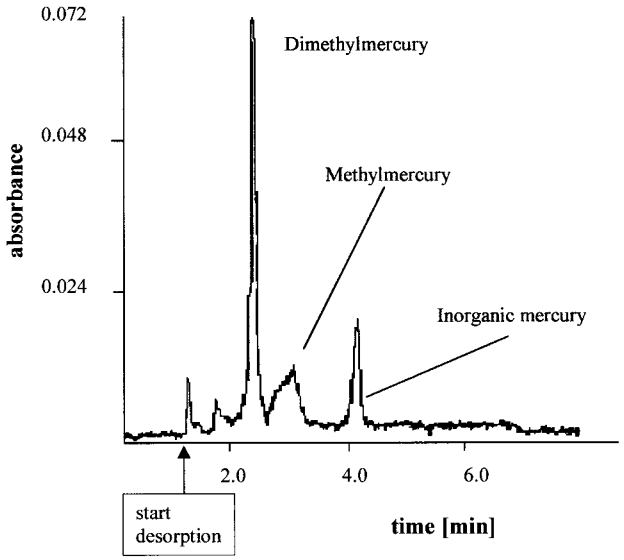

Figure 3. Example chromatogram obtained for a mixed 200 ppt stock solution of three mercury species under optimized operating conditions (chromatographic peaks are corresponding to Me_2Hg, MeEtHg, and Et_2Hg, respectively)

M buffer solution, providing a pH of 4.8, and was placed into the purge vessel for derivatization of the mercury species.

It was intended, as well, that higher volumes of the sample (1−25 mL) would be used directly for derivatization, but this line of investigation suffered several drawbacks. First, the formation of foam occurred, filling up the reaction vessel, and from there, the foam entered the dryer membrane and, later on, clogged the trapping capillary. This could be avoided by adding 50 μL of isooctanol to the entire sample volume without causing signal decrease when it was added to stock solutions. Nevertheless, highly concentrated sample solutions produced a strong matrix effect in spiked samples, resulting in signal decrease for all investigated species. Using an amount of up to 500 μL of sample matrix, effects were negligible, so the above-described procedure was used for further analysis.

RESULTS AND DISCUSSION

Capillaries Used for Trap and Transfer Line. Obviously the properties of the system strongly depend on the kind and length of the capillaries used for trap and transfer line. In this work, the two above-mentioned different kinds of capillaries at varying lengths were investigated.

Optimization was carried out by evaluating peak shape, resolution of the three analyte signals, and retention times, with the target of obtaining narrow-banded and baseline-resolved chromatograms in the shortest time possible. The optimum configuration, which was used in the ongoing investigations, was found to be a 20-cm trapping column of the deactivated fused silica capillary and a transfer line made out of 75 cm of fused silica capillary with the stationary phase. The mechanism of separation in the proposed configuration seems to be mainly based on elution in the order of the different boiling points of the derivatized species rather than real gas chromatographic separation, which is based on the shortness of the capillary selected. Nevertheless, some additional gas chromatographic separation takes place during analyte transfer to the atomizer cell of the AAS instrument via the heated transfer line.

Reductant Concentration. Optimization of the reductant concentration was carried out adding different volumes of a 0.2% $NaBEt_4$ solution to the purge vessel, containing 25 mL of the buffered analyte solution. The concentration of each mercury species in these experiments was 5 μg L^{-1}. As it is shown in Figure 4 a, the analytical response reaches a maximum by adding 500 μL of reductant solution and decreases when higher volumes of reagent are added. Applying more than 2.2 mL of reductant, the analytical response rises slightly for dimethyl- and methylmercury and considerably for inorganic mercury. Simultaneously blank values became much higher at elevated reductant concentration,

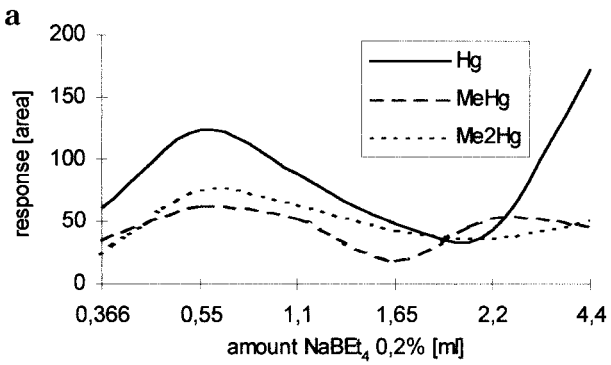

Figure 4. (a) Influence of reductant concentration on analytical response. (b) Influence of purge time on derivatization efficiency.

which obviously was caused by impurity of the reagent itself. Consequently, adding 0.5 mL of reductant was chosen to be optimum, resulting in an overall reductant concentration of 0.08%, which was found to be sufficiently high for mercury determination in the biological material.

Time Program. The precooling time, t_1, ensures that constant temperature conditions inside the whole CCT body are achieved. The trap was precooled for one minute after reaching trapping temperature and before analyte purge was started. For a given value of the carrier gas stream, the purge time, t_2, has to be optimized in order to asssure completeness of the slow derivatization process and quantitative transfer of the derivatized species toward the capillary trap. A seven-minute purge fulfilled these conditions when a helium flow rate of 28 mL min^{-1} was used. This was proven because a chromatogram similar to the blank was obtained when a new aliquot of sodium tetraethylborate was added to the remaining sample. Figure 4b represents the evolution of each mercury species response with increasing purge time. At high purge times, analyte response rose again, but reproducibility of the signal and retention times, respectively, became worse; furthermore, long purge times cause longer times necessary to complete one analysis cycle. Optimization of the remaining times are explained in the following section.

Temperature Program. The first parameter which had to be chosen was the trapping temperature. It was optimized in the range of −60 to −140 °C. The highest temperature without any species breakthrough was −100 °C, which means that at this temperature the trapping of the derivatized species is complete. Consequently, this temperature was chosen for further experiments. During desorption, the destination temperature, which is the upper set point where the controller unit reacts (not called

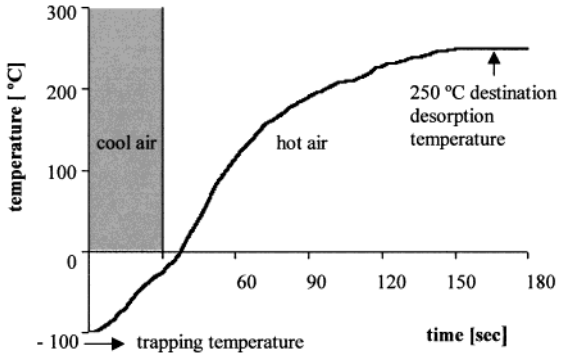

Figure 5. Temperature profile in the CCT body during desorption.

desorption temperature because analyte release may occure before reaching this limit) and parameters such as heating rate and the times of applying cold and hot air, as well as their respective flow rates, were evaluated. Destination temperature was investigated within the range of 150−300 °C, choosing 250 °C because it provided good peak separation and complete analyte release without any memory effects in the following analysis. Starting desorption directly with hot air implicates here the risk of possible mechanical damage of the resitance wires of the hot air gun and did not provide good resolution between the first analytical peaks, corresponding to Me_2Hg and MeHg. To overcome this problem, a 500 L min^{-1} ambient temperature air stream was applied during t_3, at the beginning of desorption, changing to a 300 L min^{-1} hot air stream 30 s later. In this time, the temperature in the CCT device rose to about −30°. The heating rate during the hot air desorption step could be adjusted with the help of a 300 kΩ potentiometer, regulating the output voltage toward the hot air gun. Satisfactory resolution of the analyte peaks and a complete chromatogram within four minutes could be achieved adjusting the potentiometer to half power. The temperature profile obtained under these conditions, which has been used in all subsequent experiments, is presented in Figure 5. As it can be seen, the temperature rose to about −30 °C when the system was switched to the hot air stream and analyte release occurred when the temperature was already close to the destination temperature.

Carrier Gas Flow During Purge and Desorption. The helium flow range investigated was 10−120 mL min^{-1} during trapping and 10−60 mL min^{-1} during the desorption stage. The carrier gas flows needed during the trapping and the desorption step were found to be different. While during the trapping step the gas flow should be high, to favor complete analyte transfer toward the cryogenic trap, a high carrier gas flow during desorption caused incomplete separation, peak broadening, tailing, and a decrease of sensitivity. Optimization was carried out holding the gas flow during the trapping stage constant, changing the gas flow during desorption, and vice versa.

The main criterion for optimizing these carrier gas flows has been the peak resolution, R, in the resulting chromatograms, where R is the resolution between two chromatographic peaks. As a general rule, two peak maxima can be considered separated when R reaches values of 0.5, separation is complete with $R \approx 1.5$ and analysis time is unnecessarily elevated with values of R much higher than 1.5.

The R value is plotted against different pairs of selected carrier gas combinations in Figure 6. The resolution is calculated for

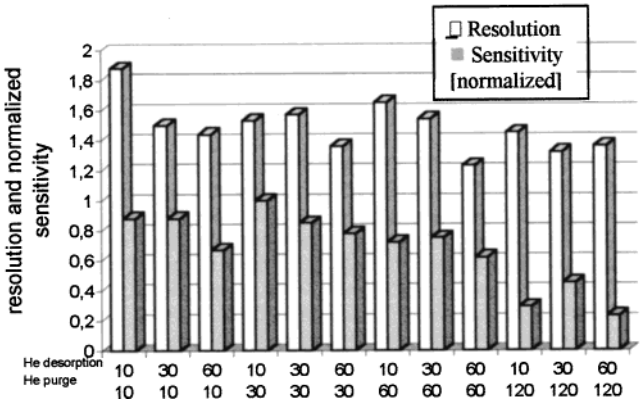

Figure 6. Chromatographic resolution and sensitivity obtained for different combinations of carrier gas flow during purge and desorption. Retention times: Me_2Hg, 1.40 min; MeHg, 2.04 min; Hg, 2.50 min.

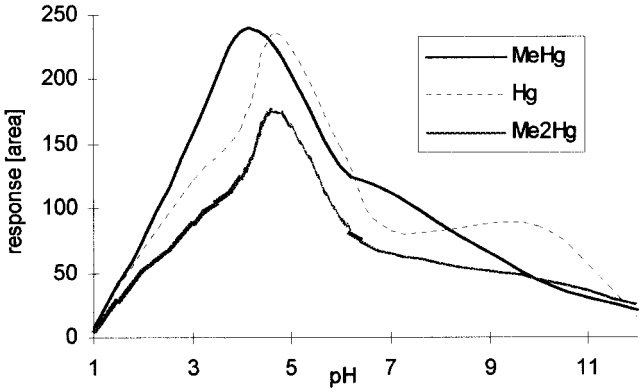

Figure 7. Optimization of pH during derivatization; analyte concentration, 5 ppb each.

the separation of Me_2Hg and MeHg, as the separation of the first-eluting species was more critical than the separation for MeHg and Hg, as Hg eluted about 1 min after MeHg. The value given for sensitivity represents the analytical response for Me_2Hg, as this species showed the smallest slope of the calibration curve, normalized with respect to the value obtained under optimum conditions. Nevertheless, the behavior for the two remaining species was quite similar. As it can be seen, chromatographic resolution is naturally more affected by carrier gas changes during desorption than by different values during the purging step, tending to decrease with higher carrier gas flows. There are several combinations of carrier gas flows which fulfill the objective of good resolution at different purge gas flows, but sensitivity tends to rise toward lower applied flows during purge. The reason why the combination of 30 mL min^{-1} for purge and 10 mL min^{-1} for desorption has been chosen as optimum is that this combination provides good resolution, the best sensitivity, and a shorter purging time than the combination 10/10 mL min^{-1}. Another reason is that reproducibility was improved using this combination, a parameter which seems to be especially affected by the purge gas flow with the tendency to decrease at high flows, possibly because then analyte could not be focused well inside the capillary trap.

Optimization of pH During Ethylation. The efficiency of the derivatization step was investigated using 5 μg L^{-1} standard solutions of the different mercury species. The reaction was carried out in buffered medium and, therefore, different buffer systems at different pH values were tested. A phosphate buffer was investigated at pH ranging from 3 to 9, a citric acid buffer at pH ranging from 4 to 7, and an acetate/acetic acid buffer between pH 1 and 12. In each investigated buffer system, the optimum pH value for the ethylation of mercury species was between 4 and 5, but the acetate buffer was the most recommendable concerning completeness of the reaction. The results of the optimization using this buffer are presented in Figure 7. As it can be seen, the optimum pH for all species is about 4.7, being slightly lower in the case of methylmercury. This coincides with the pH provided by the buffer itself, so the acetate/acetic acid buffer system was used for subsequent experiments. When standard solutions were used, a buffer concentration of 0.02 M was found to be appropiate, while in the real sample, measurements at a 4-fold higher concentration had to be used in order to provide an optimum and constant pH value without having to add acetic acid prior to each analysis.

It should be mentioned that retention times of the Hg species are slightly shifted toward elevated times, about 5 s for Me_2Hg, and 20 and 60 s for MeHg and Hg, respectively, when phosphate buffer was used. This observation could be useful in the case of more complicated chromatograms, when more mercury species are present in the sample, even though sensibility would suffer a decrease of about 50% with respect to the acetate buffer system.

Analytical Figures of Merit. The detection limits for the proposed capillary cold trap system were determined under the optimized operating conditions established in the foregoing investigations (Table 1). Signals were evaluated by measuring the peak area. Detection limits were calculated as the sample concentration equivalent to three times the standard deviation of blank measurements ($n = 7$). The calibration graphs are described by the equations given in Table 2. Absolute detection limits were 0.825, 0.975, and 1.775 ng for Me_2Hg, MeHg, and Hg, respectively. Reproducibility was tested with mixed standard solutions containing 100 ng L^{-1} of each analyte and were found to be 4.9% for Me_2Hg, 5.7% for MeHg, and 15.2% for Hg. The relatively high value for inorganic mercury can be explained with the fact that the concentration of this analyte in the test solutions was quite close to its detection limit. Upon repetition of this experiment at a higher Hg species concentration of 250 ng L^{-1}, reproducibility was found to be 5.5% for inorganic mercury.

The determination of inorganic mercury presented the most severe problems, as the cold vapor was strongly retained on the column, causing notable memory effects which were not easy to eliminate. For calibration, a blank run was done between two measurements for different concentrations.

Analysis of Biological Material. A typical chromatogram obtained for the freeze-dried tuna fish sample is given in Figure 8. This material is only certified for total mercury content with a target value of 2.89 ± 0.30 mg kg^{-1}. Speciation analysis carried out in this study demonstrated that the majority of total mercury is present as MeHg in this kind of sample; Me_2Hg could not be detected. The concentrations obtained for each species are in good agreement with the mercury content determined by other laboratories and are included in Table 2.

Table 2. Analytical Characteristics of Mercury Speciation Using CCT-AAS

mercury species	chromatographic peaks	calibration graph	R^2	retention time	detection limit
Me_2Hg	Me_2Hg	$y = 159.92x + 8.5$	0.9143	1.44 min ± 4 s	33 ng L^{-1}
MeHg	MeEtHg	$y = 233.81x + 17.5$	0.9987	2.04 min ± 4 s	39 ng L^{-1}
Hg	Et_2Hg	$y = 188.78x + 17.5$	0.9902	2.50 min ± 8 s	71 ng L^{-1}

Mercury Content in Sample No. 9/97 (T30)

Me_2Hg	MeHg [mg kg^{-1}]	Hg [mg kg^{-1}]	**total Hg [mg kg^{-1}]** certified value, 2.89 ± 0.30
not detectable	2.4 ± 0.4	0.6 ± 0.3	3.0 ± 0.4

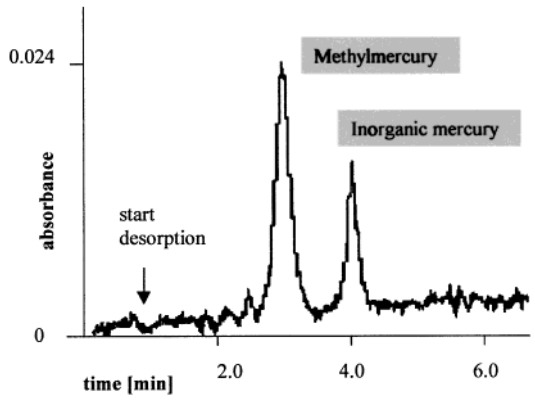

Figure 8. Typical chromatogram obtained for digested tuna fish sample (chromatographic peaks are corresponding to MeEtHg and Et_2Hg, respectively).

CONCLUSION

A semiautomated instrument, based on the idea of carrying out trapping and separation of analyte species in a single capillary, could be successfully developed. The proposed CCT system coupled with AAS detection was proven to be useful for simultaneous speciation of at least three mercury species at the part-per-trillion level. The accessory is relatively simple, provides low instrumental and operational costs, is easy to handle, and is adaptable to the demands of different environmental analyses. Chromatographic separation of the three investigated species was achieved within about three minutes with absolute detection limits of 825 pg, 975 pg, and 1.775 ng for Me_2Hg, MeHg, and inorganic mercury, respectively. The future aim of this work will be based on two important lines of investigation. On one hand, operational conditions as well as instrumental configuration for speciation of other analytes by the proposed instrument have to be established, the latter mainly by introducing new types (diameter, length, stationary phase) of capillaries into the CCT device in order to provide reliable methods for speciation of a variety of analytes. Another aim is to use the developed accessory as a sample introduction device for other detection techniques such as AFS (in the case of mercury speciation), ICPMS, or MIP-AES, with the intent being to improve obtained detection limits. Especially promising seems to be the coupling of CCT and MIP, as, for the latter, sample introduction is still critical, due to instability of these plasmas when liquid or aerosol samples are introduced.

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