Part 3 – Analytical

Fast and cost efficient semi-quantitative screening method for methylmercury determination from fish samples by solid phase microextraction-thermal desorption-atom fluorescent detection (SPME-TD-AFS).

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Abstract: The method is developed for easy and cost efficient approximation of methylmercury (MetHg) concentration in fish samples providing reliable data for decision-making in industrial quality assurance laboratories. In this concept, sample preparation was reduced to a simple ultrasonic assisted leaching step of the lyophilized, roughly ground fish tissue in 3 M HCl in a closed vial. Extracted ionic mercury species were assumed to be present in the form of chlorides, therefore selective methylmercury extraction could be carried out from the headspace based on the volatility differences between individual mercury species. Headspace SPME was performed, using a 65 μm polydimethylsiloxane-divnylbenzene (PDMS/DVB) coated fiber. The exposed fiber was subjected to thermal desorption in a heated GC inlet port. With this method selective MetHg determination was possible without any chromatographic separation, thus the GC was equipped only with a 0.5 m long, bare fused silica capillary – operating as a simple heated transfer line – instead of a "regular" GC column. Desorbed compounds were led to an atomfluorescent Hg detector via a pyroliser tube. Semi-quantitative evaluation of the method was carried out by comparing the response signals of measured samples and matrix matching "quality control" samples with known concentrations of MetHg, previously determined with a validated, independent technique.

Key words: methylmercury, fish, SPME, chloride generation

INTRODUCTION

Dietary intake is by far the dominant source of exposure to methylmercury for the general population. Nevertheless, at the average rates of fish intake, methylmercury (MetHg) exposures are considerably less than the reference dose (RfD) of 1 x 10^{-4} mg kg b.w./day[1]. However, eating more fish than is typical or eating fish that are more contaminated, can increase the risk to a developing fetus. According to an EPA "Fact sheet"[2] 10 % of women of childbearing age eat five times or more fish than does the average consumer. If the fish have average mercury concentrations of 0.1 to 0.15 ppm, the women's mercury exposures range from near or slightly over the RfD to about twice the RfD.

In this study the development of a solid phase microextraction-thermal desorption-atom fluorescent detection (SPME-TD-AFS)

method is presented for semi-quantitative MetHg determination from fish samples. With this method the approximation of MetHg concentration in real samples can be carried out even in industrial QC laboratories and cost efficient decision-making on the acceptance or rejection of a given lot of fish intended for further food processing is possible.

RESULTS AND DISCUSSION

In this work a HP-5890 gas chromatograph (GC) was applied in a non-conventional way. The GC was equipped with an approx. 0.5 m long, 0.32 mm ID bare fused silica caplillary instead of a "regular" GC column. Emerging from the GC oven, the capillary was led through a pyroliser tube before coupled to a PSA 10.750 (PS Analytical Ltd.), external atomfluorescence (AFS) mercury detector. The GC itself was serving only as a sample introduction system suitable for thermal desorption purposes with SPME and as a thermostat for the fused silica transfer line.

Three different canned/deep frozen fish products commercially available in Hungary were used for evaluation purposes. Samples have been collected in the frame of the project OTSAFE-QLK1-CT 2001-01437.

Laboratory sample preparation was carried out based on a previously published procedure[3]. Briefly, lyophilized, ground samples (0.250 g) were leached in an ultrasonic bath at 75 °C for 30 min in 30 ml glass vials using 5 ml of 3 M HCl. After cooling, pH was adjusted to approximately 2-3 by adding 4.95 ml 3M NaOH to the solution. Vials were then sealed with a PTFE lined septum cap and the headspace was subsequently sampled by SPME. Headspace sampling eliminates the need for filtration or centrifugation of the sample. Adjustment of pH was performed in order to protect the SPME fiber from acid vapors coming from the highly acidic solution.

Selectivity of the method was tested in the following experiment. A 30 ml glass vial was filled with 10 ml of either blank or 5 ng ml^{-1} Hg^{2+} or MetHgCl standard solutions. A 5 minutes long ventilation step (i.e., stirring the solution without cap) was performed prior to extraction in order to purge off elemental mercury from the solutions before starting headspace sampling. With this protocol, the undesirable Hg^0 signals could be eliminated from both blank and Hg^{2+} standard solutions, nevertheless in the case of MetHgCl standard solutions signals obtained before and after ventilation step had only a difference less than 1.5 %. It means that in the latter case the signal was produced by MetHgCl, that is volatile enough to extract from the headspace[3], but on the other hand cannot be purged as easily as Hg^0. The above described volatility differences between

Table 1. Operational values of the GC-pyro-AFS system

Parameter	*Value*
Inlet port temperature	250 °C
Carrier gas	Ar, 3.45 ml min^{-1}
Oven temperature	260 °C
Pyroliser temperature	800 °C

mercury species allowed us to carry out selective MetHg determination using the present method without any chromatographic separation. Overlapped signals of three individual samples (i.e., blank; 5 ng ml^{-1} Hg^{2+}; and 5 ng ml^{-1} MetHgCl (as Hg) respectively) obtained after 5 min ventilating followed by 10 min headspace SPME sampling with 65 μm PDMS/DVB fiber are shown below in Fig. 1.

Since this method was not intended to be a quantitative technique, therefore no attempt was made to exact quantification. Nevertheless, methylmercury concentration of the three fish samples involved in this study were determined previously with an independent and validated method[4]. Results are shown in Table 2.

In order to check the potential of this method for routine decision making, the following experiment was performed. One of the three samples was assigned as a quality control (QC) sample. Estimated concentrations of "unknown" samples were based on the known peak area-concentration relation of the given QC sample. Calculations were made in every possible experimental design in the case of these three samples. Peak areas were normalized to a dry sample mass of 0.250 grams. Results are presented in Table 3.

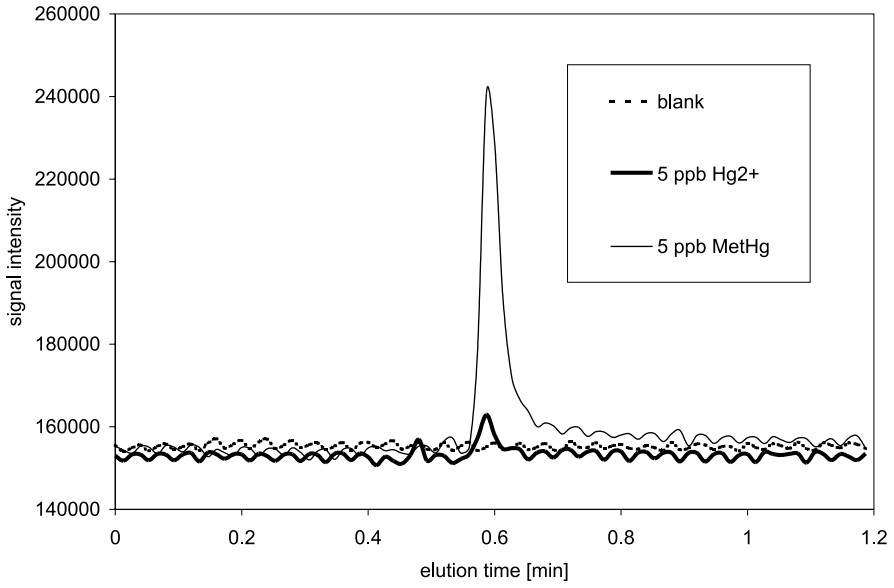

Figure 1. Overlapped signals of a blank sample and two different standard solutions.

Table 2. MetHg concentration of fish samples involved in this study. (SD1, n=3)

	Herring 2	**Hake 2**	**Sardine 1**
MetHg conc. (as Hg) μg g^{-1} d.w.	0.070±0.002	0.122±0.006	0.068±0.003

Table 3. Estimated average MetHg concentrations of fish samples. Calculations are based on different QC samples. Values are in μg g^{-1} (as Hg).

	QC: Hake 2	QC: Herr 2	QC: Sard 1
Herring 2	78	-	74
Hake 2	-	61	65
Sardine 1	127	115	-

From the results it is evident that the present method – independently from the slight matrix differences between the given types of fish products – would provide robust and sufficiently sensitive results for routine screening purposes.

CONCLUSIONS

A fast, cost efficient and easy-to-use method was developed that is purposed to use in routine industrial QC laboratories. Although several sophisticated methodology have been published for MetHg determination so far, with this method the necessity for time consuming quantitation procedures can be eliminated. One should give up the demand for highly accurate and precise results when applying such a semi-quantitative method, while the requirements of routine QC screening applications can be sufficiently fulfilled. For correct statistical evaluation of the results an adequate methodology is required, however.

Acknowledgements

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Comparison of Manual and Automated Measurements of Reactive Gaseous Mercury (RGM)

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Abstract: A measurement campaign was undertaken in Ny-Ålesund, Spitsbergen (78°55'N, 11°90'E) during April and May 2003. Four mercury depletion events (MDE) were observed during the study. Three research groups measured reactive gaseous mercury (RGM) at three different measurement spots. All groups observed increased concentrations of RGM as concentrations of GEM decreased. Recorded concentrations of RGM ranged from less than 7 to 450 pg/m^3. Differences between both measured parallels and the measurements sites were observed, even though no significant differences in the mean GEM concentrations were revealed between the measurement spots.

Key words: mercury depletion events, MDE, reactive gaseous mercury, RGM, comparison,

INTRODUCTION

Speciation of atmospheric mercury is important in order to understand the fate of mercury in the environment and mercury's implications on the environment. For the past 5-10 years a lot of work have been undertaken to develop methods to measure inorganic atmospheric forms of mercury, referred to as reactive gaseous mercury (RGM). Different groups has studied RGM at various locations through polar regions, and to ensure comparable data sets an international field campaign was undertaken in Ny-Ålesund, Spitsbergen (78°55N, 11°90E), during April and May, 2003.

This work presents measured concentrations of reactive gaseous mercury (RGM) obtained by three different research groups at three different measurement sites. One group, NILU, measured at the Zeppelin station, which is located at the Zeppelin mountain, 474 m.a.s.l. The station is typically positioned well above frequent ground inversion of the fjord valley. The second group, MSC, measured at the Italian station, which is located in the Ny-Ĺlesund village, 12 m.a.s.l. The third group, GKSS, measured at "Ny-FID Sund", which is located 500 m east of Ny-Ĺlesund at about 10 m.a.s.l. The groups used the same principle for collection and quantification of RGM as described by LANDIS ET AL. (2002). RGM was collected on KCl coated annular denuder tubes followed by thermal decomposition of RGM quantified as Hg^0. Further details are shown in Table 1.

Table 1. Summary of methods used by 3 research groups for measurements of RGM.

	NILU	MCS	GKSS
Sampling system	Manuel	Manuel	Tekran 1130
Number of parallels	2	2	1
Sampling site (m.a.s.l.)	474	12	~10
Denuder length : length of active surface (cm)	37,0 : 20,0	50,8 : 25,4	51,4 : 25,4
Sampling flow (lpm)	5	10	8,5
Sampling temperature (°C)	30 – 40	50 - 60	50
Desorbtion system	Lindberg furnace	Lindberg furnace	Tekran 1130
Desorbtion temperature (°C)	500	500	500
Quantification system	Tekran 2537A	Tekran 2537A	Tekran 2537A

RESULTS AND DISCUSSION

Four MDE's where detected during the field study, and they are labeled according to STEFFEN ET AL. (2004). During non-MDE situations all groups measured RGM-concentrations at the methods detection limit (MDL = 7 pg/m^3). In general during all events all groups measured increased concentrations of RGM while concentration of GEM decreased, as shown in Figure 1 (MDE 1 is not shown in the figure).

During MDE 1 small concentrations of RGM were observed (RGM < 16 pg/m^3) and the agreement between the sampling sites were good. During MDE 2a higher RGM was observed (max RGM = 80 pg/m^3). The precision between sets of parallels was in general good (except for one sample), but not the agreement between the sites. Both sites where at sea level, but one site shows 3 times higher values than the other. Concentrations of RGM increased further during MDE 2b. The RGM patterns observed at sea level are

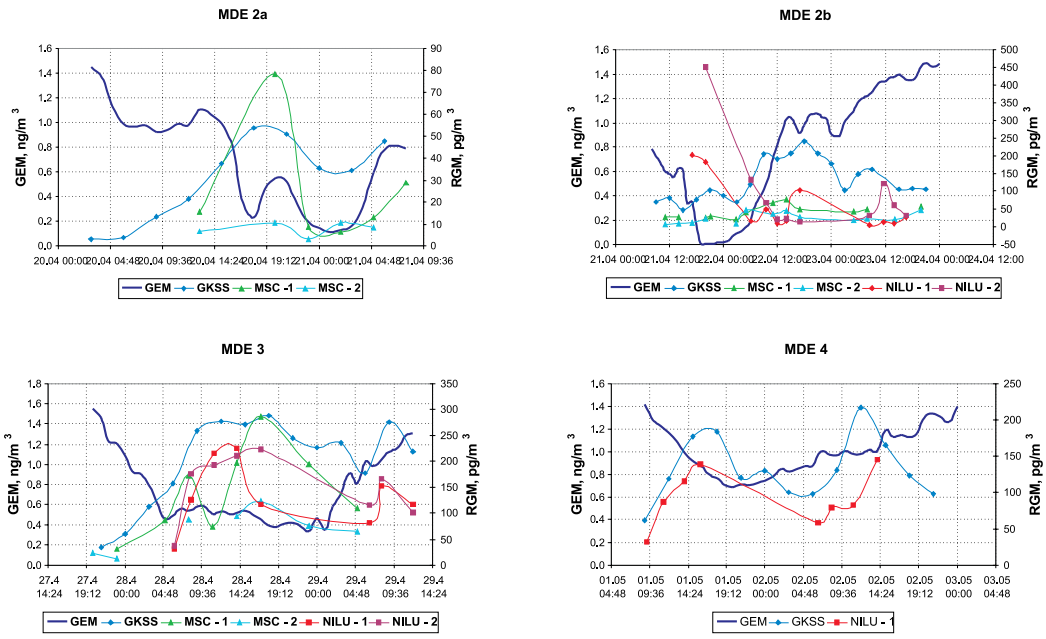

Figure 1. Development of RGM-concentrations during 3 MDE's

similar, but off-set by a factor of 3, with the highest RGM-concentration observed when GEM started to increase. RGM observed at Zeppelin were highest earlier in the event when GEM concentrations were the lowest. The precision between the parallels seemed to decrease as the concentration of RGM increased. During MDE 3 all groups measured comparable concentrations of RGM (overall precision within 30 % except for MSC – 2). The precision between parallels measured at Zeppelin was good, except for one sample (overall precision within 15 %). The variability between parallels measured at sea level was high. The RGM-pattern observed during MDE 4 shows two peaks and the measured RGM-concentrations the highest correlation ($r^2 = 0.93$). The agreement between the sites was relatively good, with a dicrepancy of 30 %.

Even though the mean GEM concentrations reveals no significant difference between sea level and the Zeppelin station (BERG ET AL., 2003; TEMME ET AL., 2004) we can not, with our current understanding, deduce that RGM measured at the same sites would show similar behavior. The authors concern is the huge differences between parallel samples. Preliminary results from Barrow, Alaska spring 2004 show similar behavior.

Of the two groups measuring manual RGM, MSC followed the guidelines set by LANDIS ET AL. (2002) whereas NILU made a few adjustments, such as reduced sampling flow and shorter denuder length. Both groups used impactors (cut off 2,5 μm) as sample inlet. The large differences between the parallel samples might be due to coarse particles entering the system and thus adsorbed to the denuder walls. This is a plausible explanation for the group using reduced sample flow. None of the above mentioned groups were able to attain comparable results. The Arctic is a harsh environment, which might be a possible explanation why comparable parallel samples were not obtained.

CONCLUSIONS

A comparative study of RGM was conducted in Ny-Ĺlesund, Spitsbergen during spring 2003. All groups observed increased concentrations of RGM as concentration of GEM decreased. The recorded concentrations of RGM differed between the sampling sites and also within sampled parallels. At this point we need more experience to understand whether the differences between the sites are due to real differences or not. The groups' inability to produce comparable parallels reveals the fact that at this point the method is not robust enough to be credible.

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Determination of Total Mercury using Thermal Decomposition with Atomic Fluorescence Detection

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Abstract: An improved apparatus based on thermal decomposition of the sample for the direct determination of mercury was constructed. The device consists of a quartz tube packed with a proprietary catalyst, coupled with gold preconcentration and an atomic fluorescence spectrophotometer (AFS) detector. Samples are weighed and inserted or injected into the system without pretreatment. The mercury vapors generated during thermal decomposition are catalytically reduced and passed to a gold-coated amalgamation cartridge. The mercury is released when the cartridge is subsequently heated and is detected by AFS. A valve system allows switching between combustion gas (air) and the pure argon carrier required for the atomic fluorescence detector. The performance of the system was tested using a wide range of samples: soil, sediment, coal, coal fly ash, petroleum coke, peat moss, seaweed, fish muscle, milk, blood, urine, gasoline, crude oils, and sulfur. Recoveries of mercury in the test samples were found to be 95 % to 110 % of the certified values. The device has a high daily throughput and requires minimal maintenance. It does not require liquid scrubbers or buffer solutions.

Keywords: mercury analysis, thermal decomposition, atomic fluorescence

INTRODUCTION

Conventional liquid digestion techniques for the determination of low levels of mercury were pioneered more than 30 years ago. Researchers also developed pyrolytic procedures for the determination of mercury in different samples.[1-5] One of the major problems with these thermal techniques was the release of other compounds along with the mercury. LIDUMS[6] developed a method based on the combustion of samples in oxygen. He also passed the combustion gases through a heated column containing a mixture of oxides that was used to remove interfering compounds from the mercury vapor. Other workers[7-11] introduced oxides or metals (Cu or Ag) in the sample decomposition train, or mixed the sample with different materials such as calcium oxide. These materials were able to transmit virtually all of the mercury in the sample while retaining the halogens and oxides of nitrogen that interfered with the trapping and release of mercury on gold or platinum. The thermally desorbed mercury was quantified using AAS. These techniques were later improved, leading to commercially available systems.[12-17] LIANG ET AL.[18] reported a thermal decomposition technique coupled with atomic fluorescence spectrophotometry (AFS) for the determination of Hg in petroleum and other environmental samples. An improved technique, which is able to measure a wide range of petroleum products, was recently published [19].

The device described in this paper is a further improvement, combining sample combustion, removal of interferent compounds, gold preconcentration, and AFS for detection.

MATERIAL AND METHOD

The sample is weighed (≤ 300 mg) into alumina boats and then introduced into a quartz decomposition furnace. This furnace is independently heated in two sections. The first is the drying & decomposition oven that is able to reach temperatures of 800 °C. The second section heats a proprietary catalyst to 615 °C continuously. Low mercury air at a flow rate of 250 mL/min is used as the oxidant for combustion. Mercury vapor is collected onto a gold-coated silica cartridge. The device is equipped with two solenoid valves. The valves switch between air and argon, prolonging the life of the gold cartridge and reducing deposition onto the detector components. When the analytical cartridge is heated, the mercury is released and swept into a Tekran Model 2600 AFS detector. A schematic diagram of the device is shown in Figure 1.

Depending on the type of sample to be analyzed, different calibration solutions were used during the tests. Aqueous mercury standards in 0.2 % HNO_3, were used for most simple matrices. Methyl mercury standard and Conostan Oil Single Element Mercury Standard were used for calibration when analyzing crude oils. Independent verification of system sensitivity was provided by injecting saturated mercury vapor through a permanent injection port into the air supply line upstream of the sample pyrolysis unit.

Initial tests included optimization of the temperature and the times for drying and decomposition of the sample, flow rate of the combustion oxidant gas and temperature of the catalyst furnace. Selected types of samples were prepared and preserved in our laboratory and run repeatedly over an extended period in order to check system robustness and catalyst life. The effect of sample size aliquot and sample non-homogeneity were also investigated. Appropriate commercially available certified reference materials were used whenever they were available. For some CRMs and for all sample matrices that have no reference material, comparison with con-

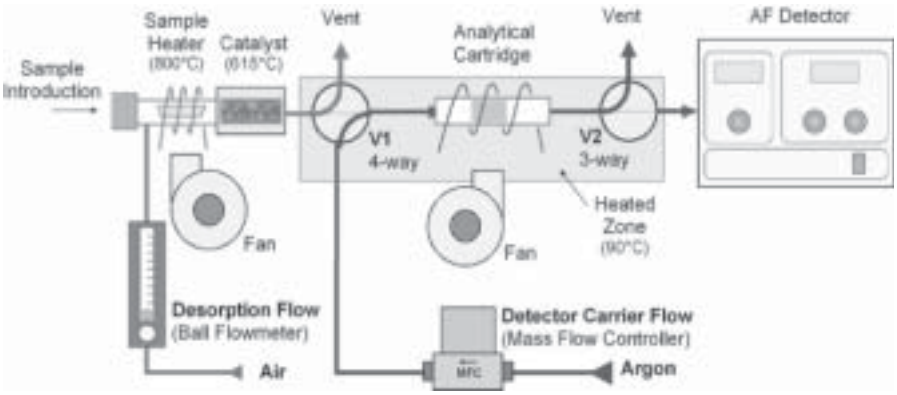

Figure 1. Flow Diagram

ventional BrCl liquid digestion / AF analytical techniques[21-23] was performed.

RESULTS AND DISCUSSION

The results for a range of samples are shown in Table 1, below. For each type of sample, the mean result and the 95 % confidence interval are shown. Where applicable, the MDL of the thermal method and comparative liquid digest results are also given. More complete results and discussions for gasoline, oil and sulfur samples will be presented in the full version of this paper.

Type of Sample	Certified Value (µg/kg)	Sample Aliquot (g)	Thermal -AFS (µg/kg)	Acid Digest-AFS (µg/kg)	MDL (µg/kg)	Recovery (%) of Certified value
NRC, Mess-3 Marine Sediment	91 ± 0.9	0.10-0.15	97 ± 0.7 (n=20)	-	-	103
NIST 2684b S and Hg in Coal	97.4 ± 4.7	0.10-0.15	96.3 ± 0.8	-	-	99
NIST 1633b Trace elements in Coal fly ash	141 ± 19	0.10-0.15	141 ± 2	-	-	100
Soil Internal Standard	-	0.10-0.15	75.2 ± 3.8 (n=20)	76.2 ± 2.5 (n=5)	-	-
IAEA-140/TM Seaweed focus	38 ± 6	0.05-0.15	40 ± 0.8	-	-	105
Peat Moss Internal Standard	-	0.05-0.15	29.2 ± 0.76 (n=20)	28.3 ± 0.2 (n=5)	-	-
NIST 966 Toxic Metals [1] Bovine Blood	31.4 ± 1.7	0.025-0.10	30.98 ± 0.9	-	-	99
Human Blood [1] (preserved in EDTA)	-	0.025-0.10	1.28 ± 0.038	-	0.12 (n=7)	-
NIST 2672a Freeze-Dried [1] Urine (elevated level)	105 ± 0.08	0.05-0.10	111.2 ± 0.1 (n=10)	-	-	106
NIST 2672a Freeze-Dried [1] Urine (low level) uncert.	-	0.05-0.10	0.63 ± 0.028	-	0.087 (n=7)	-
BCR 150 Milk Powder (Low level)	9.4 ± 1.7	0.05-0.10	9.84 ± 0.3	-	-	104
BCR 150 Milk Powder (High level)	101 ± 8	0.05-0.10	100.2 ± 1.5	-	-	99
Skimmed milk Powder Not certified	-	0.05-0.10	0.64 ± 0.03	-	0.12 (n=7)	-
NRC Tort-2 Lobster Hepatopancreas	270 ± 6	0.05-0.08	271 ± 2	-	-	100
Stripped Bass Lake fish (not certified)	-	0.25-0.30	9.05 ± 0.25	8.8 ± 0.4	1.02 (n=7)	-
Chicken Breast (not certified)	-	0.25-0.30	0.11 ± 0.013	0.10 ± 0.018	0.05 (n=7)	-
Petroleum Coke PC-1	-	0.10-0.15	2.68 ± 0.06	-	0.24 (n=7)	-
Gasoline	-	0.05-0.08	0.13 ± 0.015	0.11 ± 0.012	0.03 (n=7)	-
Crude Oil	-	0.025-0.05	0.93 ± 0.1	0.85 ± 0.1	-	-

[1] The results for blood and urine samples are expressed in µg/L

CONCLUSIONS

The thermal decomposition/AFS method is a reliable means for the analysis of mercury in a wide range of materials. The use of AFS as a detection method extends application of the thermal technique to samples with very low mercury content. The proprietary catalyst eliminates the need for frequent changes of the catalyst or gold-coated cartridge. The system does not require packing of the sample boats with additives or the use of soda lime and liquid scrubbers. The device is capable of analyzing pure sulfur samples or sulfur rich samples. The length of the analytical cycle is 6 minutes and the device is able to measure process in excess of 60 samples per day.

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Development and first tests of a laboratory flux chamber system (LFCS)

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Abstract: A Laboratory Flux chamber System (LFCS) for process studies of the air/surface exchange of mercury was developed. Initial tests and first results will be presented. The system allows investigating and controlling environmental variables that are thought to influence air/surface exchange processes, such as sunlight, air and soil temperature, soil moisture and turbulence conditions as well as physicochemical conditions of the soil. Further results are presented in accompanied contributions to this conference.

Key words: air-surface exchange, laboratory flux chamber system

INTRODUCTION

Predictive models to describe the emission of mercury from land surfaces need reliable data about the effect of major environmental variables such as soil moisture, soil temperature solar radiation and turbulent atmospheric conditions. Due to the intricacy of the processes involved in mercury emissions from natural surfaces controlled laboratory studies are necessary to elucidate the influence these variables on mercury emissions from soils We have developed a laboratory flux measurement system (LFCS) for simultaneous flux determination of Hg^0, CO_2 and water vapour under controlled environmental conditions (Fig. 1).

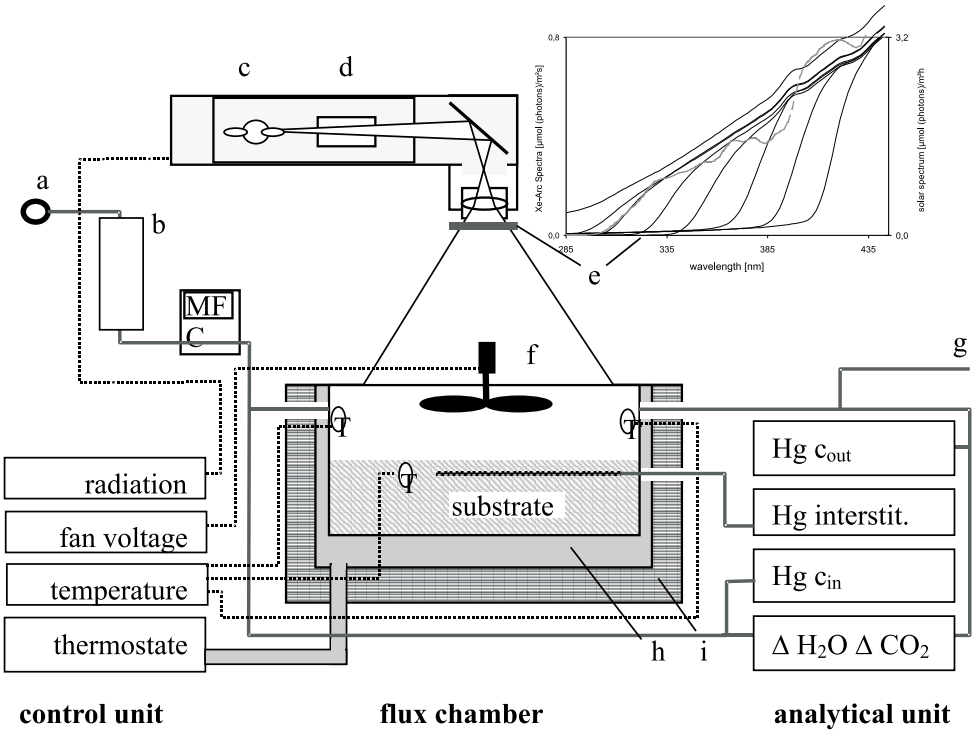
EXPERIMENTAL SET UP

The cylindrical flux chamber has a diameter of 50 cm corresponding to a surface area of 2000cm^2 and a variable height between 10 and 40 cm, resulting in a chamber volume between 20L and 80L. All system parts coming in contact with samples are made of or coated with Teflon-FEP. The bottom and the side of the chamber are made of Teflon-FEP coated stainless steel and the top is made of FEP-sheet (0.25 mm thick). Inlet- and outlet ports are on opposite sides of the chamber in a height of 8 cm over the sample surface. An additional sampling port is designated for continuous sampling of soil gas that is sampled through a Teflon line (3.2 mm in diameter and 75 cm in length), which is half-cut every 2 mm.

For continuous mixing of incoming air a fan, adjustable between 0 and 12V which corresponds to 0 to 3000 r.p.m., is installed in the centre of the flux chamber. The use of the fan avoids stagnation zones and uncontrolled induction of vertical components of airflow. Ambient air is pulled through the chamber at predefined flow rates between 0,5-30 L min^{-1} using high capacity mass flow controllers and a membrane pump. Alternatively the LFMS can operate with pressurized or synthetic air. Hg° is removed from the incoming air stream by means of a charcoal scrubber.

The bottom and the side walls of the chamber act as heat exchanger and are coupled with a thermostat (LaudaUKT 600) allowing to control of soil temperature between -15 °C and 35 °C. Insulation (6 cm thickness) at the bottom and the side of the chamber inhibits the heat exchange.

To investigate the influence of solar radiation on mercury exchange processes we use a solar simulator with a 2000 W Xenon short arc lamp as light source. The Xenon arc lamp provides a continuous light spectrum, which is quite similar to the AMO-0 spectrum in



a: gas supply ambient or synthetic air, *b*: charcoal filter, MFC mass flow controller *c*: XE-Arc light source, *d*: water filter, *e*: optical glass filter, *f*: fan, *g*: vent, *h*: heat exchanger, *i*: insulation 6 cm, T: PT 100 sensor

Figure 1. Schematic diagram of the experimental set up.

the visible UV region. About 65 % of the out coming IR-radiation are adsorbed by a water filter (thickness: 10 cm), which significantly reduces the heating of the substrate. To assess the spectral response of the Hg° flux, different Schott® glass filters with 50 % cut offs at 295, 305, 320, 335, 380, 399, 418 and nm were used.

The concentrations of Hg^0, CO_2 and H_2O_v are measured simultaneously at the inlet and the outlet of the chamber and fluxes are calculated using equitation (1)

$$F= (C_o-C_i)*A\text{-}1* Q \quad (1)$$

where F is the flux [pmol $m^{-2}h^{-1}$)] (for Hg^0), C_i and C_o are the concentrations [pmol m^{-3}] at the inlet and the outlet port respectively, A is the bottom surface area of the chamber [m^2] and Q is the flushing flow rate through the chamber [m^3h^{-1}]. All measurements are corrected for standard conditions (STP).

Hg° is measured at the inlet and at the outlet of the chamber with two Tekran Mercury Vapour Analyzers (Model 2537) with a time resolution of 5 min. The set up, accuracy and precision of this instrument has been assessed during field intercomparisons at a remote marine background location (EBINGHAUS, 1999b). The analysers were calibrated every 25 hours with an internal automatic permeation source injection.

The Δ-concentrations of CO_2 and H_2O_v are determined continuously using a Two Channel Infrared Gas Analyser (LiCor, Model Li 6262). A precise determination of these parameters requires a known and constant concentration of CO_2 and water vapour at the chamber inlet and can thus only be achieved when the LFMS operates with synthetic air. However, we found that the overall bias introduced by the diurnal variations of these compounds in ambient air is normally less than 12 % for CO_2 and less than 14 % for H_2O when the analyzer is calibrated and adjusted to the momentum concentration of these compounds every 25 h.

Temperature is measured at the inlet and outlet ports of the LFMS, in the soil in 0.5 cm depth and if required also in deeper soil layers using high precise Pt-100 sensors.

FIRST RESULTS

In order to investigate the effect of various parameters the parameter of interest is varied while all other parameters are kept constant and the response of the flux to this variation is determined. To assess possible interrelations between the environmental parameters experiments are repeated with different sets of the environmental parameters.

The LFCS provides an excellent blank performance. Under dark conditions the blanks are normally below the detection limit, which is estimated to 1 pmol $m^{-2}h^{-1}$ at a flushing flow rate of 1.0 L min-1.

After an initial acclimatisation period of about 12h fluxes remained constant within ± 7 % for the next 120 hours under constant environmental conditions and thus provide a sufficient stability to study the effect of selected environmental factors. Variations of the soil layer thickness between 10 and 1 cm showed no significant effect on mercury emission fluxes (MEFs), indicating that MEFs are controlled by the uppermost soil

layer. We found that the effect of flushing flow rate (Q) and fan voltage V_f can sufficiently be computed with a simplified form of the model provided by ZHANG (2003).

$$MEF = c(TGM_B)*Q*(1+Q*[41.3*(9.1+ V_f)^{-1}])^{-1} \quad (2)$$

Where MEF is the mercury emission flux [pmol $m^{-2}h^{-1}$) and $c(TGM_B)$ concentration of gaseous mercury in the soil gas in 1 cm depth [pmol m^{-3}] obtained from soil gas measurements. This model describes the soil-air transfer resistance as an empirical and chamber specific function of fan voltage, which is given by the term in square brackets. We verified the computed results for various soils at a soil moisture level close to field capacity by comparing them with the measured fluxes and found them in good agreement as shown by the correlation coefficient ($MEF = 1.001* MEF_{-measured}$, $n = 43$, $R^2 = 0.9736$).

Further results will be presented in accompanied contributions to this conference (BAHLMANN, 2004a, 2004b and 2004c).

CONCLUSIONS

The laboratory flux chamber system provides an excellent blank performance and a high stability of the fluxes over time under constant environmental conditions and thus the fundamentals to study the effect major environmental variables that are thought to influence the emission of mercury from soils.

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Assessment of Mercury (II) Species Bioavailability using a Bioluminescent Biosensor

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Abstract: The objective of this research was to investigate the bioavailability of various Hg(II) species in laboratory and natural solutions using a bioluminescent bacterial biosensor. The Hg(II) biosensor is a genetically engineered *E. coli* strain, which produces firefly luciferase in proportion to its exposure to bioavailable Hg(II). A new analytical protocol for the use of bacterial bioassays to study the bioavailability of trace elements and relate it to their modeled chemical speciation was developed. The influence of inorganic and organic ligands on the Hg(II) speciation and bioavailability was investigated. Kinetic experiments were performed to evaluate the Hg(II) uptake process by bacteria.

Key words: mercury, bioavailability, biosensor, chemical speciation

INTRODUCTION

Mercury is one of the most dangerous contaminants in the environment. Due to its broad dispersion through the atmosphere, Hg accumulates even in remote pristine aquatic systems, making it a global pollutant. Although significant advances in our knowledge of mercury biogeochemistry have been obtained in recent years, a key issue is still not sufficiently understood: How does the Hg(II) chemical speciation control its bioavailability to methylating bacteria? This gap is in part due to the incapacity of the traditional speciation methods to address the critical issue of bioavailability adequately. This limitation stimulated the development of new sensors that use biological components as detection devices. These biosensors have great sensitivity and specificity[1-4].

We studied Hg(II) species bioavailability using a genetically engineered bioluminescent biosensor. The Hg biosensor uses the firefly luciferase gene as the biosensor reporter gene. The engineered plasmid (pT0011) contains the reporter gene under the control of the *mer* promoter of transposon Tn21, which is induced by the intracellular presence of Hg(II). An *E.coli* (MC1061) is used as the host organism for the pT0011 plasmid. The detailed genetic construction of the Hg biosensor is described elsewhere[5].

The Hg biosensor cells used for the bioassays were cultivated in a minimal salts medium (M9) supplemented with casamino acids and kanamycin. The exposure of the biosensor to samples was performed free of the microbiological growth medium, using Hg(II) standard additions, and under different experimental conditions (i.e. variable exposure time and different Hg(II) concentrations). After the exposure, biosensor cells were resuspended into the M9 medium and incubated for luciferase production, which

should be proportional to the Hg(II) concentration inside the cells. The luciferase content of the biosensor cells was measured by the light output following addition of enzyme substrate.

RESULTS AND DISCUSSION

In the first part of the study an analytical protocol was developed and optimized using standard solutions. The major distinctive characteristic of the new procedure is that the microbiological medium used in the bioassays does not interfere with the natural trace-element speciation of the analyzed samples. Thus, the bioavailability results can be interpreted using the original chemical speciation of the analyte studied.

The biosensor assays showed good reproducibility and high specificity for Hg(II). The detection limit of the method (0.7 pM) is superior to many other Hg(II) biosensors described in the literature and it is adequate to analyze samples from pristine environments[6].

The developed protocol was used to determine the bioavailable Hg(II) concentrations in samples from two sites in the Everglades (3A15 and Lox).The experiments showed a dose-response relationship between Hg(II) added to the natural samples and the light produced by the biosensor (Fig 1). In the natural samples tested, the response to added Hg(II) seemed to be controlled mainly by natural organic ligand complexation.

In the second phase of the research, Hg(II) speciation was manipulated by the addition of ligands and the bioavailabilities of the species formed were assessed. The chloride titration results suggested that neutral Hg(II) complexes were more bioavailable than anionic Hg(II) chloride complexes (Fig. 2). The two relevant Hg(II) neutral species in oxic solutions, $Hg(OH)_2^0$ and $HgCl_2^0$, showed similar bioavailability.

These data agree with other studies performed with a different mercury biosensor, and support the hypothesis that neutral Hg(II) species may play an important role in bacterial Hg(II) uptake in the environment [7, 8].

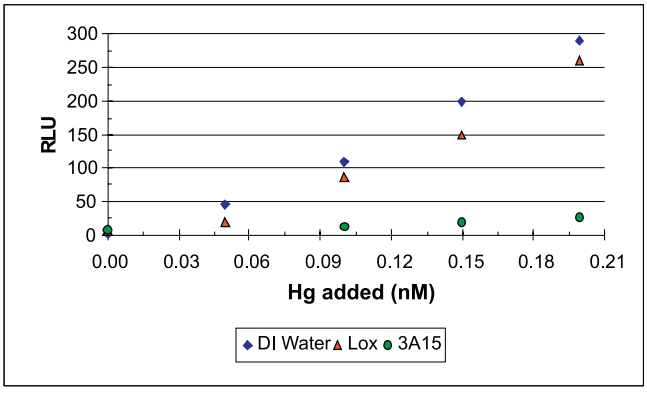

Figure 1. Analysis of Everglades samples (Water Conservation area 3A15 and Loxahatchee National Wildlife Refuge).

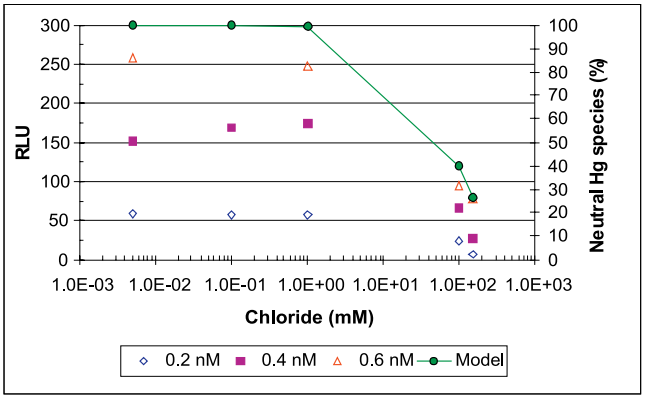

Figure 2. Hg biosensor response as a function of increasing chloride concentrations and the modeled proportion of neutral Hg(II) species

In addition, kinetic assays were performed to investigate the Hg(II) uptake process by the biosensor. The experimental data agreed with the threshold kinetic model proposed for the *mer* operon/Mer R protein response to Hg(II) (Fig. 3)[9, 10]. The half-saturation constant for the enzymatic reaction was estimated (0.249 nM) using the Hill equation [9,10], and was consistent for two different exposure times. However the maximum apparent Hg(II) uptake rates varied according to the exposure time. The Hg biosensor response displayed non-linear increases to both increasing exposure times and Hg(II) levels. Probably, both non-linear behaviors are due to the saturation of the *mer* operon/Mer R protein with Hg(II) [9-11].

The analysis of the Hg biosensor cells for the their total Hg(II) concentration, during kinetic tests, revealed no evidence of saturation of the Hg(II) uptake process. These data also allowed the estimate of the mercury uptake rate by the biosensor cells (0.7 - 1 x 10^{-23} moles $cell^{-1}$ s^{-1}) and the permeability of $HgCl_2$ (3.6 x 10^{-5} cm s^{-1}), which were similar to other values from the literature [12, 13].

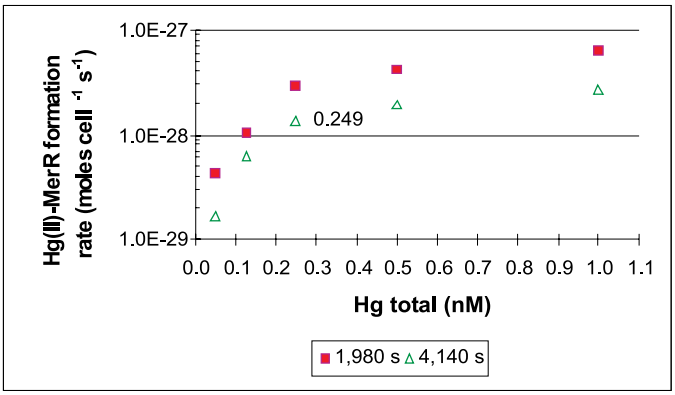

Figure 3. The Hg(II)-Mer R formation rate as function of the exposure time (1,980 and 4,140 seconds) and Hg(II) added. The Half-saturation constant for both curves is shown.

CONCLUSIONS

The Hg biosensor measured only the bioavailable Hg(II) species of the total Hg(II) present in the samples. The biosensor showed high specificity for Hg(II) and the bioassays had good reproducibility. The detection limit of this method is superior to other reported Hg(II) biosensors and adequate to analyze samples from pristine systems. The chloride titration results suggested that neutral Hg(II) complexes are more bioavailable than anionic chloride Hg(II) complexes, supporting the hypothesis that simple physical diffusion of Hg(II) neutral species is an important process for bacterial Hg(II) uptake.

The integration of the biosensor technique with other chemical speciation methods provides a powerful framework for environmental assessments. The determination of the bioavailable concentration of a contaminant in natural samples complements the total concentration analysis, and generates the information required to assess its risk to human populations and the environment.

Acknowledgements

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Comparison of High Pressure Wet Ashing and Hot Acid Extraction for the Determination of Hg and Other Trace Metals in Crude Oil

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Abstract: A comparison was made between hot oxidizing acid (0.1 M BrCl + 6 M HCl) liquid-liquid extraction and complete digestion (concentrated HNO_3) using the Anton-Parr High Pressure Asher (HPA) for the determination of Hg in petroleum. Although quantitative recovery and similar detection limits (0.2-0.5 ng g^{-1} Hg) were obtainable by both methods in most cases, the HPA proved to be superior for the digestion of crude oils and high viscosity residual petroleum products. The HPA generates a clear, simple solution in HNO_3, which is suitable for the analysis of additional trace metals by ICP/MS, whereas the BrCl extract contains too many salts and interfering isotopes to be usable in this regard.

Key Words: Mercury, Trace Metals, Oil, High Pressure Asher

INTRODUCTION

The determination of Hg and other trace metals in petroleum products at ambient levels is difficult to do, because of the recalcitrance of the matrix to complete dissolution, risks of digestion explosion, analyte loss by volatilization, and the formation of matrix components, which can interfere during the analysis step (BLOOM, 2000). In addition, regulatory interest in Hg pollution has pushed down the levels of concern in fuels to approximately 0.1–1 ng g^{-1}, a range that cannot be consistently reached using commonly used digestion methods. Although there is little published on the subject, anecdotal evidence at our laboratory suggests that these problems are even more prevalent with respect to the analysis of other metals in oil. In this study, we present the results of our recent investigation into using high pressure-high temperature wet ashing with pure HNO_3 as a way of minimizing these problems. The goal of this research is to produce a generalizable digestion method for Hg analysis that is at once suitable for petroleum, coal, plastics, and industrial chemicals.

RESULTS AND DISCUSSION

Digestion and Analysis. Most samples in this study (from the Gulf of Thailand and the USA) were waxy solids at room temperature. Prior to aliquoting for analysis, they were heated to 45 °C, and shaken vigorously. When using the BrCl liquid-liquid extraction (BLOOM, 2000), 0.5 gram aliquots were diluted with 1.5 mL of dodecane in a 40 mL glass vial, and 30 mL of 0.1 N BrCl in 6 M HCl was added. The samples were heated in an oven with Teflon caps screwed on tightly,

at 85 °C for 2 hours, with periodic vigorous shaking. The samples were then brought to 40 mL with BrCl, heated for 30 minutes longer, shaken vigorously once more, and then centrifuged while hot, in the same vials, for 20 minutes at 3,000 RPM. After removing the oily layer from the top of each sample with a pipettor, aliquots of the aqueous phase (0.01 to 2.0 mL) were analyzed using $SnCl_2$ reduction, purge and trap on gold, and cold vapour atomic fluorescence spectrometric (CVAFS) detection (BLOOM AND FIRZGERALD, 1988; BLOOM AND CRECELIUS, 1983). To digest oil samples using the Anton-Paar High Pressure Asher (HPA) approximately a 0.3 gram aliquot of oil was pipetted into a quartz vessel (50 mL), followed by the addition of 3.0 mL of concentrated HNO_3 acid. The HPA digestion is conducted at 20 Atm pressure with a gradual increase in temperature to 300 °C. Once the final temperature and pressure is reached, the duration of the digestion is 2 hours. After the digestion, samples (clear or pale yellow solutions) were diluted to 20 mL with reagent water, and analyzed by CVAFS.

Performance Comparison. Analytically, both methods performed similarly on most samples and QC measures (Table 1), with the HPA methodology giving blanks and method detection limits (MDL) approximately half as big as the BrCl extraction method. Although on most samples, both methods gave similar results (Figure 1), in those cases where a discrepancy was seen, the HPA extracted more Hg than the BrCl method, particularly when digesting heavy, viscous, sulphur-rich oils. Of particular interest was the coal CRM, NIST-1632b. This sample was completely dissolved by the HPA, yielding a concentration of 68.1 ± 2.2 ng g^{-1} (non-certified value is 74 ng g^{-1}), while using BrCl, it did not dissolve, and only 48.7 ± 4.3 ng g^{-1} was recovered. We also found that the final digest from the HPA asher was always a simple, transparent solution (colorless or light yellow), while the BrCl extracts were difficult to work with because they still contained oil, and noxious halogenated hydrocarbons. Analysis of the extracts from the BrCl procedure damaged the gold traps much more rapidly than did the analysis of the HPA digester extracts. However, the BrCl extrac-

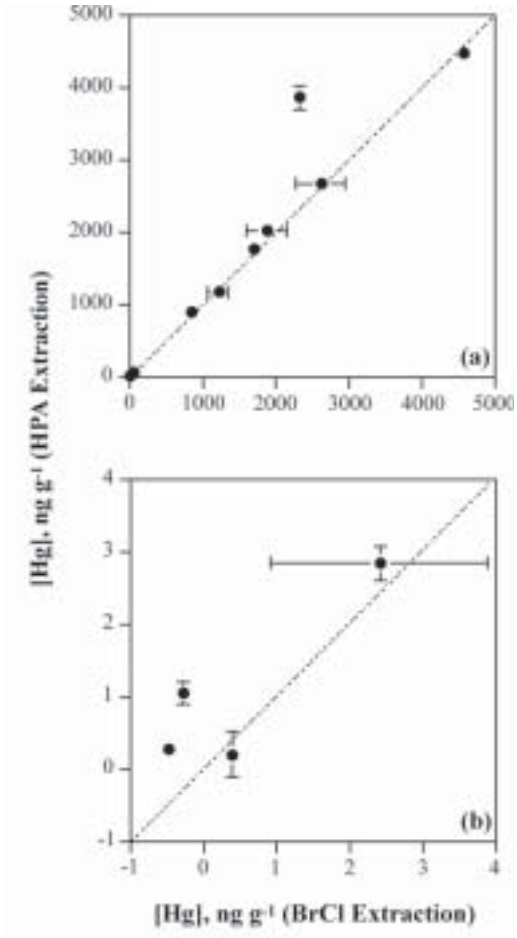

Figure 1. Comparison of Hg measured in 13 different oil samples by BrCl extraction and HPA extraction (a) all data; (b) low level data only. Most points are the mean and SD of 3 or 4 individual digestions. Dotted line indicates 1:1 correspondence.

tion is much faster. For example, a single analyst can prepare and extract 40 samples in 4–6 hours, whereas with the HPA, the same number of samples takes approximately 8–12 hours, spread over 2–3 days in the lab.

Because the HPA asher results in complete dissolution of the sample and a simple, low TDS matrix of pure HNO_3, the final solution is much more suitable for the analysis of other elements than is the BrCl extraction. In Table 2, we report the results of an initial MDL study for trace metals. In this study, As and Se were analyzed by hydride generation atomic fluorescence sprectrometry (HG-AFS) rather than ICP/MS, to obtain lower detection limits. The MDLs for these metalloids using ICP-MS are approximately an order of magnitude higher. This study showed satisfactory precision and accuracy for all 11 metals investigated, with detection limits that are at least two orders of magnitude lower than could be achieved with the BrCl extraction.

Parameter	Statistic	HPA	BrCl
mass digested	g	0.25–0.35	0.40–0.60
final volume	mL	20	40
blanks (ng g^{-1})	mean	0.05	0.28
	SD	0.11	0.22
	N	0.28	0.57
	MDL	32	46
low level spikes	mean	94.3	80.7
recovery (%)	SD	8.0	49.3
	N	12	21
high level spikes	mean	98.2	99.9
recovery (%)	SD	9.6	6.3
	N	19	34
internal reference	mean	2,005	1,883
sample (ng g^{-1})	SD	81	243
	N	12	16
	historic value	na	1,835

Table 1. Figures of merit for the determination of Hg in oil using two different digestions. Low spikes were 2–4 ng g^{-1}, and high spikes were 50–200 ng g^{-1}.

Element	Analytical Method	Mean µg g^{-1} (ppm) Blank	MDL	Mean Percent (%) Recovery	RSD
Al	ICP-MS	2	2	118.6	23.5
V	ICP-MS	0.8	0.7	92.9	8.0
Cr	ICP-MS	0.00	0.04	94.0	3.9
Fe	ICP-MS	~4	3	89.9	7.5
Co	ICP-MS	0.002	0.005	106.5	4.2
Ni	ICP-MS	0.01	0.01	91.2	4.3
Cu	ICP-MS	0.01	0.01	88.7	4.2
As	HG-AFS	0.01	0.02	90.3	7.1
Se	HG-AFS	0.003	0.005	97.8	11.5
Ba	ICP-MS	~0.01	0.04	98.2	4.8
Pb	ICP-MS	0.002	0.003	88.2	7.1

Table 2. Figures of merit for trace metals in oil after digestion using the HPA. Blanks and MDLs were determined on 8 replicates, mean recovery and precision are from 13–19 spikes and CRMs (NIST-1634c and NIST-1084a).

CONCLUSIONS

The HPA asher appears to be superior to liquid-liquid extraction with hot BrCl for the analysis of Hg and other metals in petroleum products. The HPA method yields a simple, colorless digest solution, which gives lower detection limits, higher recoveries, and is less damaging to the Au traps. However, the price of this improved performance is that the cost of sample digestion is approximately twice that of the BrCl extraction—although this cost is probably at least partially offset by reduced damage to the Hg analyzer, and less need for analytical re-runs. The HPA digestion is also advantageous in that it can digest a wider variety of samples (including coal) under one set of conditions (and so one set of QA), and the final digest solution is quite suitable for multi-metals analysis, whereas the BrCl extraction solution is not.

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Mercury speciation: A fully automatic gas chromatography/atomic fluorescence instrument

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Abstract: A sensitive, selective and reliable GC-AFS system for the speciation analysis of mercury in environmental samples is described. Extraction procedures for various sample matrices are described.

Keywords: capillary gas chromatography, environmental samples, mercury speciation

INTRODUCTION

Mercury is a widely distributed pollutant in the environment. There have been many incidents where its presence has caused damage both to humans and to production plants. Legislation is normally based on the total mercury content and the acceptable levels are always being reduced. However, its organic compounds, particularly methylmercury, are far more toxic than elemental mercury or its inorganic salts. Such widespread hazard and toxicological concern have stimulated great demand for reliable, precise and sensitive methods for the determination of organomercurials in water, sediments, fish and other biological samples. The general method for the determination of methyl and ethylmercury halides (MM and EM) involves gas chromatography with electron capture detection. However, tedious sample work-up protocols and poor chromatographic response (on packed columns) have shown the need for the development of new methods in this field. Atomic fluorescence detection offers significant advantages for the analyst and the potential of this technique is further exploited by coupling to chromatographic separation techniques.

A fully automated instrument will be described using a commercially available gas chromatograph with this highly sensitive and specific atomic fluorescence detector. This provides a sensitive method for the determination of methyl- and ethylmercury, free from deficiencies associated with earlier methods. MM and EM are first released from the sample matrix by the combined action of acidic potassium bromide and cupric ions 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 sulphate addition and subsequent extraction into a small volume or organic solvent. Capillary gas chromatography coupled with an atomic fluorescence detector system proved to be a very selective and sensitive technique with excellent separation efficiencies for methyl- and ethylmercury. The absolute detection limit for both MM and EM was found to be 0.2 pg. Data provided by the system has been used to determine the mercury speciation in

plant soils, sediments and waste samples, interesting examples of the speciation found in these types of samples will be presented.

Figure 1 shows a schematic diagram of the GC-AFS system. Samples or standards are injected onto the megabore capillary column and flushed with a stream of argon. The species, which are separated on the basis of their boiling points, then pass through a pyrolysis unit to form Hg^0. From there the mercury is mixed with a makeup gas of argon before passing into the AFS detector where species in unknown samples are identified on the basis of their retention times. Table 1 outlines the instrumental conditions used while figure 2 shows a chromatogram showing typical separation of five mercury species.

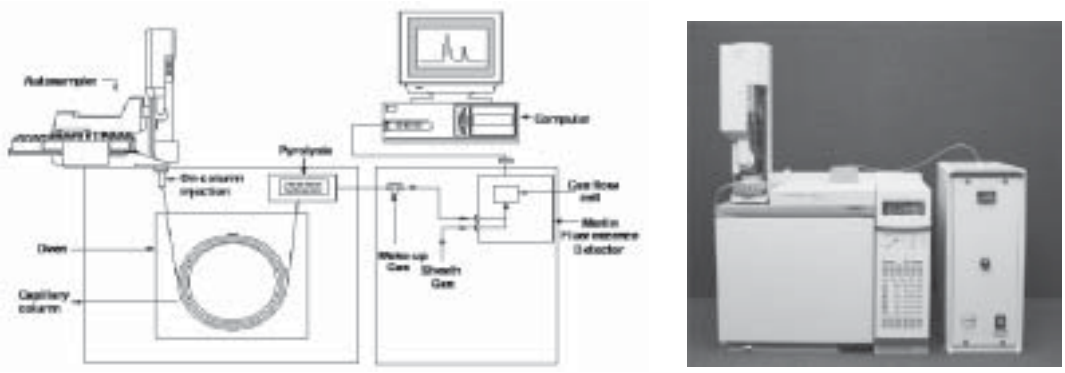

Figure 1. Schematic diagram and photograph of the GC-AFS system.

Table 1. Instrumental conditions.

Injector temperature	200 °C - glass liner & wool
Temperature program	1 min at 40 °C, 30 °C min^{-1} to 140 °C 2 min at 140 °C, 30 °C min^{-1} to 200 °C 10 min at 200 °C
Pyrolyser temperature	800 °C
Column flow rate	(Ar) 4.0 ml min^{-1}
Make up flow rate	(Ar) 90 ml min^{-1}
Column specification	DB1, 15 m length, 0.53 mm id with 1.5 μm film

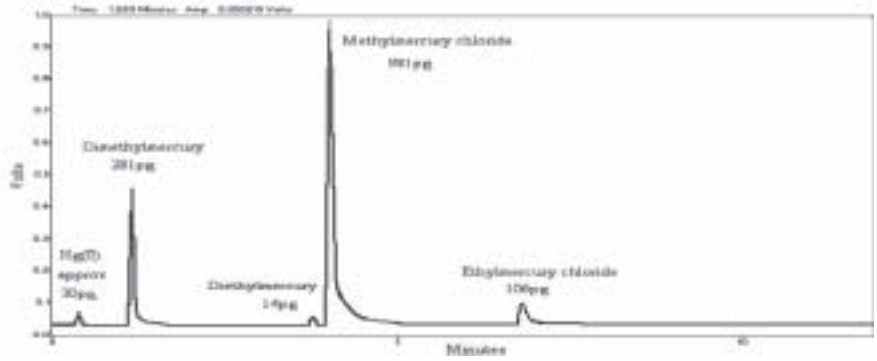

Figure 2. Typical chromatogram.

RESULTS AND DISCUSSION

Various extraction procedures can be used for the speciation analysis of mercury by GC-AFS. Typical procedures for soils and sediments and biological matrices such as fish and plant tissue are shown in figures 3 and 4.

The data presented in Table 2 shows some typical results for certified reference materials of fish, sediment and plant samples. In all cases excellent agreement was obtained with the certified values.

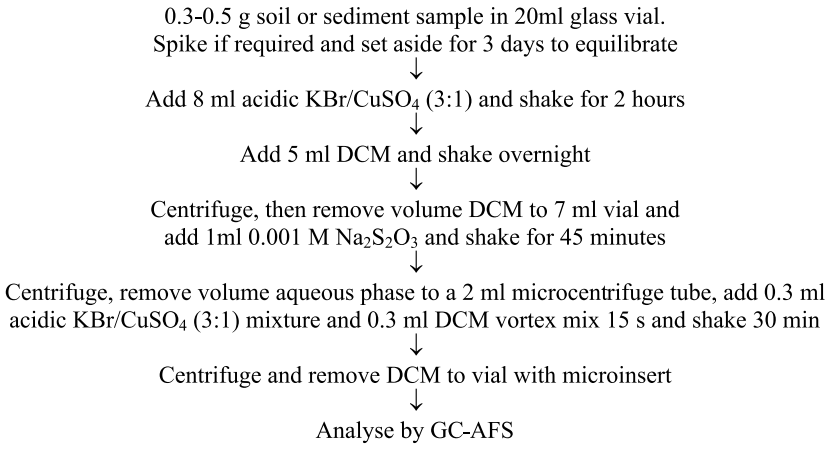

Figure 3. Organomercury extraction procedures for soils and sediments

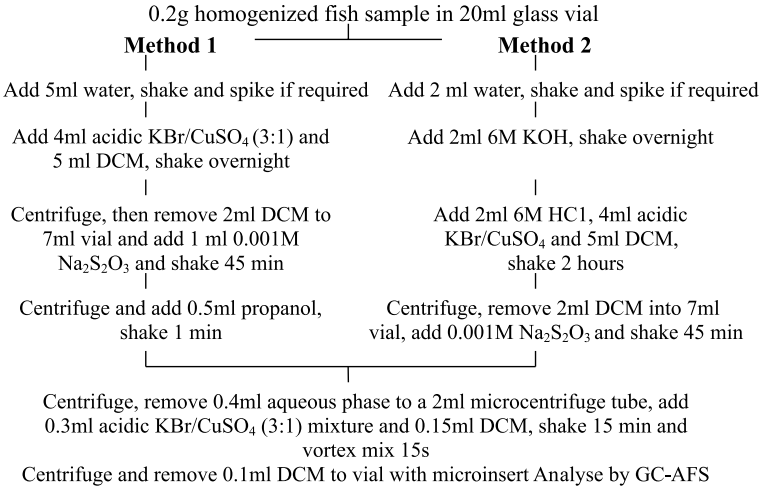

Figure 4. Organomercury extraction procedures for fish.

Table 2. Typical results for certified reference materials.

Sample	Certified MeHg (ng g^{-1})	Value obtained (ng g^{-1})
Mussel Homogenate NIST RM 8044	28 ± 2	26 ± 4
Mussel Homogenate IAEA 142	47 ± 4	45 ± 7
Dogfish Muscle DORM-1	731 ± 60	690 ± 20
Dogfish Liver DOLT 2	693 ± 53	671 ± 41
Lobster Pancreas DOLT	180 ± 1	182 ± 5
Fucus Seaplant Homogenate IAEA 40	626 ±107	630 ± 60
Polluted Marine Sediment IAEA 356	5.46 ± 0.39	5.21 ± 0.19
Polluted Marine Sediment IAEA 356 Microwave extracted	5.46 ± 0.39	5.52 ± 0.01

Marine sediment IAEA 356 was also prepared using microwave extraction to accelerate the extraction procedure. 0.3g of sample was treated in a closed microwave vessel containing 10 ml of 2 mol l^{-1} HCl. The vessel was heated at 10 % power (56w) for 3 min. The procedure in Figure 3 was then continued in the normal manner.

CONCLUSIONS

Capillary GC-AFS offers an attractive approach for mercury speciation analysis. Absolute detection limits of 0.2 pg were obtained for methylmercury and ethylmercury, this equates to 0.1 ng/g, 0.1 ng/g and 0.4 ng/g for sediments, plant and fish tissue respectively. The extraction procedure was optimized and accelerated by the use of microwave extraction and good agreement was obtained for the two extraction approaches.

Online Mercury Speciation in Flue Gas from Coal Fired Stationary Sources

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Abstract: Accurate measurement of mercury speciation in flue gas from coal fired power utilities and waste incinerators is necessary to model the fate and transportation of mercury in the atmosphere and to evaluate the effectiveness of mercury control technologies. There a numerous measurement and sampling issues that have to be addressed to ensure accurate results are obtained. Sampling in the presence of reactive flyash is problematic using conventional filtering techniques since captured flyash may collect mercury or change the speciation. To overcome this problem we have developed an inertial filter that uses a sintered porous tube. The process was evaluated using dynamic spiking of elemental mercury into flue gas with high flyash content. To perform these experiments a calibration system based on dilution of saturated mercury vapour was developed. The relative accuracy was found to be less than 5 % of the theoretical value based on saturated vapour calculations. Speciation was achieved using both wet and dry speciation modules. The purpose of these units was to generate two streams specific to elemental and total mercury. Oxidized mercury was determined by difference. The influence of flue gas components on the accuracy of the measurement will be discussed. The developed instrumentation has been successfully used in the field at various locations on power stations in Europe and the USA.

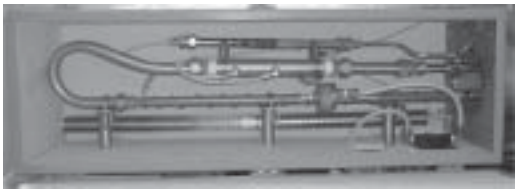
Keywords: flue gas, online instrumentation, mercury speciation, atomic fluorescence.

INTRODUCTION

Activated carbon injection and optimization of burner conditions to produce fly ash enriched with un-burnt carbon are the most promising mercury removal technologies currently being investigated. Sampling under these conditions is problematic because the gas contains appreciable quantities of reactive fly ash and carbon. Conventional methods of filtering are prone to difficulties because of high ash build up, mercury transformation and capture of Hg on the filter. Blowback filter arrangements were originally tested to overcome this problem. Unfortunately fine ash became imbedded in the filter medium and was not removed during blowback. This ultimately resulted in a loss of mercury across the filter and the expected result was never truly restored even after blowback was performed. To overcome these issues an inertial filter was developed. This paper presents a description of the probe developed and measurement technology employed for evaluation. A crucial and significant part of this study involved the use of a novel mercury calibration system. This enabled the authors to perform dynamic spiking of Hg at known concentrations into a flue gas stream heavily laden with reactive fly ash.

RESULTS AND DISCUSSION

The basic principle of operation of the inertial filter (Figure 1) is to accelerate the particulate material contained in the sample gas in a vector direction with sufficient velocity to prevent the particles from sticking to the walls of the sample tube and extract a gas sample to be transported to the Hg CEM. An eductor is used to generate a high velocity (70-100 ft/sec) axial gas flow through the inertial filter. The flow rate is dependent upon the gas density, temperature, diameter of the sampling tube, absolute pressure and particulate loading. Particulates in the high velocity gas stream continue to travel in the straight vector direction and the sample stream is withdrawn at a very low filter face velocity (0.006 ft/sec) separating the sample stream from the particulate material. Particulate deposition and penetration into the porous filter wall is prevented by the ballistic effect of the particle inertia, (Figure 2).



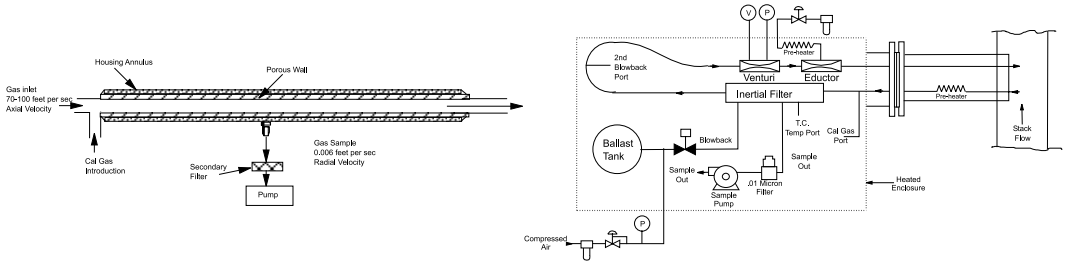


Figure 2. Inertial Probe Schematics

The P S Analytical (PSA) continuous emission mercury speciation monitor is shown in figure 3. Hot filtered flue gas is transported using a Teflon® heated line to a speciation module. This is designed so that it may operate using wet chemical impinger based reagents or solid phase adsorbents/catalysts. The sample gas is split into two streams representing elemental mercury (Hg^0) and total mercury (Hg^T). The Hg0 channel is produced by trapping oxidised mercury in a KCl solution or solid phase adsorbent and allowing Hg^0 to pass through un-retained. The Hg^T stream is produced by converting oxidised Hg to elemental Hg using SnCl2 reductant or by a thermo-catalytic process. Condensed moisture is then removed using a Peltier cooler and drain pump arrangement. The two speciation modules are shown in figure 4.

The two gas streams from the speciation module are continuously delivered to the stream selection unit. When selected the stream is passed over

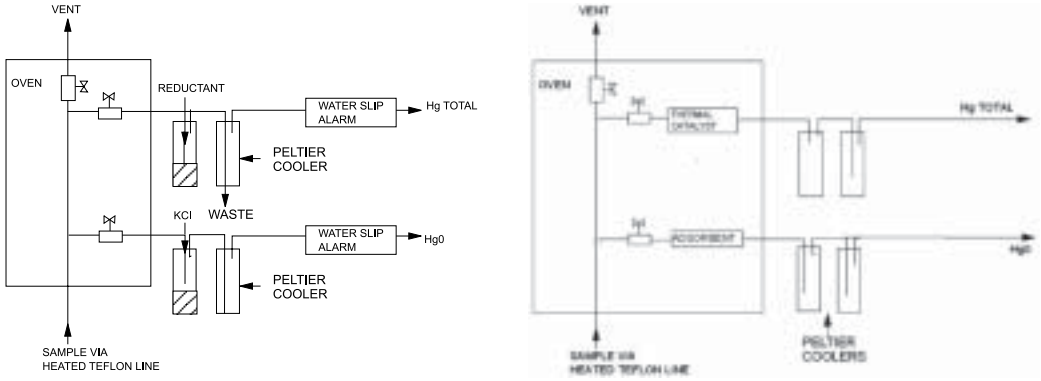


Figure 4. Schematic diagrams of wet and dry speciation modules

an Amasil® sampling tube which pre-concentrates the gaseous phase mercury by amalgamation. The flowrate and volume of gas are controlled and measured using a mass flow-controller and pump arrangement.

Amalgamation not only improves the detection limit capability but also separates the mercury from the flue gas matrix thereby overcoming potential interferences. After sampling the mercury collected is released into a carrier gas stream by thermal de-sorption. The mercury is then detected at 253.7nm using an atomic fluorescence spectrometer.

The entire sequence takes approximately 4-5 minutes. The combination of amalgamation and AFS offers an absolute detection limit of 0.1pg. This equates to 0.1ng/m^3 for a 1litre sample volume collection. One further advantage of this approach is that the linearity extends to 3000µg/m^3 without the necessity of dilution. The analytical sequence is shown in figure 5. Calibration of the mercury analyser is achieved by injecting accurate volumes of mercury saturated vapour at known temperature using a NIST certified gas tight syringe and thermometer.

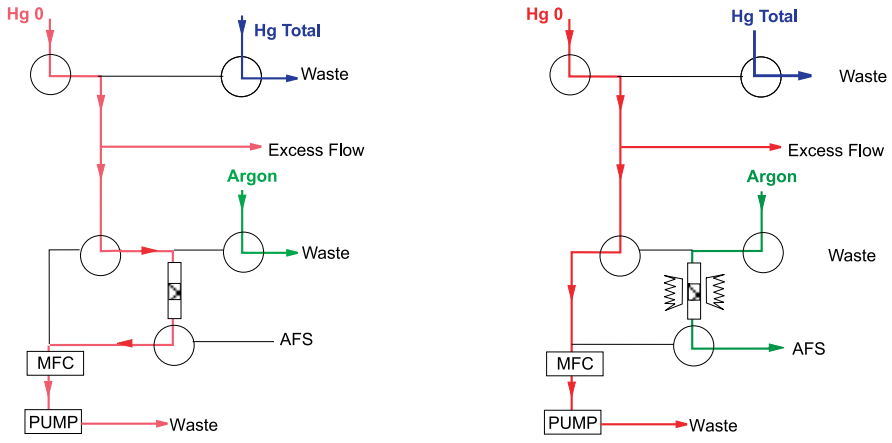


Figure 5. Analytical sequence for Hg CEM

One of the difficulties of sampling mercury from stack gas is the avoidance of mercury losses and transformation of mercury species. The original ratio of oxidised and elemental mercury should be preserved during the transport across the filter. To test for this affect an online calibration was developed.

The PSA 10.534 Cavkit calibration unit is based on accurate dilution of a saturated source of elemental mercury at known temperature. NIST certified mass flow-controllers are used to produce accurate and stable flowrates. The first mass flow-controller supplies a low flow of gas between 1-20ml/min over an Hg reservoir located in a temperature calibrated oven. This gas becomes saturated with Hg vapor. A dilution gas supplied by the second mass flow-controller then dilutes the Hg saturated gas into the concentration range of interest, by varying temperature and flowrate the device offers a wide range of concentrations from ng/m^3 to µg/m^3. A schematic of the device is shown in figure 6.

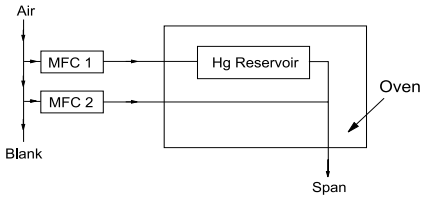


Figure 6. Flow schematic of cavkit calibration system

The inertial probe has been used and tested at various pilot scale and full scale power stations in Europe and the USA. Figure 7 shows an example of running two initial probes across an electro static precipitator (ESP). The CEM allows simultaneous measurement of mercury species at two locations thereby allowing optimisation and development of mercury removal technologies, Lissianski (2003). The coal used for this study was a blend of bituminous coals and the expected level of total mercury in the flue gas was 10µg/m^3. No mercury was found initially when burning natural gas. A steady increase in mercury was observed as the fuel was switched to coal. Mercury total at the inlet of the ESP gave extremely good agreement with the expected concentration of mercury. Approximately 10 % of the total mercury was lost across the ESP. Elemental mercury at the inlet of the ESP was found to be between 8 and 9µg/m^3, indicating the presence of oxidised mercury at 1-2 µg/m^3. A greater reduction of elemental mercury was found across the ESP. Sampling at this location using conventional filtering methods would not have been possible.

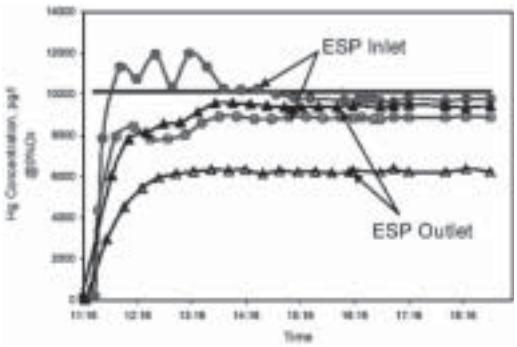


Figure 7. Hg speciation across ESP

Table 1. Spike Recovery Data

Day	Fuel & Species		Spike Conc. ($\mu g/m^3$)	Measurement Spike ($\mu g/m^3$)	% Recovery
1	Nat Gas	Hg^0	9.31	9.07	97.4
		Hg^T	9.31	9.82	105.5
2	Nat Gas	Hg^0	7.44	7.09	95.3
		Hg^T	7.44	7.18	96.5
3	Nat Gas	Hg^0	9.31	9.07	97.4
		Hg^T	9.31	10.82	116.2
	Coal	Hg^0	8.57	6.52	76.1
		Hg^T	8.57	8.25	96.3
4	Nat Gas	Hg^0	9.02	8.60	95.4
		Hg^T	9.02	8.53	94.6
	Coal	Hg^0	9.53	6.98	73.2
		Hg^T	9.53	10.30	108.1
5	Nat Gas	Hg^0	9.31	7.74	83.2
		Hg^T	9.31	10.03	92.7
	Coal	Hg^0	9.53	8.48	88.9
		Hg^T	9.53	9.17	96.2

A series of spiking experiments under different burner conditions was conducted using the Cavkit calibration system. When firing the burner with natural gas the spike recovery over 5 consecutive days ranged from 92.7 to 116.3 %. On several days the spike recovery for elemental mercury was slightly lower, possibly indicating some evidence of mercury in the flue gas or across the probe. This effect is more evident when burning coal. The results obtained are summarised in table 1. Overall the spike recoveries are very encouraging given the natural variation within the sample, difficult sample matrix and inaccuracy associated with the venturi flowmeter at process conditions.

CONCLUSION

The development of an inertial probe has enabled sampling of flue gas containing high fly ash content. This was not previously possible with conventional methods of filtration. Dynamic spiking of the probe with known quantities of elemental mercury gave excellent recoveries for natural gas. During coal calibration a small fraction of the elemental mercury was oxidised. Further work will be conducted using $HgCl_2$ spiking apparatus.

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Mercury Speciation in Crude Oil and Natural Gas Condensates using Cold Vapour Atomic Fluorescence Spectrometry

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Abstract: Crude oil is a primary feedstock for a variety of industrial processes. Understanding the mercury speciation in crude oil is critical for refining operations since the presence of mercury even at low concentrations can have a detrimental effect on numerous refining operations. Removal of mercury from crude oil and other petrochemical products is extremely challenging and the optimization of such processes cannot be achieved without knowledge of the mercury species present in the sample and how they might be transformed on the refinery. This paper we will describe various methodologies for extracting mercury species in crude oil. Cold vapour atomic fluorescence spectrometry was used as the measurement technique. Particulate mercury was established by filtering through a 0.45 micron filter and digesting/extracting the filter medium. In the particulate mercury fraction we were able to distinguish between mercury sulphide and insoluble mercury. These were done using high temperature extractions with aqua regia and dilute nitric acid respectively. In the latter case mercury sulphide was not digested and therefore the mercury sulphide content was obtained by difference. Hot aqua regia extraction was used to determine total mercury after homogenisation by ultrasonication. Ionic mercury was extracted using a saturated solution of potassium chloride. Organomercury and elemental Hg was determined using a specially designed capillary GC- atomic fluorescence spectrometer after a direct injection of the filtered samples. Results will be presented for a wide range of crude oil from different geographical locations.

Key words: crude oil, atomic fluorescence spectrometry, petrochemical

INTRODUCTION

Crude oil and condensates are primary feedstock for the petrochemical industry. Understanding the mercury speciation in these samples is critical for refining operations since the presence of mercury even at low concentrations can have a detrimental effect on numerous refining operations. These include the poisoning of expensive hydrogenation catalysts, corrosion of aluminum alloys in steam cracker cold boxes and reducing product quality. Products contaminated with mercury tend to offer a lower premium and therefore understanding the amount of mercury in the feedstock is essential. There are also environmental aspects that have to be considered, since the combustion of hydrocarbons essentially contributes to the anthropogenic emissions of mercury to the atmosphere. Removal of mercury from crude oil and other petrochemical products is extremely challenging and the optimization of such processes cannot be achieved without

knowledge of the mercury species present in the sample and how they might be transformed during refining operations.

The chemistry of mercury in crude oil and gas condensates is complex. Numerous chemical forms of mercury with different chemical and physical properties may be present in samples. The speciation of mercury is highly dependent upon the source, production stage, sampling and the age and storage of the sample. The stability of elemental mercury in hydrocarbon samples is questionable given the high volatility and readiness to adsorb on metallic surfaces and suspended material in the sample. Mercury may also be present as various oxidised forms that may be insoluble or dispersed as colloids (e.g., Hg_2Cl_2 and HgS) or soluble (e.g., $HgCl_2$,) Organomercury compounds such as mono and di-alkyl mercury derivatives may also be present and despite their high volatility they are extremely soluble in hydrocarbon matrices. Mercury coordination complexes in which Hg atoms are coordinated with sulfur and nitrogen ligands have been postulated to exist but their presence has yet to be proved. In this paper we will describe a methodology for selective extraction of mercury species with subsequent determination by cold vapour – AFS. Capillary GC Atomic fluorescence spectrometry was used for mercury speciation analysis.

Results and Discussion

An automated continuous flow vapour generation system coupled to AFS (PSA 10.015) was used to determine Hg in the various digested and extracted solutions. For the determination of total Hg, the samples were initially homogenized by shaking for 1 hour and ultrasonicated for 15 minutes. The samples were then heated in a reflux arrangement with aqua regia at 120C for a period of one hour. All samples were prepared in duplicate and analysed in triplicate. With each batch of samples a NIST certified Conostan Reference standard was prepared in base oil at 34.5 ng/ml. Samples were also spiked with this material to check for matrix interferences. Typical data is shown in Table 1.

Table 1. Total mercury in crude oil and condensate samples

Sample	Prep	Mercury (ng/ml)	Mean Result (ng/ml)
Conostan CRM	1 2	35.3 ± 0.3 33.7 ± 0.3	34.5 ± 0.4 (100 %)*
North Sea Oil 1	1 2	97.1 ± 0.2 103.6 ± 0.5	100.4 ± 0.5 (97.2 %)*
North Oil Sea 2	1 2	78.5 ± 0.1 74.3 ± 0.3	76.4 ± 2.9 (102.1 %)*
Thai Crude Oil	1 2	2896 ± 15 2991 ± 8	2944 ± 7 (96.4)*
Venezuelan Crude Oil	1 2	3852 ± 18 3926 ± 10	3889 ± 2 (95.1)*
Algerian Condensate	1 2	733 ± 14 741 ± 15	737 ± 21 (98.2)*
* Spike Recovery Data			

The North Sea and Algerian condensate were analysed after filtration through a 0.45 μm filter. The filtered medium of the North Sea oil samples was digested using two different methods in attempt to determine whether the particulate phase was Hg adsorbed onto suspended material or it was insoluble mercury species (e.g., HgS). The sample was digested, firstly shaken with nitric acid and then digested using heated aqua regia. The difference between these measurements was attributed to HgS as the nitric acid extraction was previously found not to digest the HgS species. Typical data is shown in table 2.

The determination of elemental and organic Hg was achieved by capillary GC-AFS. Samples were analysed with and without a Au/Pt gauze inline of the detector to confirm that the response was definitely Hg. The results for North Sea crude oil and Algerian condensate are shown in table 3.

In the case of the North Sea samples the elemental mercury was found to be between 43.7 and 56.8 %. In contrast to this the Algerian crude was found to contain only 2 % elemental mercury. The stability of elemental mercury was not studied. It is quite possible that the age, storage and collection method of the sample influences this measurement. In this case the samples were stored in amber glass bottles with Teflon lined caps. Both samples were analysed within one week of collection. The elemental mercury concentration did not change significantly after filtration since a closed filtration arrangement was used. No organomercury compounds were detected. At 17 minutes there was a characteristic broad hump observed eluting over several minutes. This peak was not observed after filtration so it was classified as particulate bound mercury. The response was definitely related to mercury since it disappeared when the

Table 2. Dissolved and particulate mercury

Sample	Dissolved Hg (ng/ml)	HgS in Particulate (ppb)	Hg on Particulate (ppb)
North Sea Oil 1	80.5 ± 2.35	12.1 ± 1.1	8.1 ± 0.7
North Sea Oil 2	50.6 ± 7.60	15.2 ± 2.2	10.3 ± 0.5
Algerian Condensate	20.1 ± 3.0	-	-

Table 3. Data from GC-AFS

Sample	Elemental Hg (ng/ml)	DMM (ng/ml)	DEM (ng/ml)	MMC (ng/ml)	Particulate Bound Hg (ng/ml)
North Sea Crude Oil 1 (Filtered)	43.9 ± 0.1 (43.0 ± 0.2)	N.D (N.D)	N.D (N.D)	N.D (N.D)	19.9 ± 2.3 (N.D)
North Sea Crude Oil 2 (Filtered)	43.4 ± 3.6 (4.1 ± 0.8)	N.D (N.D)	N.D (N.D)	N.D (N.D)	25.8 ± 7.1 (N.D)
Algerian Condensate (Filtered)	14.1 ± 0.2 (13.0 ± 0.8)	N.D (N.D)	N.D (N.D)	N.D (N.D)	700 ± 93 (N.D)

Table 4. Data for KCl Extractions

Reference	KCl without digestion (ng/ml)	10 % KCl digested with Aqua Regia (ng/ml)
North Sea Crude Oil 1	N.D	32 ± 3
Algerian Condensate	0.6 ± 0.1	752 ± 17

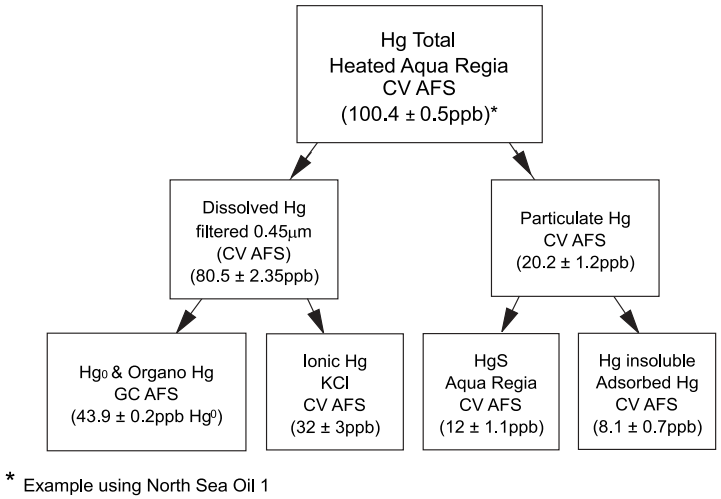

Figure 5. Procedural flowchart for Hg Speciation in Crude Oil

Au/Pt gauze was placed before the AFS and the peak area correlated well with the result for Hg total by aqua regia digestion. It was also observed that by varying the injection temperature the compound was thermally degraded to elemental mercury at a temperature of 350 °C. Although further work would be required to identify this compound its chromatographic behavior would suggest an insoluble inorganic mercury species with high polarity or mercury coordination complex such as porphyrin.

To extract ionic mercury species the North Sea and Algerian crude oil samples were shaken overnight at room temperature with saturated KCl. The aqueous phase was then analysed by continuous flow vapour generation AFS after various pre-treatments. The results obtained are shown in Table 4.

When the aqueous phase was analysed directly without oxidation virtually no mercury was found. This implies that the mercury was not free divalent mercury. When the aqueous phase was digested with hot aqua regia mercury was then found. In both cases the results corresponded well with the total concentration of mercury of the Algerian crude oil the result corresponded well with the total concentration of mercury.

CONCLUSIONS

A method has been developed for total mercury in crude oil and heavy condensate samples. Extraction with hot aqua regia gave repeatable results with excellent precision and spike recoveries. The procedure was validated using NIST certified Conostan.

Mercury associated with suspended solids was either as an insoluble mercury species or mercury adsorbed onto the surface of the particulate material. GC-AFS was used to determine elemental and organic mercury. Only the former was found in the samples studied. An unknown mercury species was present in the samples. This decomposed at 350 °C and could be extracted with a KCl solution. To recover mercury from the NaCl extract a vigorous extraction with hot aqua regia had to be employed. Further work is required to positively identify this species.

Online Determination and Removal of Mercury from Natural Gas Streams

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Abstract: Natural gas and its liquid condensates are primary feedstocks for a variety of industrial processes. Mercury in natural gas is known to cause corrosion problems with aluminum heat exchangers, rotors and condensers. The replacement of heat exchangers is a costly operation with high capital investment and huge financial losses due to unscheduled plant shutdown. Mercury has also been found to be responsible for the deactivation of expensive hydrogenation catalysts. It is therefore important to remove and accurately determine mercury from natural gas streams to ensure the protection of downstream refinery equipment. In this paper we will describe the development and application of an online process mercury analyser to monitor the efficiency of mercury removal beds. Instrumentation based on dual amalgamation coupled to atomic fluorescence spectrometry was developed and subsequently installed at numerous production facilities. Sampling strategies to ensure a representative sample was obtained without mercury losses were developed. On a plant in the USA inlet concentrations of Hg were found to be quite variable and up to 8 ug/Nm^3 whilst the concentration after Hg removal was typically less than 15 ng/Nm^3. The results for online measurements were periodically validated using offline measurements and these typically gave good agreement to within +/- 10 %. The detection limit was found to be 1 picogram Hg absolute, this equates to 1 ng/m^3 for a 1-litre sample volume collection. The measurement cycle was 5 minutes.

Keywords: mercury removal, natural gas, online instrumentation, atomic fluorescence

INTRODUCTION

Knowledge of the mercury content in natural gas is extremely important. Firstly, mercury is highly toxic and is of environmental concern and secondly, the damage caused to petrochemical plants can be financially crippling especially when unscheduled shutdowns are forced. Mercury has been found to be responsible for many cases of selective hydrogenation catalyst deactivation. Palladium based catalysts are commonly used for the selective hydrogenation of acetylenic species in the steam cracking of C_2 to C_4 cuts. Mercury is known to be the cause of corrosion problems with aluminum-based heat exchangers, rotors and condensers at natural gas refinery plants. Heat exchanger replacement is a costly operation due to the capital investment of the exchanger itself and the plant down time incurred for its replacement. This paper will describe the development and implementation of an online process analyser to monitor the efficiency of mercury removal from natural gas using activated carbon beds impregnated with sulphur. Performance characteristics of the analyser will be discussed with reference to sampling, calibration, accuracy, precision and long term reliability.

RESULTS AND DISCUSSION

Sampling natural gas for mercury is problematic due to high pressure normally involved and the ability of mercury to amalgamate to metallic surfaces. When decreasing the pressure from approximately 100 Bar to 1 bar, the associated adiabatic temperature drop is approximately –30 °C. As the pressure is decreased heavy hydrocarbon cuts are released from the vapour phases and condense as a liquid. Heavy hydrocarbons condensing on the collection mediums have been shown to reduce the collection efficiency, thereby giving lower mercury results. To obtain a representative sample gas from a high-pressure gas stream the use of heated regulators was found to be necessary during the pressure letdown stage. In this way the sample gas at ambient pressures will have the same composition as that at the higher operating pressure. Losses of mercury by surface adsorption on stainless steel components can greatly affect results. To overcome these effects it was found that a high flowrate primary bypass for the sample was also required. Given the above sampling difficulties, offline (PSA 10.537) and online (PSA 10.540) sampling devices were developed. These are described below in more detail.

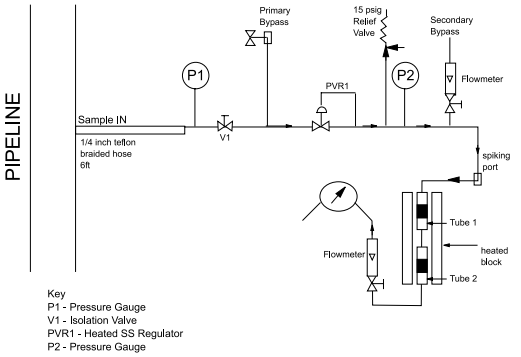

Figure 1. Schematic diagram of offline sampling unit in series mode

The unit has been designed to operate in hazardous Zone 1 areas using ExDIICT3 rated components. This enables the samples to be collected close to the pipeline and, therefore, minimizes any contamination or losses often found when sampling for mercury. A schematic diagram of the offline sampling system operating in series mode is shown in Figure 1.

In normal operation the sampling tubes are used in series to test for breakthrough of mercury. The system can be modified in the field so that the sample can be collected in parallel. To overcome condensation of hydrocarbons on the sampling tubes, the adsorbent Amasil ™ was maintained at 140 °C,

Table 1. Typical offline natural gas results for inlet and outlet of Hg removal beds

INLET

Mode	Tube1 ng	Tube2 ng	Volume L	Conc ug/m3
Series	7.547	0.072	1	7.619
Series	7.693	0.076	1	7.769
Series	15.042	0.121	2	7.582
Series	38.213	0.218	5	7.686
Parallel	7.491	7.485	1	7.491, 7.485
Parallel	15.123	15.007	2	7.562, 7.504
Parallel	39.282	38.719	5	7.856, 7.744

Mean result = 7.63±0.13µg/m^3

OUTLET

Mode	Tube1 ng	Tube2 ng	Volume L	Conc ng/m3
Series	214	25	20	11.95
Series	742	68	50	16.2
Series	1358	105	100	14.55
Series	6985	98	500	14.17
Parallel	710	740	50	14.20,14.80
Parallel	1323	1315	100	13.23,13.15
Parallel	7651	7600	500	15.30,15.20

Mean Result = 14.28± 1.24 ng/m^3

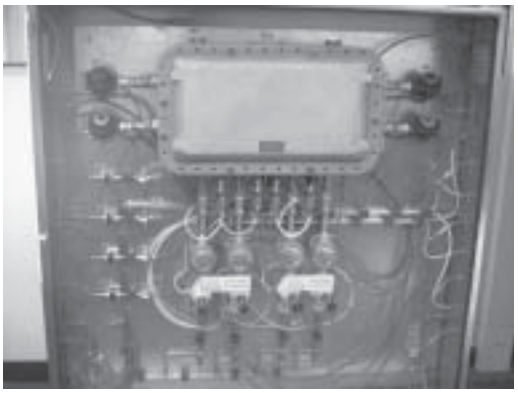

Figure 2. Photograph of online sampling system

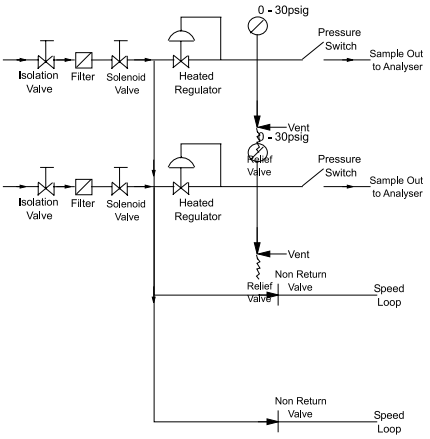

Figure 3. Schematic diagram of online sampling system for a single stream

which is well above the dew-point of the hydrocarbon gas. Offline samples were collected upstream and downstream of the Hg removal beds. Different sample volumes were collected to ensure that no matrix interference was encountered. Samples were also collected in parallel mode. The sample tubes were analysed by dual amalgamation – atomic fluorescence spectrometry.

The online sampling unit is based on the same principle as the offline device but its sole purpose is to deliver a representative gas sample to the online analyser. A sampling system for 4 streams is shown in Figure 2.

All components used in the sampling system are certified to explosion proof rating. A schematic diagram showing the sample stream flow for just one stream is shown in Figure 3. The sample was delivered from the sample point using Ľ -inch Teflon braided hose.

Figure 4. Photograph of online system for Hg in natural gas

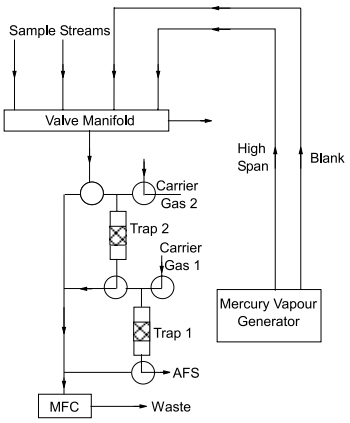

Figure 5. Schematic diagram of online dual amalgamation

Comparisons of offline and online measurements confirmed that no losses of Hg occurred for the online sampling system. For safety implications we incorporated a normally closed 110 V solenoid valve. In the event of an alarm condition a contact closure prevents the power being supplied to the valve stopping the flow of sample. The pressure of the gas was then reduced to 6 psig using a stainless steel heated regulator. A relief valve downstream of the regulator was set to 10 psig. In addition to this a pressure switch that activates at 8 pisg was also included. In the event that the regulator should fail the pressure switch activation closes the solenoid valve.

The online analyser enclosure and sampling system is shown in Figure 4. To comply with safety regulations the cabinet was continuously purged with air. The power to the analyser is only applied after the purge conditions are maintained and uninterrupted.

The purged enclosure contains an industrial computer with monitor, automatic calibration system, stream selector and a mercury analyser based on dual amalgamation-AFS.

The preconditioned sample was delivered initially to the stream selection module. A schematic diagram (Figure 5) shows the flow of the sample in standby mode. An online

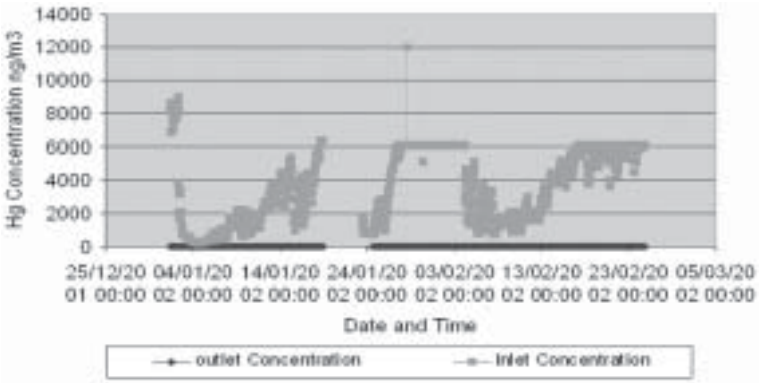

Figure 6. Online determination of Hg in natural gas for inlet and outlet

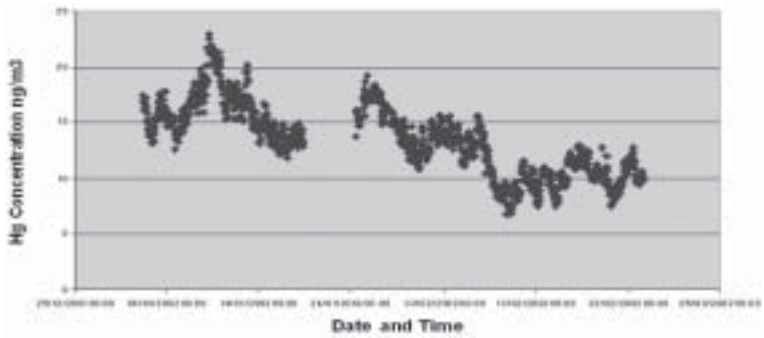

Figure 7. Outlet Hg concentration

software program allows the user the select what streams are to be analysed in a sequential fashion. On selection of the stream the valve was activated so the gas was delivered to the Hg analyser.

The sample volume collected and flow-rate over the trap was controlled using a digital mass flow-controller. During the collection period the sample tube was heated to ensure that no heavy hydrocarbons condense on the collection medium.

After the collection period the sample trap was heated to 900°C with a stream of argon carrier gas for 30 seconds. This thermally desorbs the mercury collected from the sample and delivers the mercury to secondary trap maintained at ambient temperature. Optimization of flow-rates and sampling times allows a wide concentration range to be measured with the same calibration. Inlet measurements are achieved using a sample flow-rate of 250 ml/min for a period of one minute whereas the outlet measurements were performed using a ten-minute collection.

CONCLUSIONS

Offline and online sampling units have been developed to enable representative sampling of natural gas for mercury measurements. Despite the wide concentration range of mercury between the inlet and outlet of mercury removals beds, amalgamation coupled to AFS was found to provide an accurate measurement of mercury for both streams. The system described has operated for several years with minimal maintenance requirements allowing the refinery to monitor the efficiency if the Hg removal process in real time. Excellent agreement was found for offline and online sampling.

Sialic Acid Content of Low-Density Lipoprotein (LDL) is a Marker of LDL Oxidation

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Abstract: Oxidative stress constitutes a significant etiological factor for mercury intoxication, therefore, development of assays for monitoring oxidative stress of an organism is reasonable. Recently it was *in vitro* shown that a decrease in sialic acid (SA) content of low-density lipoprotein (LDL) is only a primary step in a chain of multiple modifications, which finally yields oxidized LDL (ox-LDL). To test the hypothesis that SA content of LDL and oxidation of LDL are interrelated also *in vivo*, we measured SA content of LDL and concentration of ox-LDL in plasma of 20 apparently healthy men. An average SA content of LDL was 34.7 ± 1.8 nmol per mg of LDL protein and concentration of ox-LDL 7.24 ± 1.01 % of total LDL. Linear regression analysis revealed that lower SA content of LDL was related to higher percentage of ox-LDL from total LDL ($r = -0.7085$, $p = 0.0008$). Our study is the first evidence that desialylation and oxidation of LDL occurs simultaneously also *in vivo*. These results suggest that SA content of LDL may serve as a sensitive marker of LDL oxidation possibly useful for monitoring oxidative stress of an organism in mercury polluted environmental areas.

Key words: mercury, oxidative stress, low-density lipoprotein, sialic acid

INTRODUCTION

Current evidence strongly suggests that oxidative stress constitutes a significant etiological factor for mercury intoxication[1,2], therefore, development of assays for monitoring oxidative stress of an organism is reasonable.

Oxidation of lipids and proteins substantially modifies the physical, chemical and immunological properties of low-density lipoprotein (LDL). Most recently, desialylation of LDL, e.g. loss of sialic acid (SA) residues on apo B and glycolipids, was shown *in vitro* to be an initial step in a chain of multiple modifications, which finally yields oxidized LDL (ox-LDL)[3,4]. Thus, the decreased SA content of LDL might be a marker of the extent of LDL oxidation indicating oxidative burden *in vivo*.

To test the hypothesis that SA content of LDL and oxidation of LDL are interrelated also *in vivo*, we measured SA content of LDL and concentration of ox-LDL in the plasma of 20 apparently healthy men. This may be of help when choosing SA content of LDL for monitoring oxidative stress of an organism in mercury polluted environmental areas.

RESULTS AND DISCUSSION

Apparently healthy men were prospectively and consecutively enrolled from healthy volunteers willing to participate in the study. To be included in the study, subjects had to have 1) absence of diseases indicating excessive oxidative stress, such as atherosclerosis, diabetes, chronic renal failure, ischaemia reperfusion injury, rheumatoid arthritis or certain nervous system diseases as verified by detailed history and clinical examination 2) systolic and diastolic blood pressure ≤140 and ≤90 mmHg 3) to be nonsmoker and 4) to have serum concentration of C-reactive protein ≤ 1,5 mg/L.

SA content of LDL was determined in isolated LDL fraction with ion-exchange chromatography as previously described[5]. Briefly, plasma containing 4.42 mM EDTA was used for LDL isolation. Butylated hydroxytoluene and Trolox (Hoffmann La Roche) were added at a final concentration of 20 μM of each immediately after centrifugation of blood cells. LDL was isolated by two-step density gradient ultracentrifugation at 100 000 rpm for two hours and with TLA 100.4 rotor in Optima™ TLX ultracentrifuge at 10 °C (Beckman). Lipoprotein(a) (Lp(a)) in the isolated LDL fraction was removed by immunoaffinity gel containing polyclonal anti-apo(a)-antibodies isolated from N Antiserum Lp(a) (Behring). Electrolytes in isolated LDL fraction free of Lp(a) were further removed using a gel filtration (Biogel P-6DG, Bio Rad). Desalted LDL fraction free of Lp(a) was concentrated three times by ultracentrifugation at 100 000 rpm for 75 minutes with rotor TLA 120.2 in Optima™ TLX ultracentrifuge (Beckman) at 10 °C. The protein concentration was determined by the method of Lowry *et al*. Desalted and concentrated LDL free of Lp(a) was diluted with 10 mM Tris pH 7.4 and sulphuric acid to a final concentration of proteins of 0.88 g/L in 0.02 M sulphuric acid. The hydrolyzing solution was incubated for one hour at 80 °C with permanent shaking and stored afterwards at –70 °C until further analysis. SA was determined in one batch at the end of the study with Aminex HPX-87

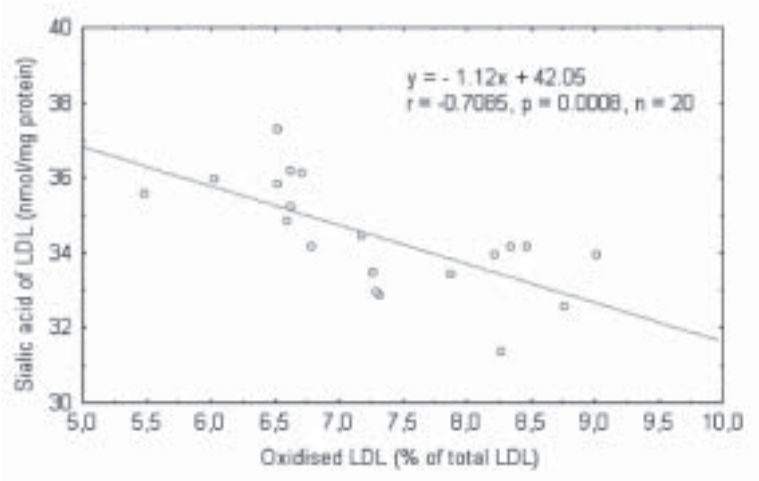

Figure 1. Correlation between the salic acid content of low-density lipoprotein (LDL) and the percentage of oxidized LDL in apparently healthy men.

cation-exchange resin column 300 x 7.8 mm (Bio Rad) and Micro-guard cation precolumn at 42 °C, a mobile phase of 0.003 M sulphuric acid at a flow-rate of 0.65 ml/min and UV detection at 206 nm. Oxidized LDL was determined in isolated LDL fraction, free of Lp(a), as previously described[6].

An average SA content of LDL was 34.7 ± 1.8 nmol per mg of LDL protein and concentration of ox-LDL 7.24 ± 1.01 % of total LDL. Linear regression analysis revealed that the lower SA content of LDL was related to higher percentage of ox-LDL from total LDL ($r = -0.7085$, $p = 0.0008$). Results obtained are graphically presented in Figure below.

A possible link between desialylation and oxidation of LDL was studied *in vitro* for the first time by Chappey *et al*. in 1998[3]. They found that LDL exposed to dialyzing buffer containing low EDTA concentration revealed to the partial oxidation, as assessed by the decrease in vitamin E and the increase in TBARS. At the same time SA content of LDL markedly decreased, which was concluded to be related to a subsequent alteration of lipoprotein integrity. Desialylation and oxidation of LDL was completely inhibited by concentration of EDTA in the dialyzing buffer above 1 mmol/L. At the same time Tertov *et al.*[4] reported a significant fall in the lipoprotein SA level after only one hour of incubation of native LDL with an autologous plasma-derived serum. While SA of LDL was continuously decreasing, LDL gradually revealed oxidative properties such as the increase of negative charge and susceptibility to copper-oxidation, the loss of alpha-tocopherol and the decrease of particle size. Thus, the desialylation of LDL was only the earliest event in a chain of multiple modifications, which finally yields highly ox-LDL.

CONCLUSIONS

We found a significant correlation between the decreased SA content of LDL and the increased percentage of ox-LDL from total LDL, which is in accordance with data previously published[3,4]. However, our result is also the first evidence that desialylation and oxidation of LDL occur simultaneously also *in vivo*. This result suggests that SA content of LDL may serve as a sensitive marker of LDL oxidation possibly useful for monitoring oxidative stress of an organism in mercury polluted environmental areas.

Acknowledgements

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CVAAS Mercury Vapor Mini-Analyzer Based on Measurements at 184.9 nm

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Abstract: A mercury mini-analyzer was developed, based on cold vapor atomic absorption spectrometry (CVAAS), by using the mercury line at 184.9 nm. The sensitivity of mercury vapor measurement was 10 times higher in comparison with the using of mercury line at 253.7 nm. The new mercury instrument consists of the following main parts: a low pressure mercury lamp, a flow cell, a detector of radiation (a special photo-multiplier tube sensitive at 184.9 nm and not sensitive at 253.7 nm) an electronic part and an air flow part. The developed mercury mini-analyzer was a non-dispersive instrument (without monochromator or any focusing or colimating system). As far as we know, till now there are no commercially available instruments for mercury analysis by CVAAS based on the use of mercury line at 184.9 nm.

Key words: mercury, mini-analyzer, atomic absorption, air analysis, mercury analysis, CVAAS

INTRODUCTION

Current environmental concern over the danger of mercury pollution has accelerated progress of analytical methods for mercury. One of the best methods for determination of mercury is the cold vapor atomic absorption spectrometry (CVAAS). This method has made possible to determine mercury at the sub-ppb (ng/mL) level in liquids or at μg/m^3 level (even tenths of μg/m^3) in air. Nowadays mercury is determined especially by CVAAS at 253.7 nm. This method for mercury analysis in different matrixes is described in a great number of papers and in several monographs on AAS, one of the most complete being the book of WELZ AND SPERLING[1].

However, some natural samples (e.g., air) contain mercury at very low concentrations, difficult to be determined by conventional CVAAS. Therefore, improved methods are required to directly determine such low-level mercury concentrations without tedious preconcentration procedures.

Almost all the studies for mercury analysis by CVAAS, so far performed have utilized the spin-forbidden resonance line at 253.7 nm. However, it is known that the main resonance line of mercury is at 184.9 nm in the vacuum-ultraviolet (VUV) region. The VUV atomic line has a higher oscillator strength (f = 1.18) than the 253.7 nm line (f = 0.026). Consequently, improved atomic absorption sensitivity may be expected at 184.9 nm compared to 253.7 nm, since the absorption coefficient is proportional to the oscillator strength of each line[2].

However only a few investigations have been reported regarding CVAAS of mercury by using the mercury line at 184.9 nm[3, 4]. This may be due to experimental difficulty in the vacuum UV (VUV) region especially because of the molecular oxygen absorption. In spite of 80 % decrease in the line intensity (it was used a flow cell of 26 cm) it was concluded that it was possible to determine mercury in air with a better sensitivity by using the line at 184.9 nm compared with the line at 253.7 nm.

RESULTS AND DISCUSSION

The new mercury mini-analyzer based on the absorption of mercury line at 184.9 nm, is composed of two main parts:

a) A source of radiation (a mercury electrodeless discharge lamp) that emits the specific radiation of mercury at 184.9 nm, that is passed through a *flow cell* with quartz windows with a length of 35 cm and 1.7 cm internal diameter, a *detector* (a photomultiplier tube with a cathode of CsI, sensitive for mercury line at 184.9 nm and not sensitive for the line at 253.7 nm) an *amplification system* and a *display unit*.

The photomultiplier cathode material is sensitive only to vacuum UV radiation, thus it will be measured effectively only the mercury line at 184.9 nm.Taking into account the literature data, appear that the analytical potential of the resonance line of mercury at 184.9 nm, has been exploited only partially to date. That is due in part to the difficulty of working in the vacuum ultraviolet. By working in air, an important part of the radiation at 184.9 nm is absorbed by oxygen and water vapors. Moreover by using a conventional spectrometer another important part of the radiation is lost in the monochromator of the spectrometer.

With the advent of special detectors of radiation that have the feature to measure the radiation intensity at 184.9 nm (photo-multiplier tube with a CsI cathode) and not at longer wavelengths, it is possible to develop a mercury analyzer without need of using a monochromator or filters (a non-dispersive instrument). This type of detectors has important advantages, the most important being: (i) the intensity of radiation that reach the detector is bigger (monochromator or filter reduce strongly the radiation intensity); (ii) a mercury analyzer that use this type of detector could be simpler and cheaper than a conventional analyzer.

b) A purification and transport system for the samples and standards of mercury vapors. The air transport system consists of a membrane pump, the flow cell, a system of trapping the water vapor of air by using of calcium chloride, a system for air purification from mercury vapor (zero mercury gas filter) and a particulate filter.

It was proved that water vapors absorb at 184.9 nm. Good results for water vapors removal from analyzed air were obtained by using a trap with calcium chloride. The filter for air purification of mercury vapors is very important in order to have the possibility to adjust the device for “zero” mercury vapors in air (the point zero of calibration curve). Very good results were obtained by using a special built gold filter. Even after passing 400 liters of 80 μg m^{-3} mercury vapor standard in air through this filter, the

capability of mercury retaining is almost 100 %. Using this gold filter, the interference of organic substances, which can absorb the radiation of 184.9 nm, are eliminated.

The mini-analyzer has a predisposition of networking. It has a RS 232 plug by which it could be connected to a computer. The mini-analyzer is 45 cm long, 42 wide and 20 cm high. It has 13 kg. In Figure 1 is presented the general appearance of the mini-analyzer.

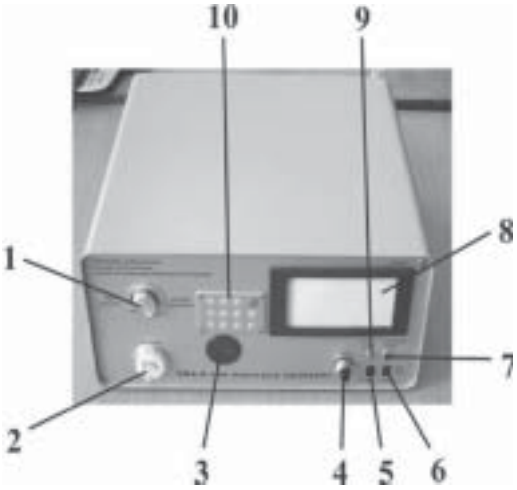

Figure 1. General appearance of the mini-analyzer. 1) three ways stopcock; 2) air inlet; 3) validation button; 4) "zero" mercury button; 5) pump power switch; 6) lamp power switch; 7) mercury lamp light; 8) display; 9) pump power; 10) keypad.

The mercury mini-analyzer was calibrated by using diluted mercury vapor standards in air with concentrations between 0.5-80 µg m^{-3} mercury. These standards were prepared by introducing known volumes of mercury saturated air (at known temperature) in Tedlar PVF bags. Using a "Perkin Elmer" AAS, type "Analyst 700" coupled with a Mercury Hydride System, type MHS-10, it was determined the actual mercury concentration of every standard inside Tedlar PVF bag and also the mercury standards stability in time. The mercury standards could be used with good results for mercury mini-analyzer calibration. The mercury standards with concentrations below 5 µg m^{-3} could be used with enough precision for mini-analyzer calibration at least in the first thirty minutes after preparation. The stability of mercury vapor standards in air is much higher at higher concentrations (see Figure 2).

The sensitivity of mercury determination in air (1 % absorption, 99 % transmittance) was of 0.77 µg Hg/m^3. The measuring range was 0.10 – 40 µg Hg/m^3. The measuring range could be extended to 100 µg Hg/m^3. The relative standard deviation for 5 µg Hg/m^3 was of 1.1 % (n = 7). A determination last 2 seconds. The mini-analyzer developed at

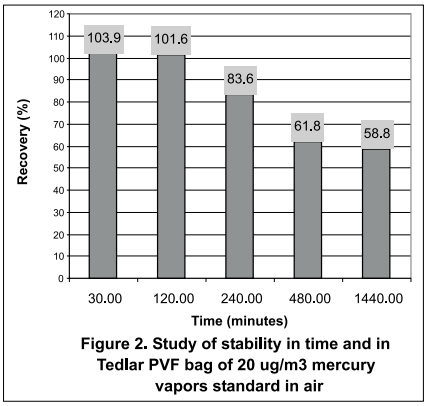

Figure 2. Study of stability in time and in Tedlar PVF bag of 20 ug/m3 mercury vapors standard in air

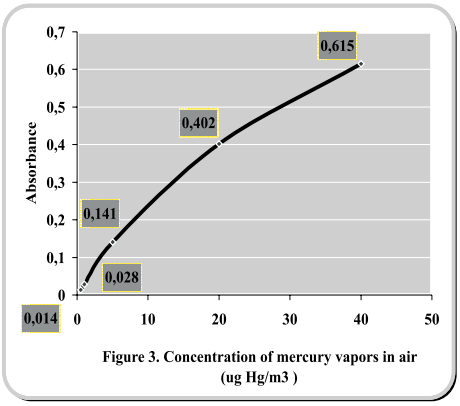

Figure 3. Concentration of mercury vapors in air (ug Hg/m3)

Bucharest University was ten times more sensitive than a conventional mercury analyzer that use for measurements the mercury line at 253.7 nm. In Figure 3 is presented the calibration curve obtained using the developed mercury mini-analyzer.

CONCLUSIONS

It was developed a non-dispersive CVAAS mini-analyzer for mercury vapors determination in atmosphere based on the absorption of mercury line at 184.9 nm. The mini-analyser presents a 10 times improvement in sensitivity of mercury vapor determination, compared with the using of mercury line at 253.7 nm.

As far as we know there are no commercially available CVAAS mercury vapor analyzers that use the mercury line at 184.9 nm. The new instrument is simpler and cheaper than a conventional mercury analyzer because it is a non-dispersive analyser without without using a monochromator or filters. A gold filter, that trap selectively mercury vapors was used to adjust the point "zero mercury concentration" for standards and samples. A calcium chloride trap was used for water vapor removal of analyzed samples or standards. The absorption of molecular oxigen from air do not interfere in determinations because its concentration is constant in air and analyzed samples.

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Determination of Mercury by Cyclic Voltammetry after its Pre-Concentration on a Carbon Paste Electrode Modified with Cadion A

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Abstract: The use of a carbon paste electrode modified with 4 nitrophenyldiazoaminoazobenzene for the determination of inorganic mercury by cyclic voltammetry was described. Mercury(II) was preconcentrated, under open circuit conditions, on the surface of a modified carbon paste electrode. Mercury accumulated from solution (0.2 M sodium acetate buffer, pH 7-7.5) forming with the reagent a complex, which was reduced to elementary mercury by electrolysis at –400 mV during a period of 60 s. Then it was determinated by anodic stripping voltammetry. Optimization of operational parameters such as: the concentration of supporting electrolyte, the pre-concentration time, the reduction potential, the reduction time and others were studied in detail. The peak current intensity increase linearly with the mercury concentration over the range 0.1 μg/mL to 10 μg/mL.

Key words: mercury analysis, cyclic voltammetry, carbon paste electrode, 4-nitrophenyldiazoaminoazobenzene, water analysis

INTRODUCTION

Mercury is an abundant heavy metal in the environment, and its toxic effects have been recognized for a long time. Due to its dangerous and harmful properties for the health of human being, the determination of mercury is very important for environmental protection. Highly sensitive electroanalytical methods, such as stripping voltammetry[1, 2], allow determining heavy metals at levels of sub μg L^{-1}. An increase in the sensitivity of stripping voltammetry, using chemically modified electrodes (CMEs) can be achieved by its combination with an effective method of separation and pre-concentration. The basic carbon electrode materials most frequently used for electrochemical measurements are glassy carbon, spectral graphite, and carbon paste. Chemically modified electrodes have the following advantages: easy fabrication, low detection limit, fast response, good selectivity, excellent sensitivity and low cost. They have drawn much attention, especially in electroanalytical chemistry. Until now, various CMEs[3, 4] for determining mercury have been reported. Carbon paste electrodes are superior to other solid electrodes in having a low residual current and noise, and in being very cheap and easy to prepare and replace; these electrodes have a wide range of anodic and catodic applica-

bilities. A very sensitive and selective procedure was developed for determination of mercury. In this paper cyclic voltammetry was used to investigate the electrochemical behavior of mercury at a chemically modified carbon paste electrode with Cadion A. Using this type of electrode, trace levels of mercury in water samples were determinated.

RESULTS AND DISCUSSION

For the voltammetric measurements was used a potentiostat linked to a Pentium computer driven by a software "Cyclic voltammetry" designed by Slavomir Kalinowsky (Olsztyn University, Poland), equipped with a voltammetric cell and three electrodes: carbon paste electrode as the working electrode, a platinum electrode as the counter electrode and an Ag/AgCl/KCl (sat.) as the reference electrode.

Working procedure: the working electrode is dipped, for a required period of time, in 25 mL buffer (0.2 M sodium acetate, pH 7-7.5), containing mercury (II), the analyte solution being stirred to ensure a good reproducibility. The accumulation time of mercury was of 10 min. Mercury accumulated from solution forms with reagent a complex, which is reduced to elementary mercury in an electrolysis step. In figure1 is presented the structure of the formed complex. Then the electrode is removed from solution, rinsed with water and then placed into the voltammetric cell, containing HNO_3, where the pre-electrolysis is taking place at the potential of -400 mV, for 60 s and without stirring. The potential was then scanned from -400 to +650 mV, at scan rate of 100 mV/s, recording the cyclic voltammograms. The electrode was then cleaned in a HNO_3 solution by scanning from +650 to -400 mV, at a scan rate of 100 mV/s until no voltammetric peak was recorded.

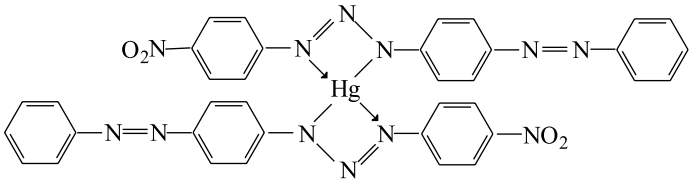

Figure 1. The mercury(II)-Cadion A complex.

In Figure 2 is presented the blank electrochemical behavior of the modified carbon paste electrode and the aspect of a cyclic voltammogram in the presence of mercury ions.

The influence of HNO_3 concentration in the solution where takes place the pre-electrolysis step on the peak current is shown in Figure 3. It was found that the peak current becomes higher with the increase of HNO_3 concentration. At concentration higher than 0.24 M HNO_3, the peak current increased very slowly. The concentration of 0.12 M HNO_3 was chosen in further experiments.

The peak current increases with increasing the reduction time. For reduction time longer than 60 s, the peak current increased very slowly. A reduction time of 60 s was chosen for all other experiments.

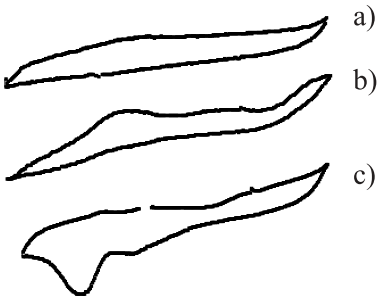

Figure 2. Cyclic voltammograms, obtained at: a) unmodified carbon paste electrode; b) Cadion A-modified carbon paste electrode, without accumulation of mercury ions; c) chemically modified carbon paste electrode, after accumula- tion of 5 μg/mL Hg(II).

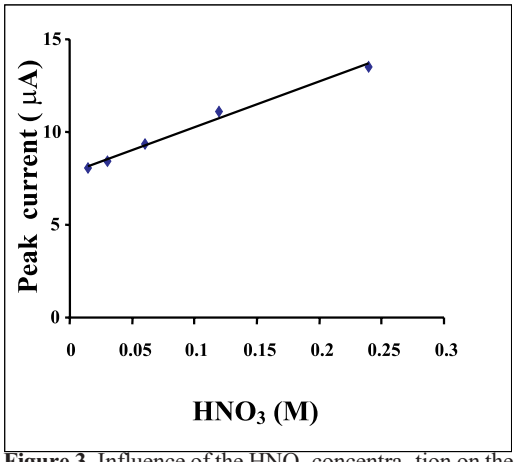

Figure 3. Influence of the HNO_3 concentra -tion on the analytical signal for Hg^{2+}. Reduction time, 60 s; reduction potential, -400 mV; accumulation time, 10 min; scan rate,100 mV/s; Hg^{2+}concentration, 20μg/mL

For reduction of mercury to elemental state it was chosen a potential of -400 mV. The accumulation time of mercury on the surface was a factor very important which influences the peak current. Under the same experimental conditions, a longer accumulation time would lead Hg^{2+} to be pre-concentrated more completely on the surface of the electrode. For this reason, it was chosen an accumulation time of 10 min. The effect of scan rate on the peak current was investigated for Hg^{2+} concentration of 1 μg/mL. The current peak increase linearly with the scan rate over 25 to 400 mV/s. For all other experiments, it was chosen a scan rate of 200 mV/s.

Calibration curve for Hg^{2+}

The relationships between the peak current intensity and the concentration of Hg^{2+} was investigated. A linear calibration graph from 0.1 to 10 μg/mL of Hg^{2+}, at a scan rate of 200 mV/s, was established (Figure 4). The curve equation is Y = 2.4005x + 0.8207, and R is 0.9899. The detection limit was 0.1 μg/mL, after the acumulation under the optimum conditions. The relative standard deviation, calculated at 20 μg/mL Hg(II), was 1.84 %, (n=6).

The influence of several metal ions was investigated under the conditions optimized for Hg^{2+} determination. It was found that the interference of some cations such as: Zn^{2+},

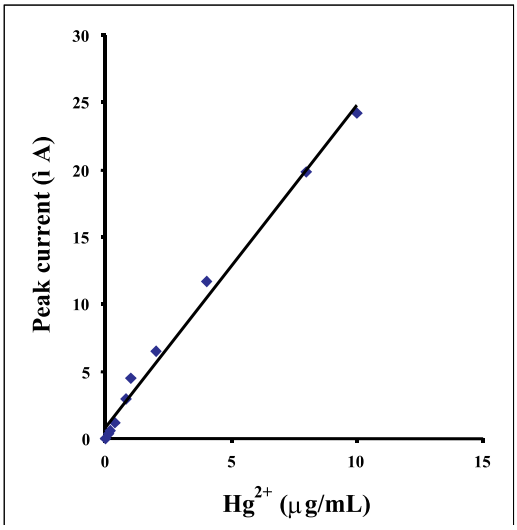

Figure 5. Calibration graph obtained in optimum conditions: HNO_3 con-centration, 0.12 M; reduction time, 60 s; reduction potential, –400 mV; accumulation time, 10 min; scan rate, 200 mV/s

Cd^{2+}, Pb^{2+}, on the peak current intensity, was low. $Zn^{2+}$and Cd^{2+} not interfere till a ratio Hg^{2+}/metal cation of at least 1/500 and 1/500 respectively.

CONCLUSIONS

It was studied the electrochemical behavior of a carbon paste electrode modified with 4-nitrophenyldiazoaminoazobenzene for the determination of Hg^{2+}. I were established the most important operational parameters for the determination of mercury by cyclic voltammetry by using that type of electrode. The proposed method of analysis allow the mercury determination within 0.1-10 μg Hg^{2+}/mL with a good selectivity. The interference other ions in mercury determination was low.

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In-field Determination of Inorganic Mercury in Urine Samples with the Portable Mercury Analyzer Hg-254-NE under Adverse Conditions of Small Scale Gold Mining Areas

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Abstract: A quantitative determination of Hg in human body fluids or specimen e.g. with CV-AAS requires a well-equipped lab, including an analyzer, pressure gases like argon or nitrogen, etc. To measure the Hg burden of patients in field, it is almost impossible to bring such an equipment to an affected site, e.g. to a small scale gold mining area in a developing country. On the other hand, for a medical pre-selection of high burdened individuals from a larger population it would be very helpfully to get a first information on the individual Hg burden just in time and in field. For this purpose it was tried to apply the Mercury Analyzer Hg-254-NE, Seefelder Messtechnik, Seefeld, Germany. This analyzer based on AES (atomic emission). It fits in a normal alu-suitcase, weighing all together approx. 25 kg. Beside an electric supply just tin(II)chloride and HCl 25 % is needed. Urine samples can be screened directly without working up procedures within a few minutes for inorganic Hg (as tinchloride does not reduce MeHg). The result of approx. 750 urine samples, measured with this analyzer under adverse field conditions in villages of small scale gold miners in Indonesia and Tanzania was compared to the re-determination of the urine samples under lab conditions with CV-AAS, after shipping the samples acidified and under cooling to Germany. It was found that the determination in field with the Mercury Analyzer Hg-254-NE is suitable at least for a rough screening of the urine samples for Hg. Together with a medical investigation for typical signs of a Hg intoxication like tremor, ataxia or disdiadochokinesia, in most cases a correct diagnose of a chronic Hg intoxication can be made just in field and in time. The method is limited to inorganic Hg in urine. Therefore it should be applied only if a burden predominantly with Hg vapor or inorganic Hg could be assumed and not in the case of a methyl-mercury burden.

Study of the Suitability of Different Extracting Agents of Mercury Species

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Abstract: The aim of this study is to compare the influence and feasibility of two common extracting agents (50 % v/v HCl and 50 % v/v HNO_3) on the leaching of Hg in soils. The solubility of a number of Hg species in each acid solution was evaluated in some selected conditions. Most of them were quantitatively dissolved in both acids being HgS an exception. The application of both acid solutions to a soil sample from Almaden mining area provided different recoveries of Hg (about 5 % in 50 % v/v HNO_3 as extracting agent and 50 % in 50 % v/v HCl). A number of experiences with both reagents was designed and developed in order to evaluate the matrix influence: (1) Study of the solubility of HgS in presence of different potential interfering compounds such as $FeCl_3$, KCl, KI and Fe_2O_3, (2) Study of the recovery of HgS spiked in soil samples, (3) Study of the extraction process in soil samples spiked with the critical interfering compounds. As a conclusion, none of these acids are totally free of matrix effects from common soil constituents, and the consequences inferred by the general application of these extraction procedures about mercury mobility must be made with caution.

Key words: mercury, extraction, HgS, Almaden, soil.

INTRODUCTION

Sequential extractions are often used for evaluating the mobility of Hg in soils and sediments. These methods are used to subdivide the mercury content of soil samples into several operational defined groups of more or less soluble fractions and they provide information on metal release when changes in geochemical conditions take place. The most extraction methods generally used to study Hg[1-3] in soils include a highly concentrated acid leaching stage with HNO_3 or HCl prior to the extraction or digestion of the least available Hg fraction. Since the interaction between Hg species and the extracting solutions are affected by the soil characteristics, the leachability of Hg from soils may greatly differ depending on the selected extracting agent and its concentration. Moreover, the solubility of Hg could be affected by the presence in the soil of some critical compounds as chloride compounds (e.g. KCl, $FeCl_3$), iron(III) compounds (e.g. $FeCl_3$ and Fe_2O_3) or iodide compounds (e.g. KI).

In the present study, the extractability of Hg in 50 % v/v HNO_3 and 50 % v/v HCl was studied. As a previous step, the solubility of a number of mercury species ($HgCl_2$, yellow HgO, red HgO, HgS, Hg_2Cl_2, $HgSO_4$ and

$Hg(NO_3)_2$) in both reagents was evaluated. All of them were quantitatively dissolved with the exception of HgS and Hg_2Cl_2. While the latter is not usual in environmental samples, HgS represents a common source of mercury in soils, especially in soils from mercury mining areas. In addition, the solubility of HgS in presence of different potential interfering compounds such as KCl, KI, $FeCl_3$ and Fe_2O_3 was estimated. A soil sample from Almaden mining area with a high Hg concentration was selected for carrying out the subsequent experiences. With the goal of evaluating the matrix influence we designed and developed a number of experiences with both acid solutions: (1) Study of the recovery of HgS spiked in soil samples, (2) Study of the extraction method in soil samples spiked with the critical interfering compounds. All the extractions were carried out at the same conditions.

The quantification of Hg remaining from the first stage was carried out by digestion of the residue with aqua regia in a microwave oven. Total Hg in the samples was determined by digestion of soil with a mixture of aqua regia and hydrofluoric acid in a microwave oven. Cold Vapour Atomic Absorption Spectrometry (CVAAS) and Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) were the analytical techniques used to determine the Hg content throughout this study.

RESULTS AND DISCUSSION

Study of the solubility of Hg species in the extracting agents

Results of solubility are shown in Table 1. All Hg species were quantitatively dissolved with the exception of HgS and Hg_2Cl_2. An additional solubility assay was performed to evaluate the solubility of a sample of cinnabar ore from Almaden founding that no significant Hg amount was dissolved in both extracting solutions.

Table 1. Percentage of Hg species recovered in 50 % v/v HNO_3 and 50 % v/v HCl

Species	HNO_3	HCl
$HgCl_2$	95.4	93.0
Yellow HgO	101.2	98.4
Red HgO	97.8	95.0
HgS	0.1	0.1
Hg_2Cl_2	4.7	0.6
$HgSO_4$	95.6	97.6
$Hg(NO_3)_2$	98.7	103.2
Cinnabar	0.3	0.4

Experimental conditions: 0.1g of each Hg species with 10 ml of 50 % v/v HNO_3 or 50 % v/v HCl

Study of the solubility of HgS in presence of potential interfering compounds

The aim of this study was to investigate the solubility of HgS in both acid solutions in the presence of different potential interfering compounds. The assays were carried out at both room and high temperature (approximately 70 °C). Experimental conditions: 0.1 g of HgS + 0.5g of the corresponding

reagent with 10 ml of the acid solution. Results of this study are summarized in Figures 1 and 2.

Quantitative Hg recoveries were obtained for HNO_3 in presence of KCl and $FeCl_3$ at room temperature. A partial dissolution was obtained in presence of KI at high temperature. In the case of HCl, KI has a marked effect on the solubility of HgS whereas the rest of tested compounds only could promote the solubility at high temperature.

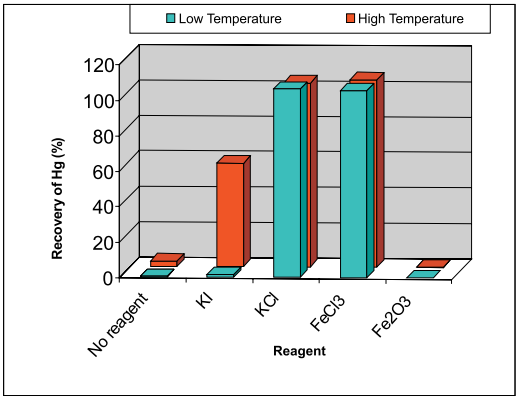

Fig. 1. Solubility of HgS in 50 % v/v HNO_3

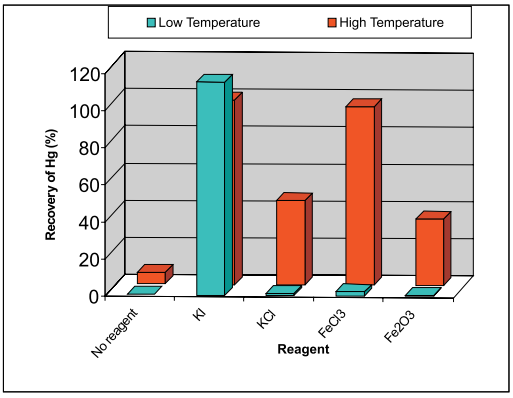

Fig. 2. Solubility of HgS in 50 % v/v HCl

Quantitative Hg recoveries were obtained for HNO_3 in presence of KCl and $FeCl_3$ at room temperature. A partial dissolution was obtained in presence of KI at high temperature. In the case of HCl, KI has a marked effect on the solubility of HgS whereas the rest of tested compounds only could promote the solubility at high temperature.

Study of the extractability of Hg in soils spiked with HgS

Spikes of 1 mg/g, 10 mg/g, 25 mg/g and 100 mg/g on a soil sample from Almaden were prepared by the addition of the adequate amount of HgS and then homogenized. All spiked samples were extracted at the same conditions: 0.25 g sample weight, 10 ml of 50 % v/v acid solution and a contact type of 1 day in an end-over-end shaker. Results are shown in figures 3 and 4.

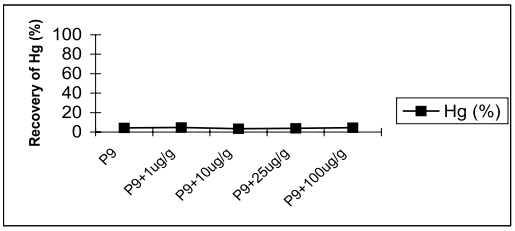

Fig. 3. Extraction of a soil with 50 % v/v HNO_3 alone and spiked with different concentrations of HgS

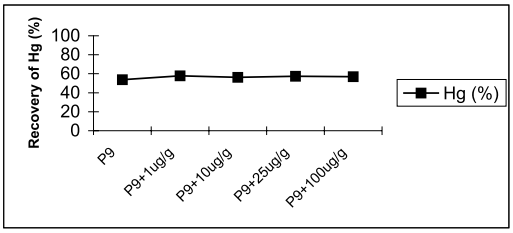

Fig. 4. Extraction of a soil with 50 % v/v HCl alone and spiked with different concentrations of HgS

Results showed a different leachability of Hg for both extracting agents. Hg recovery from HNO_3 leaching was about 4 % whereas the

recovery was higher than 50 % when hydrochloric solution was used. By other hand, no significant differences of Hg recoveries are observed with increasing the amount of HgS spiked for the two extracting agents, suggesting that the matrix influence does not depend on the amount of HgS (cinnabar) present in soils.

Study of the extractability of Hg in soils spiked with potential interfering compounds Spikes of KCl, KI, $FeCl_3$ and Fe_2O_3 were prepared at the same way with 10 % w/w concentration. All spiked samples were extracted at the same previously cited conditions. Results are summarized in figures 5 and 6.

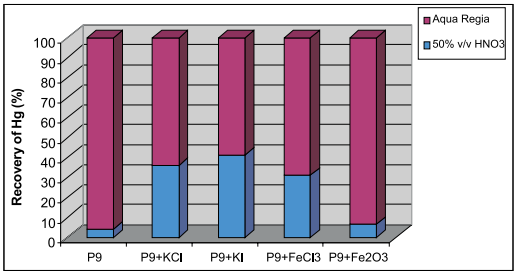

Fig. 5. Extraction of a soil with 50 % v/v HNO_3 alone and spiked with different compounds

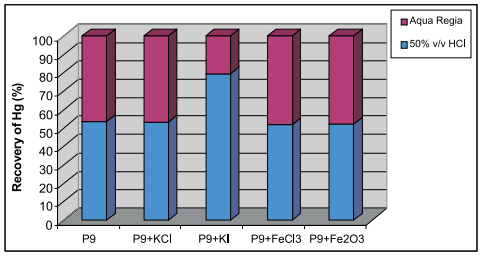

Fig. 6. Extraction of a soil with 50 % v/v HCl alone and spiked with different compounds

It can be observed that Hg recoveries are markedly increased in presence of KCl, KI and $FeCl_3$ for the HNO_3 leaching ranged between 30-40 %. However the presence of Fe_2O_3 has an insignificant effect on Hg extractability. In the case of the HCl leaching, the only reactive that has a marked effect on the extractability of Hg in the soil sample was KI, whereas the other reagents do not affect the leachability of Hg.

CONCLUSIONS

Results obtained from the application of both extracting agents showed that none of the acids are totally free of matrix effects from common soil constituents. Extractability of Hg was much higher when we employed 50% v/v HCl as extracting agent, indicating that the matrix effects are more pronounced for this acid. No changes in matrix influence were observed when the amount of HgS was increased. On the other hand, the presence of the tested interfering compounds was more critical in the case of the nitric acid leaching with the exception of Fe_2O_3. Therefore, although both acids are commonly used in sequential extraction schemes for evaluating Hg mobility in soils, results are not comparable and the choice of one of them in soil studies must depend on specific purposes.

Acknowledgement

Authors thank the Spanish Ministry of Science and Technology for the financial support (project BQU2003-07509-C02-02).

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Determination of highly precise isotope ratios by using multi-collector inductively coupled plasma mass spectrometry

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Abstract: The use of an on-line Hg reduction technique (stannous chloride used as the reducing agent) to generate a continuous steady signal has been developed for isotope ratio determinations by multi-collector (MC)-ICP/MS. The technique was applied to investigate the extent of Hg fractionation in a variety of sediments from different locations for which sources of mercury are various and have been identified. The ratios $^{198}Hg/^{202}Hg$, $^{199}Hg/^{202}Hg$, $^{200}Hg/^{202}Hg$ and $^{201}Hg/^{202}Hg$, all expressed as d-values (per mil deviations relative to an in-house standard) were clearly significantly different among samples. The measurements demonstrated the ability of the proposed method to detect significant differences in Hg isotope ratios within one type of samples (e.g., between different sediments) and so far have unequivocally shown that natural variations in Hg isotope ratios exist in nature.

Key words: mercury, stable isotopes, isotope ratios, multi-collector ICP-MS, sediments.

INTRODUCTION

Developments of Multi-Collector Inductively Coupled Plasma Mass Spectrometry (MC-ICP/MS) have led to resurgence in stable isotope geochemistry of heavy elements, where mercury is still one of the more uncommon elements to study. Recent measurements have suggested that isotope signatures of Hg in various environmental compartments (KLAUE ET AL., 2000; LAURETTA ET AL., 2001) and, more recently, among samples of Hg ore from various sources (HINTELMANN AND LU, 2003) may be different. However, it is still debated, whether mercury from anthropogenic sources is isotopically different from geogenic mercury, which would allow tracing of mercury sources according to their isotopic fingerprint.

This work describes the use of an on-line Hg reduction technique (stannous chloride used as the reducing agent) to generate a continuous steady signal, which can be processed for precise isotope ratio measurements by multi-collector (MC)-ICP/MS. Special attention has been paid to ensure optimal MC-ICP/MS conditions allowing precision measurements (1 SD < 50 ppm, 0.005 %) enough to be able to detect the anticipated small differences in Hg isotope ratios in nature (FOUCHER ET AL., 2003). The method was applied to investigate the extent of Hg fractionation in a number of sediments from different locations for which sources of mercury are various and have been identified.

MATERIALS AND METHOD

Instrumentation and data acquisition

The experimental system consists of a Thermo-Finnigan Neptune multi-collector inductively coupled plasma mass spectrometer interfaced with an LI-2 cold vapour generation system. The cup configuration of the double focusing multiple-collector ICP-MS usually used is shown below:

Collector cup configuration

Cup#	L4	L3	L2	L1	C	H1	H2	H3	H4
Hg-isotope	xxx	198	199	200	201	202	xxx	xxx	xxx

Stannous chloride is used as the reducing agent in the formation of volatile elemental mercury. Ar gas for the ICP-MS is passed directly through the cold vapour generation system, sweeping the Hg vapours into the injector of the ICP. During the time of analysis, the solution of mercury is sampled continuously, creating a steady signal of mercury. The raw isotope ratios ($^{198}Hg/^{202}Hg$, $^{199}Hg/^{202}Hg$, $^{200}Hg/^{202}Hg$ and $^{201}Hg/^{202}Hg$) were determined as the average of a number of 300 measurements of 2 seconds integration time each, giving a global acquisition of 10 minutes for a single sample. Due to a lack of a precisely characterized Hg isotope ratio standard, the accuracy of our method was checked by comparing relative per mil (‰) deviation (using the d-notation) of all our measurements to a common in-house standard solution (mercury atomic spectroscopy standard – Fluka Chemica), according to the formula:

$$\delta^{198/202}Hg = 1000 \times \left(\frac{^{198/202}Hg_{sample}}{^{198/202}Hg_{standard}} - 1 \right)$$

with $^{198/202}Hg_{sample}$, the measured value of the sample and $^{198/202}Hg_{standard}$, the reference value of our in-house standard solution calculated as the average of one acquisition done before and after every sample. The external precision (1SD) of the measure for certified reference materials was determined from values obtained for digest replicates (minimum of 6).

Samples preparation

Sediment samples (typically between 200 to 400 mg of dried sediments) were digested in a hot (100-120 °C) mixture of high purity concentrated sulfuric acid and nitric acid (7:3, v/v). Sediments were digested to obtain final Hg concentrations of 2 to 5 $mg.L^{-1}$, the minimum concentration required to obtain the precision necessary for this type of measurement (FOUCHER ET AL., 2003). For samples with higher total mercury contents, sediment digests were diluted before analysis with Milli-Q water to a concentration of ~ 5 µg $Hg.L^{-1}$, so that a minimum of 200 mg of dried sediment were digested each time.

RESULTS AND DISCUSSION

The extent of Hg fractionation has been investigated in a variety of sediments from different locations for which sources of mercury are various and have been identified. The samples consisted of (1) certified sediment reference materials (listed in *Table 1* below) naturally or anthropogenically contaminated and (2) a well characterized and dated sediment profile from the Lake-658 of the Experimental Lakes Area (METAALICUS study lake, Ontario, Canada).

An internal precision of 10 to 70 ppm (1SE) was obtained across all ratios and the various sediment samples investigated. The external precision of the measurements for replicate sample digests (n=6) was between 0.02 and 0.24 ‰ (1SD) depending of the certified reference material. The range of d values observed (Table 1) was extended from 0.15 to 5.93 ‰ for the certified sediments and from 0.51 to 1.52 ‰ for the sediment profile (ELA, Lake-658). As Table 1 shows, the magnitude of the Hg fractionation per amu was constant within one type of sample.

Table 1. δ-Values per mil (‰). Errors for certified sediments represent 1SD, calculated from the mean of digest replicates (n=6). Errors for ELA-658 sediments represent 1SD, calculated from the mean of samples from several different depths (n=3 for 0-10cm, n=7 for 10-30cm and n=9 for 30-70cm).

Certified materials	THg ($mg.kg^{-1}$)	Sediment matrix
CRM MESS-2	0.092	estuarine sediment
CRM MESS-3	0.091 ± 0.009	estuarine sediment
NIST SRM-1944	3.4 ± 0.5	freshwater sediment
CRM BCR-580	132.0 ± 3.0	marine sediment
ELA Lake-658 0-10cm	0.25 ± 0.06	freshwater sediment
ELA Lake-658 10-30cm	0.16 ± 0.10	
ELA Lake-658 30-70cm	0.10 ± 0.02	

Certified materials	$\delta^{198/202}$Hg (1SD)	$\delta^{199/202}$Hg (1SD)	$\delta^{200/202}$Hg (1SD)	$\delta^{201/202}$Hg (1SD)	δ per amu (1SD)
CRM MESS-2	5.93 ± 0.22	4.68 ± 0.16	2.94 ± 0.10	1.57 ± 0.05	1.52 ± 0.05
CRM MESS-3	4.20 ± 0.24	3.36 ± 0.19	2.11 ± 0.12	1.05 ± 0.10	1.07 ± 0.03
NIST SRM-1944	0.38 ± 0.12	0.36 ± 0.08	0.20 ± 0.05	0.14 ± 0.02	0.11 ± 0.02
CRM BCR-580	0.41 ± 0.15	0.41 ± 0.13	0.23 ± 0.08	0.15 ± 0.04	0.13 ± 0.02
L658 0-10cm	1.52 ± 0.13	1.34 ± 0.20	0.89 ± 0.09	0.48 ± 0.15	0.44 ± 0.04
L658 10-30cm	1.95 ± 0.32	1.49 ± 0.24	1.06 ± 0.17	0.47 ± 0.12	0.50 ± 0.02
L658 30-70cm	2.15 ± 0.26	1.53 ± 0.23	1.11 ± 0.16	0.41 ± 0.10	0.51 ± 0.07

The isotopic signatures were significantly different (comparing values with internal or even external precision) among samples (certified materials) and, to a smaller extent, within near surface and deeper sediment of the single core. The surface sediment (0-10 cm), which shows elevated levels of Hg from presumably anthropogenic activities, appears to be enriched with lighter isotopes.

CONCLUSIONS

The measurements demonstrated the ability of the proposed method to detect significant differences in Hg isotope ratios within one type of samples (e.g. between different sediments) and so far have unequivocally shown that natural variations in Hg isotope ratios exist in nature. Future research will focus on the differentiation between natural and anthropogenic sources in the global Hg cycle. There is a need to get better understanding of the range of Hg isotope fractionation that can be expected in nature, i.e. among matrices (air/water/sediment/biota) and a single matrix (sediment cores). This information needs to be reconciled with observed differences to ultimately assess, whether variations in Hg isotope ratios are caused by natural fractionation processes or are a result of anthropogenic activity.

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Validation of a mercury analyser: Lumex RA915+/RP91C (solid configuration)

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Abstract : The Lumex is a portable mercury analyser on air, soils and water. This study presents the methodology used for the analytical validation of this device on soils and sediments. On ten reference materials, the following characteristics of the method have been assessed: linearity, quantification limit, repeatability, reproductibility, trueness. They were found very close to the characteristics of our reference method (Aqua Regia – CVAAS) and even better for quantification limit. On real samples analyses with the two methods were quite comparable with a slight underestimation for some samples with Lumex.

Key words: validation, mercury, soils, Lumex, reference materials.

INTRODUCTION

In the "Global Mercury Project" of UNIDO (United Nations Industrial Development Organization) BRGM is implied in environmental assessment of mercury release by artisanal and small-scale gold miners. In this framework, BRGM purchased a "portable" mercury analyser called LUMEX (LUMEX Ltd Co, www.lumex.ru) adapted to different matrices, especially soils and sediments (the sample is introduced in an oven heated at 800 °C, the mercury vapour is then analysed by atomic absorption with Zeeman correction). The use of such device in measurement program raise the problems of results reliability, data interpretation and comparison of results with reference methods.

This study is also included in the two following frameworks:

- the recent development of on site analyses and the necessity of results validation.
- the program of accreditation by the french committee COFRAC of the activity "adaptation, development and conception of methods" in the BRGM.

This study presents the methodology used in our laboratory for the analytical validation of the mercury analyser LUMEX.

RESULTS AND DISCUSSION

The first part of the study consisted of a simplified robustness study, by assessing the influence on the signal of three parameters. The airflow across the oven and analyser was found the main point to be followed during the analyses. Due to the lack of precision of the regulation, this parameter has to be checked regularly.

The validation was mostly made according to french standard XP T90210. The following characteristics of the method were evaluated: linearity, quantification limit, repeatability, reproductibility and trueness. In this part of the study and, in order to work on homogeneous and well known solid material, only reference material were used (dried an ground materials).

The method showed good linearity in a working range reduced by a factor two with regard to the range given by the manufacturer. In the higher sensitivity of the device the upper limit of the working range is close to 20 mg/kg. In a less sensitive configuration mercury levels up to 100 mg/kg could be analysed.

The quantification limit was estimated by repeated analyses of a low mercury level material. This limit was found to be 2 ng of mercury introduced in the oven, which is equivalent to 10 µg/kg for 200 mg of solid.

In order to assess the absence of bias in the method, ten reference materials (various matrices and mercury level: SRM 2709, 2711, LGC6156, STSD1, ...) were analysed. The recoveries were between 90 and 110 % of the certified value (see Figure 1: some material appear twice because of analysis at two different levels).

Repeatability and internal reproducibility were lower than 10 and 15 % respectively. These values are classical value of laboratory method.

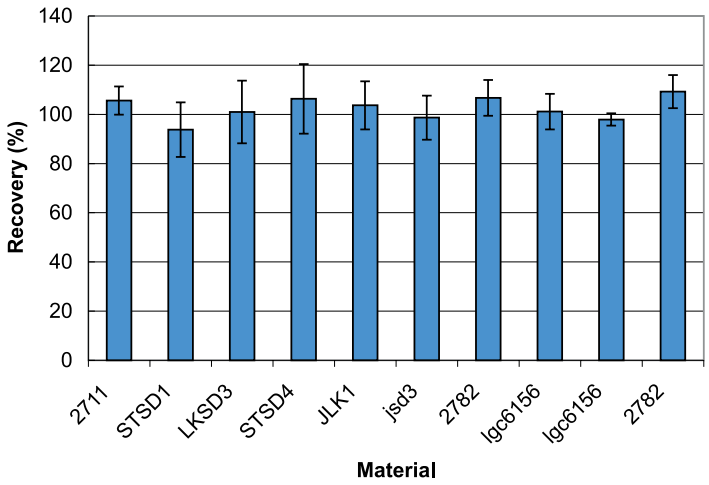

Figure 1. Evaluation of the bias of the method with reference material: lumex value (mean of 5 data) divided by certificate value (%).

All the tested performances revealed quite comparable with the performances of the reference method (aqua regia mineralisation and CVAAS according to EN 1483) used in our laboratory (even better for quantification limit).

The following part of validation concerned "real" samples analysed both with LUMEX and the reference method. These samples have been previously treated with two different preparation procedures:

- dried at 40 °C and ground to 80 µm,
- only 2 mm sieved to be close to "on site conditions".

With dried and ground samples, homogeneity is quite good; the results were compared and no significant differences were observed excepted for two samples (see Figure 2). For these samples results with Lumex were slightly lower than with the reference method (approximately 20 %). No explaination was found yet for these samples (the relative high concentration of these samples doesn't seem to be an explaination; this should be further checked).

Regarding "on site samples", differences with reference values were up to 100 % but mostly lower than 30 %. As expected, the repeatability on three measures increased due to inhomogeneity of samples (mass of analysed sample is about 100-200 mg wich is low compared to the considered fraction < 2 mm). This study on "non prepared samples" is not a part of the validation but has to be considered only as an illustration of the possible limitation of the method in "on site conditions".

The tested device was also transported near a mercury-contaminated site. One part of samples was immediately analysed with LUMEX and another part was analysed in laboratory conditions. The results are not known yet but will be presented.

Finally, the LUMEX will be used in ONUDI campaigns (Laos, Sudan, ...) with about 10 % of samples being analysed by reference methods. This will give complementary data for validation.

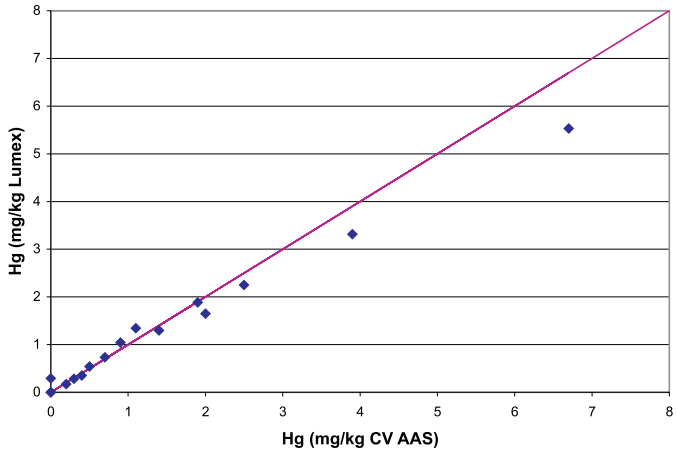

Figure 2. Mercury levels in 15 samples (sediments, soils, rocks) : comparison beetween results with lumex and with aqua regia-CVAAS.

CONCLUSIONS

The performance of the mercury analyser Lumex RA915+ (solid configuration) has been tested on soils and sediments following a validation procedure. Results were quite good on the tested reference materials, showing analytical performance comparable to a reference method. Two different uses of the device could then be proposed. **In the laboratory**, this device could give, on prepared samples, reliable results. However, the feasibility and efficiency of mercury extraction on some samples (compared with *aqua regia* mineralisation), should be further checked. **On site**, reliable results could also be obtained as far as they are not interpreted as laboratory results. They could be used as screening analyses or could help in the choice of laboratory samples.

REFERENCES

XP T90210: Protocol for the evaluation of an alternative quantitative physico-chemical analysis method against a reference method.

Optimisation of cold vapour atomic absorption spectrometry for determination of high levels of total mercury in activated carbon

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Abstract: The relative efficiency of digestion/leaching procedures for the determination of high mercury concentrations in activated carbon obtained from natural gas treatment facilities was investigated. The method is based on acid digestion/leaching, reduction by $SnCl_2$, gold amalgamation and detection by cold vapour atomic spectrometry. Sample decomposition was carried out in sealed Pyrex ampoules and closed Teflon vials, as well as in "cold finger" vessels. We used various combinations of acids (HNO_3/H_2SO_4, HNO_3, HNO_3/HCl, HNO_3/HF/HCl and HCl), digestion time, temperature and filtration. The efficiency of decomposition was obtained by comparison with results obtained by the Eschka method, radiochemical neutron activation analysis (RNAA) and k_o-instrumental neutron activation analysis (k_0-INAA). Our results showed that for samples of activated carbon containing up to 6 % of mercury, good results could be obtained using various digestion procedures (HNO_3/HCl, HNO_3/HF/HCl and HCl) with the exception of HNO_3 or HNO_3/H_2SO_4, which resulted in lower values. In addition, for samples of activated carbon with more than 6 % of mercury, efficient digestion/leaching can be obtained by treating the activated carbon in a "cold" finger vessel with 20 mL of concentrated HCl or aqua regia (HCl:HNO_3 (3:1)).

Key words: atomic absorption spectrometry, mercury, activated carbon

INTRODUCTION

Many analytical techniques have been developed for the determination of total mercury, especially for low mercury levels in environmental samples, using CV AAS. When samples with very high mercury concentrations (e.g., in the mg/g concentration range) are to be analysed by such a sensitive technique the major source of error may be due to large dilution factors. Also, preparation of such contaminated samples in trace analysis laboratory may lead to contamination of the laboratory and/or the measurement system. The activated carbon studied in this work originates from natural gas treatment facilities, where it is used for removal of mercury from the natural gas stream. On average, the concentrations of Hg in such carbon can reach up to 30 % (w/w) of mer-

cury. The second problem is the preparation of a homogeneous and representative sample of activated carbon, and the third important problem to be mentioned is related to the efficiency of digestion/leaching procedures. In order to overcome these difficulties the granules of activated carbon were ground in a stainless steel mixer.

The classical approach to determine Hg at high concentration is based on the gravimetric principle that was for centuries used in the Hg mining industry (the Eschka method). There are a number of alternative methods that can also be used, such as radiochemical neutron activation analyses (RNAA) or instrumental NAA (INAA), but these methods are only available in specialized institutions. The goal of this study was to investigate the relative efficiency of digestion/leaching procedures for subsequent determination of high mercury levels in activated carbon using gold amalgamation and detection by cold vapour atomic absorption spectrometry (CV AAS)[1, 2]. Sample decomposition was carried out in sealed Pyrex ampoules and closed Teflon vials, as well as in "cold" finger vessels. We used various combinations of acids (HNO_3/H_2SO_4, HNO_3, HNO_3/HCl, HNO_3/HF/HCl and HCl), digestion time, temperature and filtration. The efficiency of decomposition was compared with results obtained by Eschka method[5], radiochemical neutron activation analysis (RNAA)[3, 4] and k_0-instrumental neutron activation analysis (k_0-INAA)[4] as reference methods.

EXPERIMENTAL

The activated carbon studied in this work originated from natural gas treatment facilities, and was received in granulated form. Since the efficiency of wet digestion and leaching of mercury from the sample also depends on the size of the particles, the granules of activated carbon were ground in a stainless steel mixer. About 50-100 mg of ground activated carbon was weighed directly in a Teflon vial, Pyrex ampoule or "cold" finger digestion vessel. After addition of different acids the vessel was closed, Pyrex ampoules were sealed and the mixture was left to react at room temperature for 1 hour. Digestion/leaching was finished by heating the mixtures in an Al block at 100 (135) °C for 3 or 12 hours on a hot plate. Some digests were filtrated through Whatman GF/C filter prior dilution. To the digest was added 10 mL of BrCl and Milli-Q water to the desired volume. An aliquot of the digest was added to the reduction vessel and after reduction with $SnCl_2$, mercury was swept from the solution by aeration and concentrated on a gold trap. Mercury was then released from the gold trap by heating and measured by cold vapor atomic absorption spectrometry (CV AAS).

The Eschka method is used for fast quantitative determination of Hg in the ores and is based on amalgamation process on a pure-golden pot. Ground and dried sample was weighed in a porcelain dish and 3 g of iron chips and 30 g of ZnO were added. The porcelain dish was covered with a previously weighed pure-golden pot and heated on an electric furnace at 600-800 °C for 30 minutes. Meanwhile fresh deionized water was constantly added on the surface of the golden pot, so the temperature of water did not exceed 40 °C. When the reaction was finished, the porcelain dish was left to cool down for 10 minutes. The golden pot was dried with a

filter paper and weighed again. The % of Hg was calculated from the difference between the mass of a golden pot before and after the amalgamation process, and divided with the mass of the sample.

RESULTS AND DISCUSSION

Samples of activated carbon were analyzed in both granulated form and in powder form, obtained by grinding. The acid digestion/leaching involved 6 mL of an HNO_3/H_2SO_4 (4:2) mixture and heating in an Al-block on a hot plate at 100 °C for 3 hours. Before dilution with Milli-Q water 1.0 ml of BrCl was added. The measurement proceeded as described above. The differences in homogeneity and digestion/leaching efficiency between the granulated and powder form of activated carbon in 9 parallel aliquots are presented in Table 1. Table 2 presents results

Table 1. Comparison of results for total mercury (%) in granulated and powder forms of activated carbon, determined by CV AAS

	Hg (%)								
Parallel	1	2	3	4	5	6	7	8	9
Sample form:									
1. Granulated	1.24	0.916	0.666	0.463	0.536	0.421	-	-	-
2. Powder	4.23	3.42	3.56	3.59	3.87	3.82	4.22	3.84	4.41

Table 2. Results for total mercury (%) in four samples of activated carbon (A, B, C, D) obtained by the Eschka method, RNAA, k_o-INAA, and CV AAS after different digestion/leaching procedures

	Method	Sample			
		A	B	C	D
	Eschka method	30.7	5.5	5.7	18.2
	RNAA[3, 4]	25.6	5.2	6.1	15.0
	k_o-INAA[4]	31.9	5.9	-	18.9
CV AAS	6 mL HNO_3:H_2SO_4 (2:1) 100 °C, 3 hrs, Teflon vial	19.8	4.0	2.7	5.7
CV AAS	6 mL HNO_3:H_2SO_4 (2:1) 100 °C, 3 hrs, Teflon vial, filtered (GFC)	18.0	4.9	-	14.3
CV AAS	10 mL HNO_3: HF (2:1) + 1.5 mL HCl 135 °C, 12hrs, Teflon vial	15.7	-	5.8	13.1
CV AAS	3 mL HCl:HNO_3 (4:1) 100 °C, 12hrs, Pyrex tube, filtered (GFC)	24.6	-	5.3	12.6
CV AAS	20 mL HCl:HNO_3 (3:1) 100 °C, 3hrs, cold finger vessel	33.5	-	-	-
CV AAS	20 mL HCl 100 °C, 3 hrs, cold finger vessel	31.4	-	-	-
CV AAS	5.0 mL HCl 100 °C, 12 hrs, Teflon vial, filtered (GFC)	22.4	-	6.1	17.6
CV AAS	20 mL HNO_3 100 °C, 3 hrs, cold finger vessel	3.9	-	-	-
CV AAS	3.0 mL HNO_3 100 °C, 12 hrs, Pyrex tube, filtered (GFC)	-	-	3.5	1.9

for total mercury (%) in four samples of activated carbon obtained by the Eschka method, RNAA, k_0-INAA, and CV AAS with different digestion/leaching procedures.

In the granulated form of activated carbon concentrations of mercury were of only about 10-35 % of those found for the powdered form of the sample. The granulated sample was also non-homogeneous. Results from Table 1 show that the size of the particles of activated carbon is extremely important for more efficient acid digestion and leaching of mercury from the sample. Samples of activated carbon with high Hg concentrations of the order of 300,000 mg/kg (30 %), digested with HNO_3 as the major acid, showed about 40 % - 90 % lower results compared to the results obtained by RNAA, k_0-INAA, and the Eschka method. After digestion/leaching in sealed Pyrex ampoules or Teflon vials using aqua regia (HCl/HNO_3 (4:1)) or concentrated HCl for 12 hours mercury concentrations were underestimated by about 25 %. These results may reflect inefficient decomposition of the sample and losses with Hg volatilisation during longer extraction. Slightly higher Hg concentrations compared to results obtained by RNAA, k_0-INAA and the Eschka method were found after digestion/leaching in a "cold" finger vessel using 20 mL of aqua regia (HCl/HNO_3 (3:1)) for only 3 hours. Samples of activated carbon with Hg concentrations in the order of 60,000 mg/kg (6 %) digested with HNO_3 as the major acid showed about 50 % lower results than those obtained by RNAA, k_0-INAA and the Eschka method. Results obtained by digestion/leaching with HNO_3/HF/HCl, aqua regia or HCl alone showed good agreement with the results obtained by these other methods.

CONCLUSIONS

For determination of mercury in very contaminated samples of activated carbon containing more than 6 % of mercury the CV AAS method can be applied, if appropriate wet digestion/leaching of the sample is used. The efficiency of wet digestion/leaching depends on the size of the particles. Grinding before wet digestion/leaching is therefore a very important step. However, by far the best method in laboratories routinely analyzing very contaminated samples is based on gravimetry (Eschka method), while radiochemical methods are useful as reference methods for occasional quality control.

Acknowledgment

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Mercury at Ultratrace Concentrations: Target in Environmental Analyses, Challenge for the Analyst

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Key words: mercury analysis, atomic fluorescence, mercury

Since many years mercury belongs to the elements, which are controlled at very low concentrations below 1 µg/L in environmental samples such as drinking water or surface water. In spite of rigorous control in many countries the global pollution of mercury is increasing according to the United Nations Environment Program (UNEP). As a result UNEP decided to undertake a global assessment of mercury to be presented to the Governing Council at its 22nd session in 2003. The report confirms that the global worldwide mercury pollution is higher than previously estimated. The findings confirm that mercury is in fact one of the most critical heavy metals in the environment and in the biological organism. The U.S. EPA Method 1631 „Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry" requires a limit of determination of 0.5 ng/L with an instrument detection limit of 0.2ng/L. As described in the title of EPA and corresponding European standards the analytical method of choice in this concentration range is atomic fluorescence spectrometry of mercury vapour, which is carefully separated from matrix by gas/ liquid separation and amalgamation.

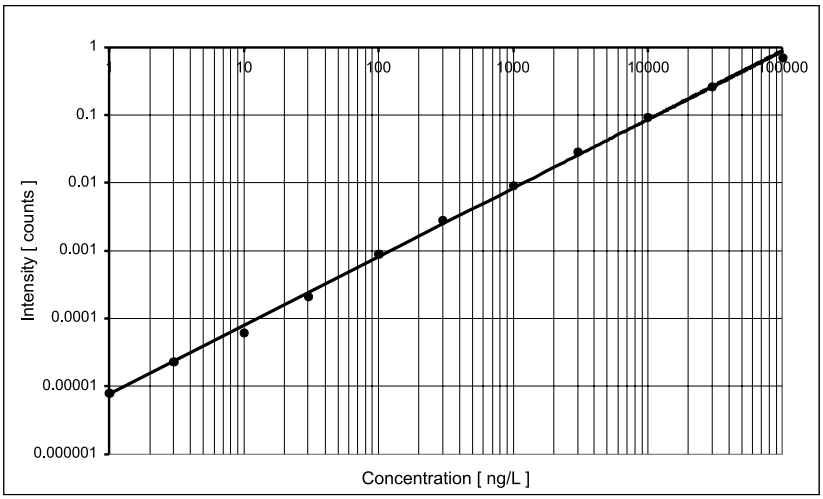

Figure 1. Linear dynamic range from 0,001 µgL^{-1} to 100 µgL^{-1} at 280V multiplier gain

In this paper the instrumental and analytical prerequirements for the routine and automated mercury determination in the concentration range of 0.5-100 ng/L are discussed. The mercury concentrations in typical environmental samples are determined with a novel atomic fluorescence spectrometer following U.S. (EPA) and European (CEN) norms. The detection limit of the method based on 3 standard deviations of the blank was found to be < 0.5 ng/l without amalgamation and < 0.1 ng/L with amalgamation. In each case only about 1 mL per sample were required for a single determination. One measurement cycle requires less than 1 minute in the direct measurement mode. The linear dynamic working range is 4 orders of magnitude.

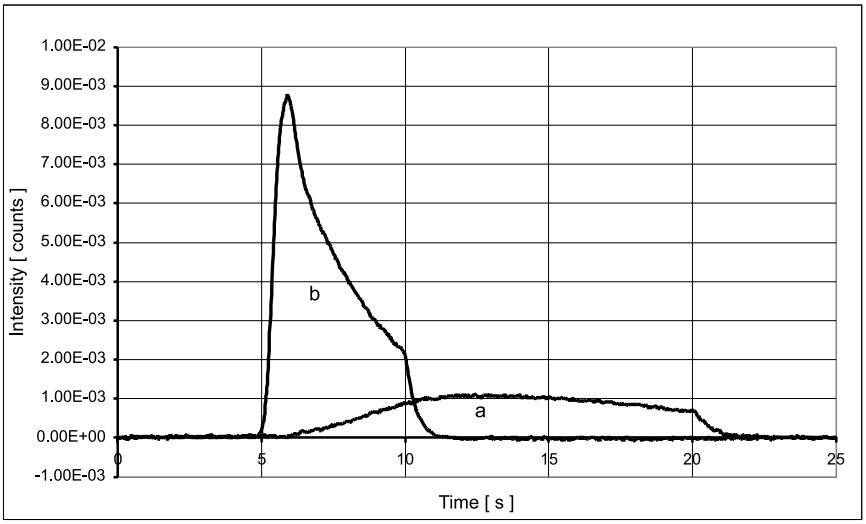

Figure 2. Time resolved intensity of 10 $ngL^{-1}Hg$: (a)direct reading; peak intensity=0.0011, integrated intensity=0.012 and (b) amalgamation, peak intensity=0.0087, integrated intensity=0.023

Although contamination control is of great importance, blanks in the range of 1 ng/L Hg can be obtained even in routine laboratories. Other important parameters such as adsorption/desorption effects, influence of the oxidant concentration and chemical reaction times etc., will be discussed in the paper.

Apart from the procedures strictly defined by regulations, which always include significant sample pre-treatment, solid sampling and direct gas sampling become more and more important for mercury determinations.

An overview of the method and some typical interesting applications are introduced in this paper.

The Production and use of $^{197}Hg^{g}$ Radiotracer to Study Mercury Transformation Processes in Environmental Matrices

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Abstract: This work shows the applicability of the radiotracer $^{197}Hg^{g}$, which was employed successfully in mercury methylation/de-methylation experiments in soils and sediments. This radiotracer can be produced in non-high flux reactors, using non-enriched Hg. The experiments consisted of amending triplicates sediment and soil samples, and incubating with labeled Hg for different time periods. $HgCH_3^+$ was extracted using toluene. The specific activity of $^{197}Hg^{g}$ obtained was high enough to allow minimum addition of total mercury to our experiment design of 5-10 ng, which is comparable to the radiotracer ^{203}Hg and other non-radioactive tracers used for this purpose. $HgCl_2$ was irradiated to produce $^{197}Hg^{2+}$ tracer, while $HgCH_3Cl$ was used for $^{197}HgCH_3^+$. Well, coaxial, and planar HPGe detectors were used in the experiments to measure the radiotracer. Spectra peaks associated to $^{197}Hg^{g}$ decay were determined by using usual peak fitting programs and also by direct spectrum integration.

Key words: radiotracer, ^{197}Hg, Hg methylation, Hg de-methylation.

INTRODUCTION

The use of radioisotopes to trace different transport and transformation processes is widespread; in the case of mercury the most frequently used radiotracer is ^{203}Hg, which in recent years is no longer regularly produced and therefore difficult to purchase. However, when adequate facilities are available $^{197}Hg^{g}$ can be also employed successfully, as it was demonstrated in mercury methylation/de-methylation in soils and sediments performed at the Department of Environmental Sciences, Jozef Stefan Institute, and Laboratorio de Análisis por Activación Neutrónica, Centro Atómico Bariloche. $^{197}Hg^{g}$ ($T_{½}$=64.14 h; TULI, 2000) can be produced in a research nuclear reactor by irradiating non-enriched Hg targets with thermal neutrons (for the $^{196}Hg(n,\gamma)^{197}Hg^{g}$ reaction σ_{th}=3080±180 b; production with epithermal neutrons is not relevant: Ig=413±15 b; MUGHABGHAB, 1981). $^{197}Hg^{m}$ ($T_{½}$=23.8 h; TULI, 2000) is also produced, and 93 % of its decay feeds the ground state, but with 30 times less probability (σ_{th}=109 ± 6 b and Iγ=58.9 ± 2.4 b; MUGHABGHAB, 1981). Figure 1 shows the decay scheme of ^{197}Hg. $^{197}Hg^{g}$ has a production rate, for short irradiation periods, about 50 times higher than

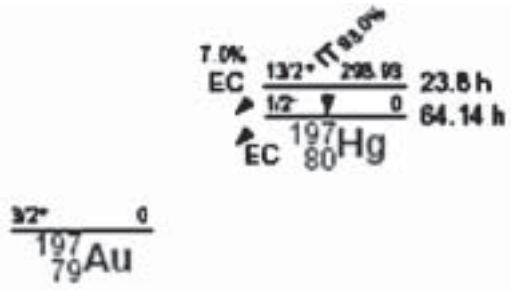

Figure 1. Decay scheme of ^{197}Hg (FIRESTONE, 1996).

that of ^{203}Hg, and hence it is possible to produce it with high specific activity in shorter irradiations, in non-high flux reactors (10^{12} to 10^{13} n.cm^{-2}.s^{-1}), using non-enriched Hg. Another advantage of the use of ^{197}Hg^{g} to trace processes is that, because of its short half life, the cleaning of devices and tools of the ^{197}Hg^{g} contamination associated to their use or caused by accidents, can be done just letting the tracer to decay away, hence assuring no interference from previous experiments.

RESULTS AND DISCUSSION

For the methylation/de-methylation experiments in soils and sediments, $HgCl_2$ was irradiated to produce the $^{197}Hg^{2+}$ tracer, while $HgCH_3Cl$ was used to produce $CH_3{}^{197}Hg^{g}$. In both cases the tracer is ready to be used after a few hours of cooling time, to allow ^{38}Cl ($T_{½}$=37.24 m; TULI, 2000) to decay. $HgCl_2$ was dissolved in 3.2 % HNO_3 after irradiation, and $HgCH_3Cl$ was dissolved in isopropanol. Working solutions of both mercury compounds were prepared by appropriate dilution. Since the $HgCH_3Cl$ decomposes during irradiation, purification has to be done immediately before each application. $HgCH_3^+$ and Hg^{2+} in 6M HCl solutions were separated by anion exchange chromatography (Dowex 1x8 resin, Cl-form, 100-200 mesh) using minimal light conditions. The $HgCH_3^+$ is then collected and the solution neutralized for further tracer experiments. In our experiments we observed about 20 % decomposition of $HgCH_3Cl$ during irradiation (20 h in 10^{12} n.cm^{-2}.s^{-1} thermal neutron flux).

The more relevant emissions associated to ^{197}Hg^{g} decay are X-rays 67.0 keV (21 %), 68.8 keV (35 %) 77.9 keV (12 %) and 80.4 keV (3.3 %), and g-ray 77.3 keV (18 %) (BROWNE, 1986). Typical spectra obtained with high purity germanium detectors (HPGe) are shown in Figures 2 and 3. Spectra obtained with planar detectors (see Fig. 2) have higher resolution compared to the well detector, but the efficiency of the detection system is much lower. The peaks associated with 67.0 and 68.8 keV emissions are clearly defined in the spectrum collected with the planar detector (see Fig. 2), but they are not resolved when the well detector is used (see Fig. 3). The 77.3 and 77.9 emissions are included in a single peak, superposed to the 80.4 keV peak, in the spectrum collected with the well detector (see Fig. 3), but these two emissions can be distinguished, but not resolved, using the planar detector (see Fig. 2). HPGe detectors allow, in general, discriminating three main peaks by using usual peak fitting programs, namely 67.0 keV, 68.8 keV, and 77.3 + 77.9 keV. But the manual determination of peak areas in two regions, one including 67.0 and 68.8 keV X-rays, and the other including 77.3, 77.9, and 80.4 keV emissions, when low resolution detectors are used, also provide accurate results. This is because these kinds of studies imply relative measurements with respect to a reference, and no absolute measurements are required. Also direct spectrum

integration procedures are much simpler. This procedure can also be applied to the peak area determinations for the 77.3 + 77.9 keV region when high-resolution detectors are used. Well, coaxial, and planar HPGe detectors were used successfully in the experiments mentioned before. For very low activity measurements, X-rays generated in the lead shielding (72.8 keV, 75.0 keV, 84.5 keV, and 84.9 keV) may affect the 77.3 + 77.9 keV measurement region of the spectra, but the 67.0 + 68.8 keV region remains undisturbed. The use of a 1 cm thick copper plate lining inside the shielding was effective to prevent the appearance of the Pb X-ray peaks in the spectrum.

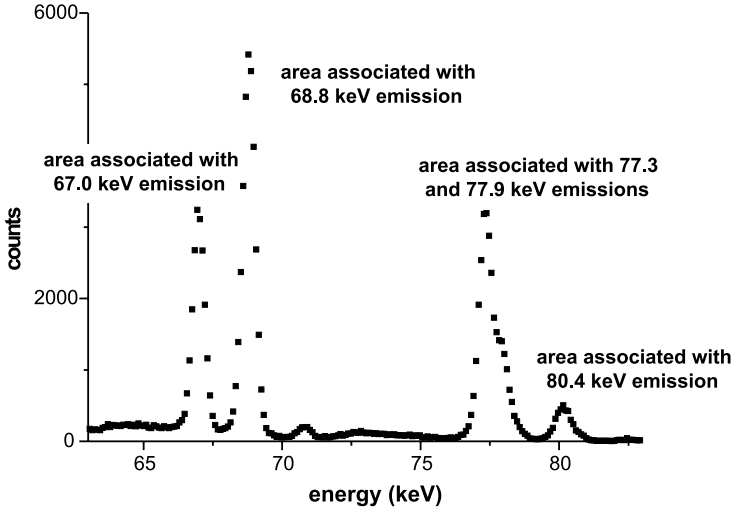

Figure 2. Spectrum obtained from a $^{197}Hg^{g}$ liquid source with an HPGe planar detector.

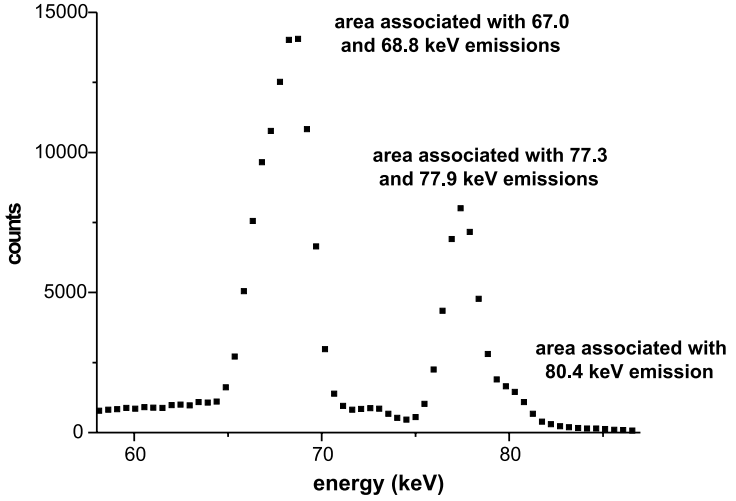

Figure 3. Spectrum obtained from a $^{197}Hg^{g}$ liquid source with an HPGe well detector.

By simple methylation/de-methylation experiments performed so far in soils and sediments the specific activity of $^{197}Hg^{g}$ was high enough to allow minimum addition of total mercury. Experiments consisted of amending triplicates sediment and soil samples, and incubating with labeled Hg for different time periods. In addition, blanks and samples in which microbial activity was inhibited by flash freezing just after inoculation ("killed control samples") were also assayed. $HgCH_3^+$ was extracted using toluene, which was then dried using anhydrous Na_2SO_4 (MARVIN-DIPASQUALE, 2003). An additional clean-up step by aqueous solution of thiosulphate was used in lake sediment experiments, in order to examine the presence of inorganic Hg^{2+} in toluene extracts. Methylation experiments performed on sediments by incubation of labeled Hg^{2+} showed $^{197}Hg^{g}CH_3^+$ recoveries as low as 0.105 ± 0.020 % to 0.133 ± 0.018 % for toluene extraction on "killed control samples", and 0.0354 ± 0.0078 % to 0.0716 ± 0.0035 %, also on "killed control samples" using the more extensive extraction. Uncertainties reported are the standard deviations of triplicates. Total Hg inoculated in methylation experiments with sediments ranged from 50 to 100 $ng.g^{-1}$ wet sediment, and Hg inoculated in de-methylation experiments with soils ranged from 50 to 400 $ng.g^{-1}$. The specific activity of the radiotracer can be further improved with proper optimization of the irradiation; for our experiments design an inoculation of 5-10 $ng.g^{-1}$ can be achieved. The total Hg amounts of labeled Hg inoculated for the experiments performed are comparable to the amounts amended when ^{203}Hg and other non-radioactive tracers are used for this purpose. In addition, the sensitivity of the results strongly depends on experimental design and counting equipment.

The tracer allows an assessment of mercury methylation and de-methylation potentials in soil and sediments, and also mercury reduction potential. The latter is also very important to assess the mass balance of the added radiotracer. Appropriate separation procedures have to be employed, including solvent extraction for $HgCH_3^+$ and trapping of volatile mercury species, if present. In the case of reduction potential measurements, mercury can be trapped on solid adsorbents, such as gold traps for total gaseous mercury or Tenax if speciation of gaseous Hg is intended. Direct trapping of total gaseous Hg in aqueous solutions of permanganate is also possible. Based on trapping system an appropriate detection system should then be selected.

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Dimethyl Mercury in Municipal Waste Landfill Gas: Measurements and Analytical Method Development

LUCAS HAWKINS & ERIC PRESTBO

Abstract: Municipal waste landfills have been gathering increased attention due to the release of mercury species and other potentially harmful compounds to the atmosphere as constituents of landfill gas (LFG). Quantification of methylated species in LFG presents a unique set of challenges due to the complex nature of the matrix and the limitations of the sampling media employed. In this study we investigated the use of a pre-trap to reduce collection of high molecular weight volatiles, manipulated sample volumes to determine the effect on analytical results, collected numerous field duplicates to compare direct sample injection to pre-concentration, and collected 32 laboratory-prepared spiked traps in an effort to investigate matrix effects and analyte migration along the sampling train. A total of 16 landfill sites across the United States were sampled for gaseous dimethyl mercury (DMM) and total mercury using previously published methods. Briefly, DMM samples were collected using two serial traps (primary and backup) containing a 10 cm long by 0.4 cm diameter adsorbent bed of CarbotrapTM packed between silanized glass wool plugs in a silanized glass tube. Total mercury samples were collected using a similar technique, but employing a sorbent total mercury (STM) trap where the adsorbent beds consist of chemically impregnated carbon. DMM samples were analyzed by thermal desorption, isothermal GC separation, pyrolytic reduction, with detection by cold vapor atomic fluorescent spectrometry (CVAFS). Total Hg samples were analyzed by hot acid leaching, SnCl2 reduction, with detection by dual gold amalgamation CVAFS. Total mercury concentrations were observed between 10 – 8230 ng/m^3 and DMM levels were observed between 0.2 – 637 ng/m^3. To date there appears to be no strong correlations between landfill age, location, methane content, CO_2 content, and the expected levels of DMM in the produced LFG. While matrix spike recoveries appear to be highly site-dependant, we were successful at improving the average primary trap recoveries from 17.2 % to 55.5 %. The largest observed factor affecting recovery was sample volume, as is to be expected with matrix interference. Signal was reduced by as much as 60 % in instances where the guard column was removed, but this effect was not observed at all sites tested. At selected sites, the Carbotrap TM DMM method compared favorably with an alternate sampling method where the DMM is trapped by passing the LFG sample stream through methanol impinger solutions.

Key words: emissions, dimethyl mercury, Landfill gas

Results from the METAALICUS Intercalibration Program on Measuring Ambient and Excess Isotopic Concentrations of HgT and MeHg in Environmental Samples

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Abstract: This is the first report on an intercomparison exercise measuring not only ambient mercury levels, but also excess isotopic concentrations of mercury originating from isotope spiking in lake water. The work was carried out to support the on-going QA/QC activities of the METAALICUS (Mercury Experiment To Assess Atmospheric Loading In Canada and the US) project.

Key words: stable mercury isotope, intercomparison, total mercury, lake water, METAALICUS

INTRODUCTION

It is strongly advised that environmental studies investigating the fate of mercury in the natural environment demonstrate the reliability of obtained data by implementing adequate QA/QC protocols. One important piece of such protocols is the use of certified reference materials and regular participation in laboratory intercomparison to prove the ability to accurately measure levels of HgT and MeHg. More and more, funding agencies demand such activities before they commit to funding, particularly for major projects. While the situation regarding the availability of certified reference materials has steadily improved, the advent of new investigative tools has generated new chal-

lenges. Increasingly, research groups utilize enriched stable isotopes of Hg in their studies. The whole ecosystem project METAALICUS Mercury Experiment To Assess Atmospheric Loading In Canada and the US) introduced the large scale application of stable Hg isotopes. Early on in the project, the METAALICUS felt the necessity to implement a mandatory interlaboratory testing program for all participating labs to ensure validity and comparability of results among research teams. This exercise did not only concentrate on the determination of total Hg levels, but also established for the first time the measurement of individual isotopic concentrations of Hg in environmental samples. A total of nine laboratories measured total mercury concentrations (ambient and added isotopic Hg combined) and 4 laboratories participated in the intercomparison of excess isotopic mercury concentrations. This presentation will show the results for intercalibrations measuring HgT and MeHg in lake water, sediments, air, zooplankton, and zoobenthos. All measurements were made on unamended samples obtained during the initial phase of the METAALICUS study.

SAMPLING

Water samples were collected in September 2001 from the west basin of Lake 658 at the Experimental Lakes Area, Ontario, Canada. At this time, the first season of isotope additions (Hg enriched with ^{202}Hg) was almost completed. Water was filtered in-line using pre-cleaned QF/F filters. All sampling equipment was made out of Teflon that was rigorously acid cleaned prior to sampling. Water was collected into 10 individual Teflon bottles (500 mL), acidified with HCl (2 mL conc. HCl per 500 mL of sample) in the field-laboratory and shipped to Trent U. Prior to distributing samples were combined to a composite sample in a 5 L Teflon coated carboy. After mixing, samples were redistributed into new 500 mL Teflon bottles and shipped to the participating laboratories.

EVALUATION METHOD

While laboratories using AFS detection submitted values for ΣHgT only, participants using ICP/MS detection reported values for ambient HgT (calculated, measuring the concentration of an isotope other than ^{202}Hg) and excess ^{202}HgT (using a mathematical algorithm to deconvolute the contribution of the spike solution to the total measured concentration of ^{202}Hg). ΣHgT was then obtained from the sum of all isotopes measured by ICP/MS. For each lab, mean and standard deviations were calculated separately for the concentration of excess isotope ^{202}Hg as well as the ΣHgT concentration (ambient HgT plus isotope spike).

An overall mean and standard deviation was calculated for a given sample using the individual means. A Q-test (outlier test) was performed on the highest and lowest mean value for each sample. Finally "z"-scores for a given sample and laboratory was then calculated as follows:

z = (reported laboratory mean – overall mean)/overall standard deviation

Z-scores are interpreted as follows:

$|z| \leq 2$: satisfactory performance

$2 \leq |z| \leq 3$: questionable performance

$|z| \geq 3$: unsatisfactory performance

RESULTS

Figure 1 one shows the individual and overall means of results for the measurement of ΣHgT in lake water. The dotted lines represent 2 sd of the overall mean and indicate the range within a score of $z \leq 2$. Individual means ranged from 2.93 ± 0.11 to 3.98 ± 0.19 ng/L. No outlier was detected. The overall mean of individual means was 3.72 ± 0.36 ng/L. All participating results were within the acceptable range of $z \leq 2$, except for lab #1, which was just outside this range.

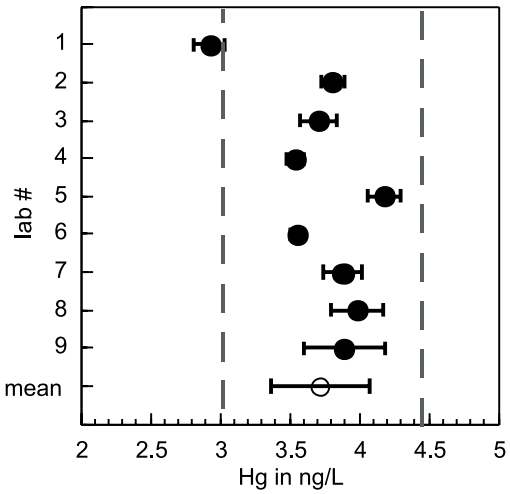

Figure 1. individual (solid circles) and overall (open circle) mean of the ΣHgT METAALICUS intercomparison measurement in lake water

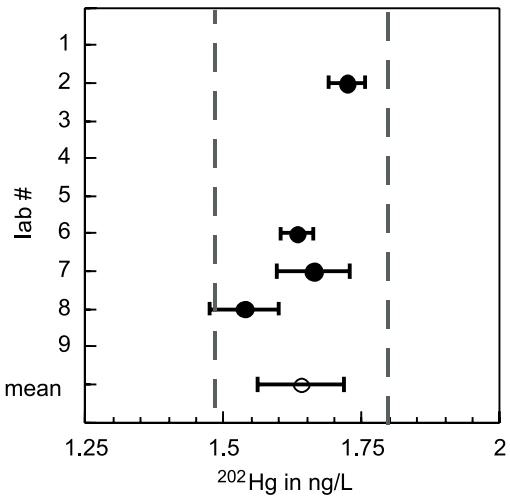

Figure 2. Individual (solid circles) and overall (open circle) mean of the ^{202}HgT METAALICUS intercomparison measurement in lake water

Figure 2 one shows the individual and overall means of results for the measurement of excess ^{202}HgT in lake water. The dotted lines represent 2 sd of the overall mean and indicate the range within a score of $z \leq 2$. Individual means ranged from 1.54 ± 0.06 to 1.72 ± 0.03 ng/L. No outlier was detected. The overall mean of individual means was 1.64 ± 0.08 ng/L. All participating results were within the acceptable range of $z \leq 2$.

DISCUSSION

This results from the first interlaboratory experiment of METAALICUS demonstrated excellent agreement of measurements among METAALICUS laboratories for both measurement of ΣHgT and excess isotope concentration of 200HgT, representing the lake addition. To our knowledge, this represents the first ever intercalibration exercise for measuring unknown levels of added isotopes in environmental samples.

Acknowledgements

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Bismuth is replacing mercury in modern sensor science

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Abstract: Bismuth electrode is presented and characterized as an attractive non-toxic replacement for the commonly used mercury electrode in advanced electrochemical detection of trace heavy metals and some selected organic compounds. Bismuth electrodes were prepared as conventional size electrodes and as micro-electrodes, the latter imparting great possibilities for application in micro-volumes and at micro-locations. In particular, for trace heavy metal detection, bismuth electrodes compare favorably with those of mercury or in certain cases even surpass them. In connection with stripping voltammetry and stripping potentiometry, bismuth electrodes allow multi-element detection down to low μg/L levels of heavy metals.

Keywords: bismuth electrode, trace heavy metals, electroanalysis

INTRODUCTION

Mercury has attracted immense attention since it was recognized as an element with many adverse effects upon the biosystem. One of the fields where mercury has been commonly present is certainly that of the electroanalysis of trace heavy metals and some organic compounds. Its first application as an electrode in polarography was reported in 1922 by Prof. Jaroslav Heyrovsky, who was later awarded a Nobel prize. Since then, because of several electrochemical advantages such as high overpotential for hydrogen reduction, mercury electrodes have found widespread application, in particular for trace heavy metal detection in connection with stripping voltammetry and stripping potentiometry. Both techniques are based on mercury's inherent ability to electrochemically preconcentrate heavy metals, usually as amalgams, intermetallic compounds or as adsorbed metal complexes, thus allowing measurements down to μg/L concentration levels. However, due to the well known toxicity of mercury and inconvenience in its handling, the popularity of mercury electrodes has considerably declined in the past, particularly in the last decade. There have been many attempts to replace mercury with other electrode materials and coatings, such as gold, platinum, iridium, different carbon modifications, etc., but the overall performance has not approached that of mercury. Thus, there remains a growing interest in finding new electrode materials and coatings to replace mercury.

Very recently, the "environmentally friendly" bismuth electrode[1] was presented as an attractive alternative for the detection of some trace heavy metals and selected organic compounds. It possesses better mechanical stability together with an electroanalytical performance that compares favorably with its mercury counterparts[2-7]. Preliminary stud-

ies have revealed that the non-toxic bismuth electrode holds great promise, particularly in meeting growing demands for environmental and industrial monitoring, decentralized clinical testing and remote sensing, where the presence of mercury is undesirable or even restricted.

RESULTS AND DISCUSSION

With the aim of assessing the electrochemical performance of the bismuth electrode, a critical comparison with the mercury electrode was performed. Figure 1 displays stripping voltammetric signals for 50 μg/L of zinc, cadmium and lead obtained at mercury (a) and at bismuth (b) micro-electrodes. The stripping voltammograms exhibit undistorted and well-defined signals for all three heavy metals, together with excellent resolution. The peak potentials for zinc and lead are nearly the same, whereas the signal for cadmium appears at a more negative potential (at -0.79 V) in the case of the bismuth electrode. This characteristic presents the possibility for simultaneous detection of thallium in the presence of cadmium and lead, which is a common problem at the mercury electrode due to signal overlapping (not shown). In addition, it is evident that the bismuth electrode does not compromise the signal to background ratio in the presence of dissolved oxygen.

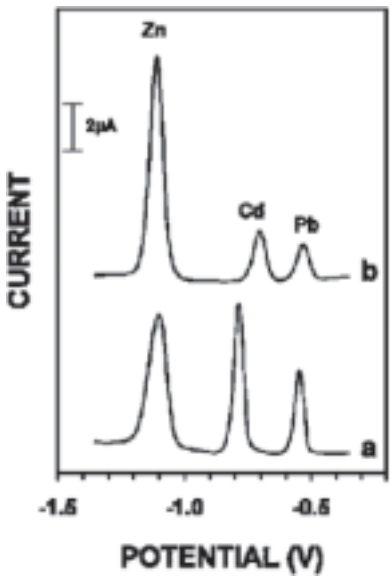

Figure 1. Stripping voltammograms for 50 mg/L of zinc(II), cadmium(II) and lead(II) at mercury (a) and bismuth (b) micro-electrode in 0.1 M acetate buffer solution (pH, 4.5) in the presence of dissolved oxygen. Deposition for 120 s at -1.4 V. Square-wave voltammetric stripping scan with a frequency of 20 Hz, potential step of 5 mV, and amplitude of 25 mV.

The use of bismuth electrode revealed an excellent reproducibility for all three metals investigated with a calculated limit of detection of, e.g., 0.3 μg/L for lead, in combination with a 10 minute preconcentration period. Similarly, several other heavy metals can be measured, such as indium, thallium, copper, cobalt, and nickel. Research efforts to expand the scope of applications of the bismuth electrode for the detection of some other heavy metals are in progress.

CONCLUSIONS

Bismuth electrode imparts great possibility for tailoring different kinds of electrochemical sensors for trace heavy metals and some organic compounds. It enables the introduction of electrochemical detection to those areas, where the use of mercury electrodes is not convenient or not possible, e.g., *in vivo* measurements, flow analytical techniques, on-field environmental measurements, etc. In addition, bismuth electrode obviates the need for special handling, which is required

for mercury and addresses the problems connected to mercury disposal. Therefore, the successful replacement of mercury with nontoxic bismuth raises expectations for a renaissance in stripping electrochemical detection in modern analytical chemistry.

Acknowledgements

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The Effect of Sampling and Sample Pretreatment on MeHg Concentration in Coastal Marine Sediments

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Abstract: The effect of sampling on monomethylmercury (MeHg) concentration in coastal marine sediments was investigated. It was shown that samples taken under nitrogen atmosphere provided significantly higher results compared to those processed under open atmospheric conditions. This study confirms that the sampling is the most important factor influencing the accuracy and uncertainty of MeHg in sediments.

Keywords: MeHg, coastal sediments, accuracy, sampling

INTRODUCTION

Two mercury contaminated coastal sites were investigated in the current study. The Minamata Bay in Japan was chosen as a case study due to its well-known history of mercury pollution. It was severely contaminated with mercury and MeHg from the Chisso acetaldehyde and vinyl chloride plant in Minamata City until 1968 (KUDO AND TURNER, 1999; TOMIYASU ET AL., 2000). After extensive clean-up actions, Minamata Bay was again open for fishing in August 1998. The second study area was the Gulf of Trieste located in the North eastern part of the Adriatic Sea (Mediterranean Sea) where the origin of mercury is due to riverine transport of mercury enriched particles from the former mercury mine in Idrija, Slovenia (HORVAT ET AL., 1999, 2002). In order to control the environmental behavior of Hg in the both study areas continuous environmental monitoring is necessary. This should include determination of Hg-T and MeHg in marine organisms for the purpose of health monitoring, while spatial changes and trends of Hg pollution require accurate measurements of mercury and its species in air and in sediments and water samples. This would allow an assessment of the current status and model the future trends of Hg pollution in this coastal environment. Reliable results for Hg-T and MeHg are, therefore, essential for further biogeochemical studies, the assessment of Hg-T and MeHg fluxes from sediment into the water column and the mass balance of Hg ts exchange with the outher seas (RAJAR ET AL., 2004).

The focus of this study is the accuracy of the results for MeHg obtained in sediments. Comparison of the results obtained by the use of different analytical techniques has been demonstrated previously (LOGAR ET AL., 2002), however the main problem associated with the accuracy of the data is related to the representativenes of the sample and the effect of sampling. Sediment is considered as the primary source of MeHg in the aquatic environments. The process of MeHg formation is still not well understood and a number of studies have shown that this process depends on various environmental conditions such as pH, temperature, presence of sulfato-reduction bacteria, redox conditions etc. Although, this is well documented in the literature a number of research groups still determine MeHg in sediments sampled under uncontrolled sampling conditions, which may result in decomposition of MeHg during sampling. As a result, concentrations of MeHg in the sediments may significantly be changed and poorly represent MeHg status in the sediments.

EXPERIMENTAL

In this study we compared the results obtained for MeHg in two contaminated coastal areas: (1) Minamata Bay, Japan was chosen as a case study due to its well known history of mercury pollution due to industrial pollution and (2) the Gulf of Trieste in the Northern Adriatic due to past mercury mining in Idrija. Sampling in Minamata was conducted in 2000 and the sampling in the Gulf of Trieste was conducted in 2003. Core samples of the bottom sediments were taken at several locations in each study area. After the cores were removed from the sea, the samples were cut in 1 to 2 cm slices under nitrogen atmosphere on-board ship in order to keep the redox conditions unchanged. The slices were stored in plastic containers and kept under nitrogen until further processing in the laboratory, where slices were divided into two portions. One was kept under the nitrogen throughout the sample homogenization, weighing and first extraction step in which MeHg was extracted from the sediment into the organic solvent. The second aliquot was transferred into another glass container, and the samples were further processed under the normal laboratory conditions, exposed to normal laboratory atmospheric conditions.

During sample preparation in Japan in 2000, pore water was also removed from the sediment core slices by centrifugation in nitrogen atmosphere, and the solid phase was then also analyzed for MeHg under the normal laboratory conditions.

The samples were analyzed using the different analytical methods verified for their comparability in another study (LOGAR ET AL., 2002). Analytical methods for determination MeHg in sediments analyzed by the NIMD consisted of acid leaching and extraction of MeHg dithizonates into toluene followed by a clean-up step, back extraction into toluene, separation by packed column gas chromatography and detection of MeHgCl by an electron capture detector (GC ECD) (AKAGI ET AL., 1991). The method used at IJS was based on acid leaching and solvent extraction into CH_2Cl_2, followed by back extrac-

tion into water phase, ethylation, room temperature pre-collection on Tenax, gas chromatography, pyrolyses and CV AFS detection. Comparability of the results obtained by two different methods was demonstrated by intercomparison exercises and by the analysis of CRMs (HORVAT ET AL., 1993; LOGAR ET AL., 2002).

RESULTS

The results obtained for sediments in Minamata area are presented in Figure 1. Two stations in Minamata area were investigate: (1) the central station of the Minamata Bay (left figure), and (2) the Fukuro Bay affected by the local wood industry (right figure). Evidently, the concentration of MeHg in sediments treated under nitrogen atmosphere are much higher than those treated under open laboratory conditions. Moreover, the results obtained for MeHg after the removal of pore water are even higher, but the differences are not so high. Comparison of the results obtained in Fukuro Bay sediments are similar to those obtained in Minamata Bay, except for MeHg in sediments after the removal of pore water. The results obtained in solid phase after the removal of pore water and the whole sediment prepared under open laboratory conditions are similar, and much lower from the results obtained under the nitrogen atmosphere. Evidently, the sampling and sample pretreatment may significantly influence the results for MeHg in sediments. These are also dependant on the type of sediments. MeHg concentrations in Minmata area were generally higher at the subsurface layer, which generally provides favorable conditions for MeHg formation.

The results obtained in sediments of the Gulf of Trieste shown in Figure 2 also confirmed that the results obtained under nitrogen conditions are higher than those obtained under the open laboratory conditions, however the differences are much smaller as compared to Minamata Bay. This again confirms the above observations that the differences are very much dependent on the type of the sediments.

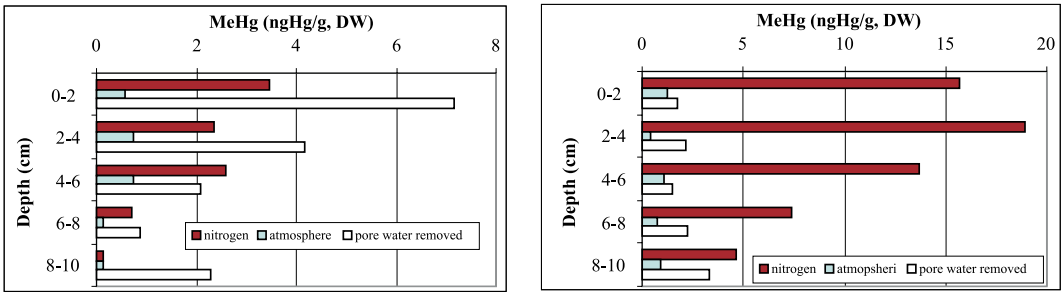

Figure 1. Concentrations of MeHg in sediments obtained during different sample preparation procedures in Minamata (left) and Fukuro Bay (right), November 2000. Left: Minamata Bay, where the total Hg concentration varies between 2 to 6 mg/kg, DW; right: Fukuro Bay , total Hg concentration varies between 7 to 8 mg/lg, DW.

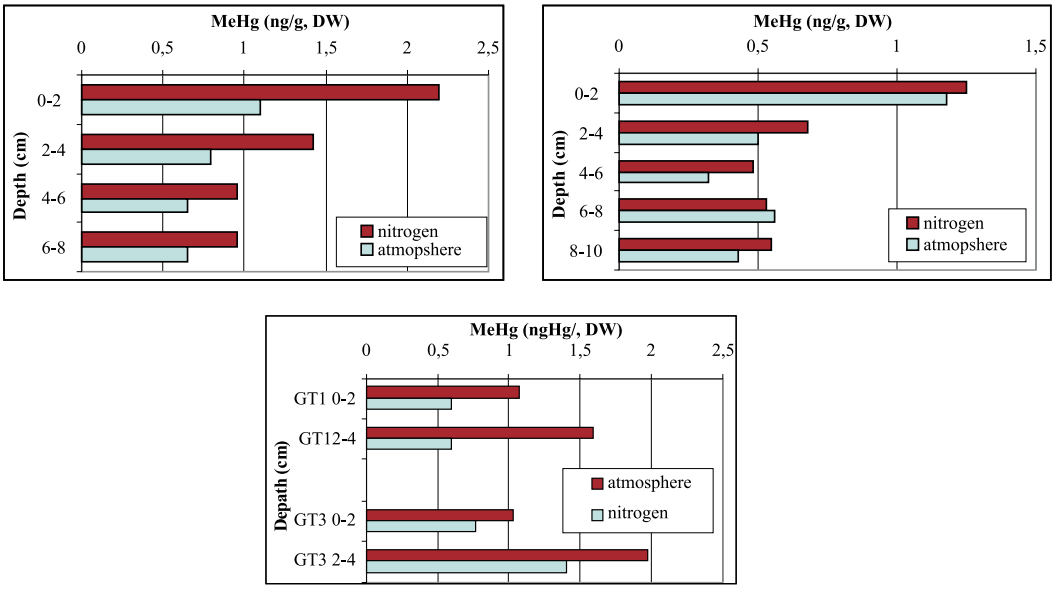

Figure 2. Concentrations of MeHg in sediments obtained using different sample preparation procedures in the Gulf of Trieste, September 2003. Left: Station GT3 with total Hg concentration between 2 to 4 mg/kg and right at the station GT1 where total Hg concentration is below 1 mg/kg. The figure below shows the results obtained in duplicate cores.

CONCLUSIONS

The results of this study suggest, that the results of MeHg in sediments are very dependent on the sampling protocol. The results reported for MeHg in the literature obtained under uncontrolled sampling conditions should, therefore, be treated with great caution. It seems that the sampling protocol may be the most significant source of uncertainty for MeHg in sediments.

Acknowledgements

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Optimisation of an Analytical Technique for Studying $^{14}CH_3Hg^+$ Demethylation Potential

VESNA JEREB

Abstract: Radiotracer $^{14}CH_3Hg^+$ is used to follow demethylation products $^{14}CH_4$ and $^{14}CO_2$ which indicate the detoxification mechanisms. In general, two approaches are used to measure CO_2 and CH_4: (i) separation of gases on gas chromatoraphy coulmn followed by detection in gas proportional counter or (ii) trapping of products into an appropriate absorption solution followed by liquid scintillation counting (LSC).

We prepared a simple system to follow $^{14}CH_3Hg^+$ demethylation by using Packard Tri-Carb 2550 A/B LSC. The gaseous products from $^{14}CH_3Hg^+$ demethylation were trapped in NaOH solution and counted on liquid scintillation counter after the addition of scintillation cocktail. CH_4 was combusted to CO_2 in CuO column at high temperature prior to trapping in NaOH solution. Analytical parameters such as counting efficiency, NaOH trapping efficiency, quenching effects, repeatability and limit of detection were determined by varying experimental factors (such as flow of purging gas, concentrations and volumes of NaOH solutions, sample / scintillation cocktail mixing ratios etc.).

For this demethylation experiments, soil sample IAEA Soil-1 was tested. Sample was spiked with different amounts of $^{14}CH_3Hg^+$ radiotracer of high specific activity and incubated in dark for several days at room temperature and under anaerobic conditions. Results of the study suggest reductive demethylation in soil, as the oxidative reductive demethylation potential ratio was about 0.1.

Key words: $^{14}CH_3Hg$ demethylation, liquid scintillation counting

Mercury Pollution and Speciation Methods Development in China

GUI-BIN JIANG, LI-NA LIANG & JIAN-BO SHI

Abstract: Mercury pollutions have been occurred in many countries of the world, including China. The mercury-mine reserve in China accounts for the third in the world and mainly focuses in southwest China, especially Guizhou Province. The exploitation of mercury mines caused severe mercury pollution in air, water, sediment and organism in that region. Besides, the wastewater and waste residue drainage from chemical industries in other regions hastened the mercury pollution in China.

The most three famous mercury pollution sites in China were Guizhou Province, Songhua River and Tianjin Jiyun River. Mercury pollution in Guizhou Province was mainly caused by the mercury mining exploitation and the coal combustion. Guizhou Province had mercury reserve once high up to 31700 tons and was praised as Mercury Capital though the mercury resources have been dried up now. The average mercury contents in coal from Guizhou were 0.55mg/g [1], which was far beyond the mean value 0.1mg/g [2]. Mercury pollution in Songhua River was mainly caused by the waste drainage from China s biggest chemical industries in the upper river. It was reported that the mercury accumulation in Songhua River made the river mercury concentrations exceeded the maximum permission levels of 0.05mg/L in industry wastewater. The deaf patients in fisherfolk were 3-4 folders of those in other regions in the 1970 s. Even in the 1990 s, methylmercury levels in catfish were still 0.34mg/g [3]. The cause of mercury pollution in Tianjin Jiyun River was just the same as Songhua River. The mercury contents in Jiyun River s sediment were once high up to 845mg/g in the drainage entrance in 1976 and declined to 450mg/g in 1982 [4, 5].

Due to the severe mercury pollution in the above-mentioned sites, many methods have been established in succession. The equipment of GC coupled with AAS [6, 7] and HPLC coupled with AFS [8] were obviously the most successful ones among all the methods. The interface of GC with AAS was a T-shape quartz tube and this equipment was successfully used in the determination of DDM, DEM, DMC and EMC in air samples and biological samples [6]. The hyphenation of HG-SPME with this system had finished the speciation of MMC, EMC and PMC in sediments and biological samples [7]. The newly established HPLC-MD (microwave digestion)-AFS system was especially suitable for the speciation of MC, MMC, EMC and PMC at the same time and it was proved to be very effective for environmental and biological samples [8].

Key words: mercury pollution, method, china

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Speciation Analysis of Mercury in Mollusks using High Performance Liquid Chromatography On-line Hyphenated with Atomic Fluorescence Spectrometry

GUI-BIN JIANG, LI-NA LIANG & JIAN-BO SHI

Abstract: Mercury pollution in China could track back to several hundred years ago, which was mainly caused by the exploitation of mercury mines in Guizhou Province. However, the high economic development in China since the 1950's caused more severe mercury pollution in broad regions of China. Northeast China was well known for heavy industries and the incidental heavy metal contamination had been brought out in Bohai Sea due to the wastewater and waste residue drainage to river waters. Bohai Sea was the largest semi-closed continental shelf marginal sea in China and the heavy metal pollution would exist for many years due to the low exchange fluxes with Huanghai Sea.

In our study, HPLC coupled with AFS was used for the speciation of methylmercury in mollusk samples[1]. The contamination levels of methylmercury and total mercury in 13 species of gastropods and bivalves collected from eight coastal sites along the coastline of Bohai Sea were investigated. Methylmercury was detected in all samples, with methylmercury levels ranging from 4.84 to 168.42 ng of Hg g-1. The species-dependent bioaccumulation capacity was observed in this study and gastropods showed higher capacity to bioaccumulate mercury than bivalves. Maybe this was because that the bivalves were grass-eating mollusks and the collected three gastropod species were all predatory flesh-eating mollusks and the main food of which were bivalves. The results also indicated that mercury contents in two gastropods presented uplifted trends with the increasing of the shells' dimensions. Due to the Hg drainage from the chemical industries in the adjacent area, mollusks collected from Huludao were obviously the most severely polluted samples.

Key words: mercury speciation, Mollusks, HPLC-AFS

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Speciation Analysis of Mercury in the Polar Environment by Multi-Capillary Gas Chromatography-Inductively Coupled Plasma Time-of-Flight Mass Spectrometry

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Abstract: The benefits of purge-and-trap injection and solid-phase microextraction as solvent-free preconcentration techniques in combination with rapid multicapillary gas chromatography separation and fast detection by inductively coupled plasma time-of- flight mass spectrometry are discussed for mercury speciation analysis. The analytical process is illustrated with data obtained by the analysis of snow and ice samples from Greenland and Antarctica.

Key words: mercury speciation; purge-and-trap injection; solid phase micro-extraction, Greenland, Antarctica

INTRODUCTION

A better understanding of the global cycle of mercury in polar environments is important as *i)* many metals and metal species appear to be accumulated in the Arctic environment and biota especially in fish and/or sea mammals, which represent the main component of native populations diet[1]; *ii)* the snow pack consists of an important reservoir of toxic elements, as it covers up to 50 % of land in the Northern Hemisphere during the winter; *iii)* the polar ice contains a record of ancient metal depositions, which provides information about both natural geochemical cycling and the impact of recent anthropogenic emissions[1]. In this general context, monitoring of mercury and in particular mercury speciation analysis is of great importance for understanding the polar environment.

Developments over the past decade in the speciation analysis of mercury replaced conventional capillary gas chromatography (GC) by multicapillary (MC) systems, leading to high-speed separations while using larger sample injection volumes without sacrificing efficiency. During the last years emphasis was also placed on the use of solvent-free preconcentration techniques to accomplish state of the art mercury speciation analysis. A method based on purge-and-trap injection (PTI) in combination with MC separation and inductively coupled plasma time-of-flight mass spectrometry (ICP-TOFMS) detection was developed and applied to ultra-trace mercury speciation analy-

sis in the remote environment[2 3 4 -5]. More recently, solvent-free preconcentration by means of solid phase microextraction (SPME) has become a more promising approach for speciation analysis of mercury. This technique ensures derivatization, extraction and preconcentration in a single step, with a significant increase in simplicity and sample throughput enhancement and leads to significant figures of merit in combination with MC GC separation and ICP-TOFMS detection. In previous work[6], it was found that the most efficient extraction of methylmercury (MeHg) and inorganic mercury (Hg^{2+}) was obtained by using a carboxen/polydimethylsiloxane (CAR/PDMS) fibers.

The present work reports the development of an analytical approach for mercury speciation analysis at ultra-trace levels on the basis of SPME with MC GC separation and ICP-TOFMS detection. The capabilities of SPME with the CAR/PDMS fiber and PTI as organic solvent-free preconcentration techniques are compared. The benefits of using rapid MC separation and fast detection by ICP-TOFMS are also discussed. The analytical process is illustrated with data obtained by the analysis of snow and ice from Greenland and Antarctica.

RESULTS AND DISCUSSION

Samples and sampling procedure

Description of samples and sampling procedure for the snow collected in Greenland is given in detail elsewhere[4]. The Antarctica ice samples were collected at Dome C within the framework of the European Project for Ice Coring in Antarctica (EPICA). The samples analyzed in this work correspond to six ice core sections taken at a depth of 229, 516, 1313 and 1643 m[7], which cover a period from the Holocene back to at least the penultimate glacial-interglacial transition. A special decontamination procedure of the samples was performed in a cold laboratory at the LGGE in a class 100 clean bench as described elsewhere[8].

Derivatization, extraction, separation and detection

To enhance both extraction/preconcentration and MC GC separation derivatization of ionic mercury species was performed at pH 5.0 using of sodium tetraethylborate ($NaBEt_4$, 100 µl solution 0.2 % m/m). Propylmercury (PrHg) was used throughout, as internal standard (IS) to correct for ion signal variation and instrumental drift. A Chrompack PTI system (Middelburg, The Nederlands) was used for the extraction of the derivatized volatile species from the solution (10 ml) and their subsequent injection into the MC GC column. The conditions optimized for achieving maximum efficiency of extraction by PTI are described elsewhere[2]. In brief, the (*in situ*) derivatized analytes (together with IS) were purged and trapped during 10 minutes using a purge flow (He) of 40 ml min^{-1} and a trapping temperature of –75 °C. The desorption/injection of analytes was achieved by flash heating the capillary trap to 125 °C. SPME was carried out using a manual device (Supelco, Bornem, Belgium) equipped with a 75 µm CAR/PDMS fiber. A standard/sample aliquot together with the IS was buffered at pH 5.0 in a 25 ml sampling vial and then diluted to a volume of 7.9 ml with milli-Q water. Then, an aliquot of 100 µl $NaBEt_4$ solution was added and the vial was immediately

closed. The extraction was carried out at room temperature by exposing the SPME fiber to the headspace during 8 min while stirring the sample at 1400 rotations min^{-1}. The fiber was then withdrawn into the needle and the SPME device transferred into the GC injector for the introduction of the analytes into the chromatographic separation column. The mercury species were isothermally separated at 100 °C using a MC GC column (MC-1 HT, Alltech, Belgium) housed in a gas chromatograph CP 9001 Chrompack (Bergen-op-Zoom, The Netherlands). For detection of the chromatographic signals an ICP-TOFMS instrument (LECO Corp., St. Joseph, MI, USA) was used with 102 ms integration time when using PTI and 204 ms when using SPME.

Analytical performance characteristics

A comparison of PTI and SPME combined with MC GC and ICP-TOFMS in terms of analytical performance characteristics is given in Table 1. In both cases, integrated peak area obtained in analog mode was used, as it provided better analytical characteristics than pulse counting. Method detection limits (MDL) are reported as 3 times the standard deviation calculated for 10 successive injections of the analytical blank. Repeatability in terms of relative standard deviation (RSD, %) was calculated for 10 successive injections of a standard mixture containing 10 pg MeHg (as Hg) and Hg^{2+} and using PrHg as an IS.

The accuracy of the measurements of the snow/ice samples was assessed on the basis of recovery studies on samples spiked (one level) with MeHg and Hg^{2+}, just prior to analysis. Quantitative recovery factors (deviation below 10 %) were obtained for both species.

Table 1. Analytical performance characteristics of the methods based on PTI and SPME with MC GC separation and ICP-TOFMS detection for mercury speciation analysis

	MDL (pg g^{-1}, as Hg)		Precision (RSD, %)	
	PTI	SPME	PTI	SPME
MeHg	0.016	0.027	1.2	3.3
Hg_i	0.26	0.27	4.1	3.8

Analysis of Greenland surface snow and Antarctica ice

The PTI method was applied to analysis of Greenland surface snow. A selection of results for a few samples is given in Table 2.

Concentration levels for MeHg are very close to MDL, whereas those of total mercury

Table 2. Results obtained by PTI and SPME coupled to MC-ICP-TOFMS for mercury speciation analysis in surface snow from Greenland and ice from Antarctica

Concentration (pg g^{-1}, as Hg) [a]						
Greenland surface snow			Antarctica ice			
No.	MeHg	Hg_T [b]	Depth (m)	Age (yr BP)	MeHg	Hg_T [b]
1	0.11±0.01	3.03±0.70	229.35	7,100	0.20±0.02	1.01±0.02
2	0.08±0.05	1.86±0.13	515.9	22,300	0.13±0.07	9.09±1.26
3	0.07±0.01	0.84±0.04	1313.4	93,300	0.36±0.09	3.92±0.54
4	0.05±0.03	1.75±0.27	1643.4	124,700	0.12±0.05	0.12±0.05

[a] mean ± standard deviation (n=3); [b] total mercury, the sum of MeHg (as Hg) and Hg^{2+}

(Hg_T) range between 0.84 and 3.03 pg g^{-1}. The SPME method was applied to mercury speciation analysis in Antarctica ice. A few preliminary results for the analysis of ice aging from between 7,100 and 124,700 years before present are also reported in Table 2.

CONCLUSIONS

This work demonstrates that the combination of both PTI and SPME with MC GC separation and ICP-TOFMS detection allows rapid, simple, accurate and precise speciation analysis of mercury at pg g^{-1} levels in snow/ice samples from remote polar environments. Both methods are comparable in terms of analytical performance characteristics but in terms of cost, simplicity and sample throughput SPME is preferable. Signals with very narrow peak width as obtained by MC GC systems can be recorded with ultra-trace sensitivity without the loss in precision or the introduction of spectral skew in the chromatograms as a result of the very high data acquisition rate of the ICP-TOFMS instrument.

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Studies on the Sorption of Hg^{2+} and CH_3Hg^+ on *Coriandrum Sativum*: Development of a Possible Reference Material for the Analysis of Mercury Species

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Abstract: A sorbent prepared from the plant *coriandrum sativum*, commonly known as coriander or Chinese parsley, was evaluated for its potential to sorb inorganic (Hg^{2+}) and methyl mercury (CH_3Hg^+) – from aqueous solutions. Batch experiments were carried out to determine the pH dependency in the pH range 1–10. Sorption capacities of 24 mg/g and 7 mg/g were found for Hg^{2+} and CH_3Hg^+ respectively. Elution of the sorbed species was optimized using mixture of hydrochloric acid and L-Cestine solutions. CH_3Hg^+ was with 1M HCl whereas 6M HCl was required for the elution of Hg^{2+}. Sorption and elution studies also showed that no interconversion of species occurred. The studies suggest that the sorbent can be used to hold known amounts of both forms of mercury and would be useful in the development of methodologies for mercury speciation.

Key words: coriander, sorption, mercury, methyl mercury

INTRODUCTION

Mercury finds wide spread usage in chloro-alkali plants, extraction of gold, dentistry, science and military operations[1]. Effluents from these industries and subsequent use of products constitute an important anthropogenic source of mercury in the environment. Exposure to methyl-mercury can cause central nervous system disorders, intellectual deterioration and even death[2]. Mercury is considered by the Environmental Protection Agency (EPA) as a highly dangerous element because of its accumulative and persistent character in the environment and biota[3].

Some of the various sorbents that have been used for removal of mercury from waste solutions are coal-fly ash[4], peat moss[5], coffee grounds[6], chemically modified cotton[7] and barks of trees[8].

In the present work we have investigated a sorbent prepared from coriander - a cheap and commonly available edible plant – that absorbs Hg^{2+} and CH_3Hg^+ from aqueous solutions as a potential material for preparation of a reference material for mercury speciation.

RESULTS AND DISCUSSION

Effect of pH on the uptake of inorganic and methyl mercury

Experimental results showing the removal of both inorganic and organic mercury species by the sorbent as a function of pH in the range of 1-10 are presented in Fig. 1. It has been observed that the sorption of both inorganic and methyl mercury reached a maximum value (>95 %) around a pH of 4 and remained constant till a pH of 10. An efficient removal of mercury from the aqueous solutions occurred over the pH range 4 - 10 irrespective of the chemical form in which it was present in the solution.

The final pH of the solutions was observed to change with sorption of the mercury ions by the sorbent, the pH reduced with sorption to lie between pH 3.5 to 5.5 when the initial pH of the aqueous solution was varied from 1-10.

Kinetic studies also indicated that the binding of both species of mercury is rapid. About 80 % CH_3Hg^+ was removed from solution at the end of 10 min. The percentage of removal of inorganic mercury reached >95 % by the end of a contact period of 45 min, whereas methyl mercury removal reached its maximum value within a contact period of 30 min. Further increase in contact period to 60 min had no significant effect.

The capacities of the sorbent for inorganic and methyl mercury (in terms of absolute amount of mercury) were determined to be ~24 mg/g and ~7 mg/g respectively. The lower capacity for methyl mercury and the more rapid desorption of CH_3Hg^+ ions (discussed later) might indicate the bulkier group's inability to diffuse inside the sorbent and absorption is essentially on the surface of the sorbent.

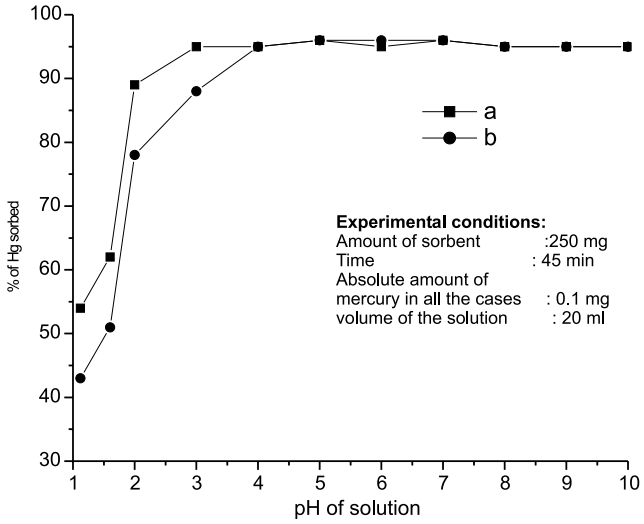

Figure 1. Effect of pH on the sorption of a) Hg^{2+} and b) CH_3Hg^+

Desorption studies

Desorption of the mercurial species sorbed by coriander was investigated as a function of concentration of HCl, in the range of 1-6 M. The mercury content in the filtered supernatant was determined.

As seen from Fig. 2, more than 95 % desorption of methyl mercury occurred at an HCl concentration of l M, whereas desorption (> 95 %) in the case of Hg^{2+} was achieved with 6M HCl.

But high acid concentration lead to deterioration of the sorbent. To reduce acid strength L-Cystein was added to the eluent. Optimum desorption of Hg^{2+} could be obtained with 10 % HCl – 0.025M cystein.

Further experiments are necessary to determine species integrity during sorption, storage and desorption.

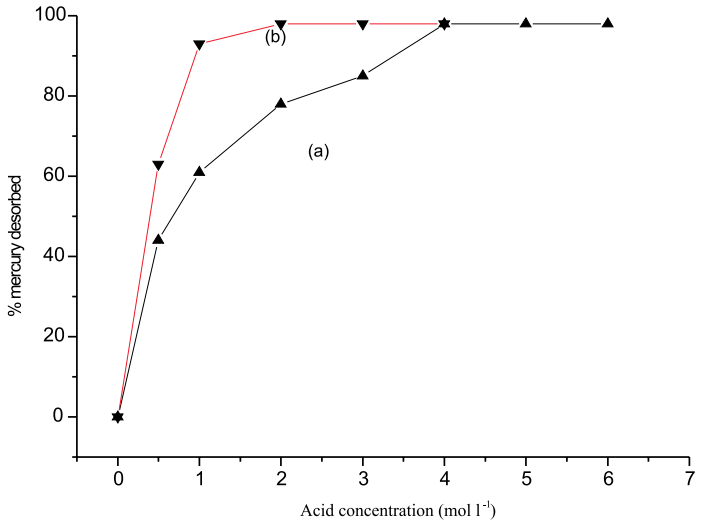

Figure 2. Desorption of mercurial species with HCl: a) Hg^{2+} b) CH_3Hg^+

Functional groups responsible for sorption

As seen in Fig. 1 the sorption of mercury initially increased with pH and a plateau occurred pH 4 onwards. This pH dependent trend indicates that the mechanism of mercury binding is through the deprotonation of functional groups, similar to another sorbent investigated by us, for sorption of mercury, prepared from the soil fungus, *Aspergillus niger*[9]. It was shown in that study, by esterification and de-esterification of the sorbent that carboxylic acid groups played a major role in the binding of the mercurial species. The similarities in the sorption characteristics and the pH profiles of the sorption and desorption in the present sorbent prepared from coriander indicate that the carboxylic acid groups play an important role in the binding of mercury.

CONCLUSIONS

The sorbent coriandrum sativum was found to sorb mercury from aqueous solutions with good efficiency. Maximum absorption occurred at a pH of ~6 with capacities for Hg^{2+} and CH_3Hg^+ of ~24 mg/g and ~7 mg/g of dry sorbent respectively. Coriander appears an attractive material, which could have, potential for use in decontaminating mercury from aqueous solutions and also a potential material for developing as a reference material for mercury speciation.

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Investigation of Mercury Isotopic Mass Fractionation as a Novel Tracer for Sources and Pathways of Mercury in the Environment

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Abstract: A novel approach to investigate the sources of mercury pollution as well as the pathways and degree of reprocessing is the determination of isotopic fractionation signatures of the seven mercury isotopes. For heavy isotope systems like mercury (atomic mass units 196, 198, 199, 200, 201, 202, 204) the range of mass fractionation is very small and was basically impossible to measure with traditional mass spectrometric methods for small sample amounts. Only for the past few years multi-collector inductively couple plasma mass spectrometry (MC-ICP-MS) has been established as a reliable and robust method to measure isotopic fractionation of non-traditional isotope systems at precision levels down to 0.002 % (20 ppm, 2s). Using a state-of-the-art NU Plasma multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS) we have developed a method that allows the routine measurement of the mercury isotopic composition for samples sizes of less than 100ng Hg with an external precision of 0.003 %. The sample introduction system consists of a high efficiency continuous-flow cold-vapor generator. For mass bias monitoring and internal precision improvement the Hg vapor is mixed with a dry thallium (NIST 997) aerosol from a micronebulizer desolvation unit. The isotopic composition of mercury in the solar system and on earth was previously poorly characterized. Before any valid conclusions about possible isotopic signatures for various natural systems and anthropogenic sources can be drawn, we started to investigate the isotopic composition of primitive meteorites, which reflect the composition of the early solar nebular. Despite earlier reports of certain large anomalies our study of 20 carbonaceous meteorites confirmed that all solar mercury is isotopically similar to mercury found in terrestrial sources. In detailed studies of various ore deposits we established that the degree of mercury isotopic fractionation within different boiling zones of single deposits spans a range of over 0.1% per amu or 0.5% for the 198Hg/202Hg isotope ratio (100times larger than the analytical resolution). The analysis of various organic materials such as fish, lobster, human hair, leaves, and sediments show fractionation spanning 0.02-0.07 %/amu. Initial mechanistic studies of fractionation during methylation by anaerobic sulfate reducing bacteria cultures under optimal growth conditions did not exceed 0.03 %/amu. Mechanistic studies of isotopic fractionation by various bacterial processes will be investigated in detail under realistic conditions. Sampling efforts for important point sources such as coal fired power plants and waste incinerators are underway. Several sediment cores from lakes and rivers in the vicinity of point sources such as a tannery, chlorine-alkali plant, and heavy industry have been obtained. Historical records of global mercury pollution in sedimentary records will reveal if there is a measurable anthropogenic isotopic signature. It can be concluded at this point that there is significant isotopic fractionation for mercury isotopes up to permil levels in natural systems that can easily be resolved by MC-ICP-MS measurements. The current data set is too small to distinguish between source profiles and isotopic signatures from chemical, physical, and bacterial processing.

Key words: mercury isotopes, MC-ICP-MS, isotopic mass fractionation

Thermal Characterization and Quantification of Mercury Compounds in Atmospheric Particulate Filter Samples by Thermal Analysis Isotope Dilution Coldvapor Generation Inductively Coupled Plasma Mass Spectrometry (TA-ID-CV-ICP-MS)

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Abstract: The true chemical composition of particulate-phase mercury is currently unknown. Because of the small sample amounts in complex mixtures conventional techniques cannot be applied. Chemical binding could be in the form of ionic species such as mercury chloride and sulfate or elemental mercury adsorbed or amalgamated on carbon and metallic phases. Recent studies demonstrated that simple filter sampling procedures are prone to artifact formation. Positive artifacts are expected from the impact of reactive gaseous mercury (RGM) while negative artifacts may occur during evaporative losses. We developed a thermal analysis method for atmospheric quartz fiber filter samples with total mercury loads in the range of typically 10-150 pg total. The thermal release of Hg in an argon atmosphere is measured as a function of a linear heating ramp at a rate of 1 °C/s from 25-750 °C by ICP-MS. The quantification of the mercury released from the samples is quantified online by isotope dilution through the addition of an enriched 200Hg and 201Hg double-spike generated by a continuous-flow high efficiency coldvapor generator. The isotope dilution quantification accuracy for the thermal release profiles was evaluated with NIST standards. The NIST 1633 "mercury in fly ash" standard was chosen as a routine external control. Recoveries were consistently 108±1 % for aliquots of 200 mg with an average value well within the certified range. Measurements of very small aliquots with Hg loads comparable to the filter samples revealed the large inhomogeneity of NIST 1633 for aliquots in the 10-30 mg range of up to 30%. The precision for the quantification of larger aliquots is quite remarkable given the fact that the thermal release for the NIST fly ash spans a temperature range of almost 400 °C/ 400s. Unlike simple thermal decomposition quantification methods with gold focusing this method does not just provide a total value but the true absolute amount released from a sample in integration windows of 1 - 3s. The sensitivity or detection limit for each 3s integration window is in the order of 20fg Hg, which is about factor 20-50 lower than any atomic fluorescence detector could provide in general but still not with the same temporal resolution. The quantification of pg level filter samples was also tested by conventional analysis of parallel filter samples by microwave digestion and CV-AFS analysis, which yielded excellent agreement between the two methods.

Parallel filter samples were collected in Detroit, Michigan with both KCl denuded and undenuded sampling lines. Because of a suspected impact of ozone levels on the RGM collection we also employed KI denuders in front of the KCl denuders.

The release profiles of denuded and undenuded filter samples revealed some common features but also great complexity. All three sampling approaches showed differences in both release profile and total Hg load. Most release profiles show two main release maxima at 210 – 250 °C and 380 – 410 °C with the majority of samples releasing the most Hg in the temperature range of 150-300 °C around the first peak. The first maxi-

mum may be accounted for by physisorbed elemental mercury and the second one may represent ionic forms. The release temperatures are in general higher than expected from published literature data about the decomposition temperatures of pure Hg compounds. Experiments with some of the pure salts such as $HgCl_2$, $HgSO_4$, HgS, HgO etc. show that all of these compounds decompose in the temperature range above 300°C so that no clear distinction between them can be achieved by the release profiles of the filters. In most cases the undenuded filter samples showed the higher Hg loads compared to the denuded samples. The excess was found to be mostly in the lower temperature peak. The addition of the KI denuded samples also typically increased the Hg load of the lower temperature range, which may be caused by iodine release and subsequent elemental mercury conversion in the aerosol or on the iodized filter substrate. It can be concluded that this fast and powerful new technique reveals distinctive features of the mercury binding in the particulate phase mercury. The method provides full quantification at sub-picogram levels and thermal characterization with total analysis times of less than 20 min with no other sample preparation or external calibration. The differences in the release profiles for denuded and undenuded samples clearly demonstrate that possible artifact formation even with the use of denuded filter sampling have to be further investigated. While the thermal release profiles cannot clearly distinguish between individual ionic Hg species it does reveal significant information regarding the classification of mercury binding forms.

Key words: particulate phase mercury, thermal speciation, isotope dilution

Application of the Sequential Extraction Scheme for Mercury in Contaminated Coil

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Abstract: The main aim of this study was to test and apply sequential extraction and quantification of different Hg phases in order to estimate the mobility and potential bioavailability of Hg in contaminated soils in the Idrija Hg-mine region, Slovenia. Separation of Hg phases was performed by means of a selective sequential extraction procedure complemented by volatilization of elemental mercury (Hg^0). Fractionation measurements indicated cinnabar as the predominant Hg fraction, followed by Hg^0. Accumulation of cinnabar predominantly occurred in coarse grained flood plains sediments, where on average it constituted more than 80 % of total Hg. In contrast non-cinnabar fractions were found to be enriched in areas where fine grained material was deposited, reaching up to 62 % of total Hg. The strong positive correlation (R^2=0.71-0.99) among non-cinnabar fractions suggested that these fractions predominantly control the mobility and potential bioavailability of Hg. Sample pretreatment before fractionation influenced the partition of Hg between different fractions, and therefore fractionation in fresh, nontreated samples is suggested. Good agreement (R^2=0.81-0.95) was found between the non-cinnabar fractions and evaporation of Hg^0. Both the temperature and sample moisture had significant effects on mercury volatilization.

Key words: mercury fractionation, soil, sequential extraction

INTRODUCTION

The biogeochemical and especially the ecotoxicological significance of Hg input is determined by its specific binding form and coupled reactivity rather than by its accumulation rate in the solid material. Consequently, these are the parameters that have to be determined in order to assess the potential for Hg transformation processes (such as methylation, reduction, demethylation), and to improve data for environmental risk assessment. One of the aims of the study presented here was differentiation of Hg compounds in soils into different behavioural classes by the sequential extraction scheme adopted from BLOOM ET AL.[1] The sequential extraction scheme consisted of six steps, including (a) water soluble (F1), (b) 'human stomach acid' soluble (F2), (c) organo-chelated (F3), (d) elemental Hg (F4), (e) mercuric sulfide (F5) and residual fraction (F6).

Emissions of volatile mercury species from natural sources are believed to be a significant contributor to the atmospheric burden of mercury.[2] In contrast to anthropogenic point sources of atmospheric Hg, natural sources are long lived (>10^4 years) and their emissions enter the global atmospheric Hg pool. In the past decade significant progress has been made in development of methods for the measurements of mercury emission, using both dynamic flux chambers and mi-

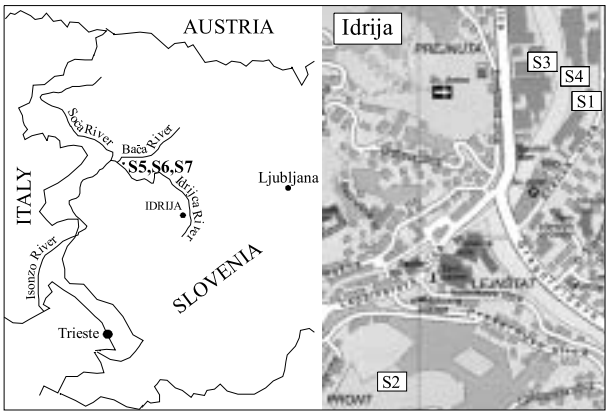

Figure 1. Sampling sites (S1-S7)

cro-meteorological methods. A good model should simulate all the processes in their proper importance, but as no *ideal* model of mercury soil-to-atmosphere emission exists, it is most important to know the relative importance of different parameters. For this purpose a simple mercury volatilization simulation experiment was applied. The study focuses on the estimation of the amount of volatile mercury in soil and on the influence of temperature and sample moisture content on mercury volatilization.

Samples were taken in the city of Idrija and its surroundings (Fig. 1). Two types of samples were analysed: fresh and homogenized, to investigate the influence of sample pretreatment on fractionation results. The fresh part was stored under refrigeration until analysis. The other part was dried at 35 °C, homogenized and sieved through a mesh of 200 μm pore size. The procedure for simulation of mercury volatilization from soils was applied to fresh samples.

RESULTS AND DISCUSSION

Volatile mercury. Mercury fluxes were measured for 14 h in one-hour intervals follow-

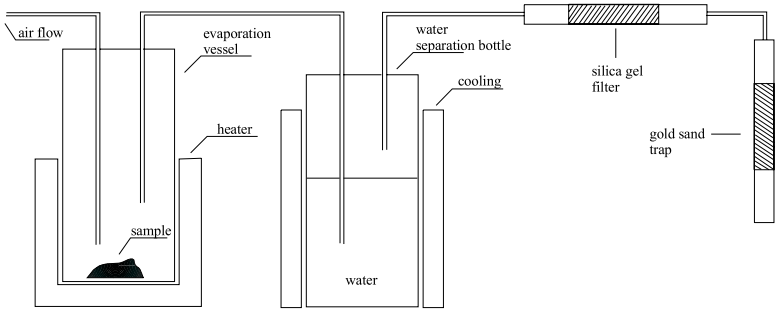

Figure 2. System for measuring soil Hg volatilisation: A sample is placed in a flow of Hg-free nitrogen in a teflon evaporation vessel connected to a water separation bottle and a gold sand trap. The gold sand trap is analysed by thermal desorption, double amalgamation and CVAFS.

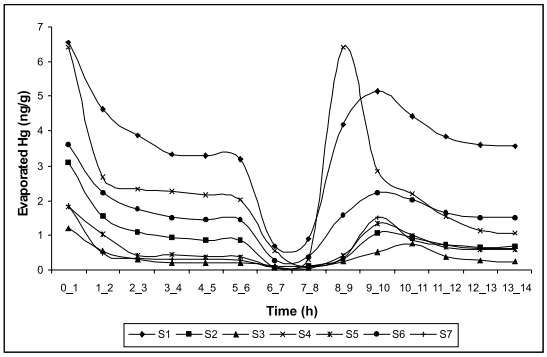

Figure 3. Results of Hg volatilization simulation experiment (one-hour intervals)

ing the procedure illistrated in Fig. 2. There is a similar trend in all samples (Fig. 3). The highest fluxes were determined in the first hour. Afterwards, during the second and third hour, fluxes gradually decreased. During the next three hours, when samples were already dry, fluxes within one-hour intervals became constant. This fact indicates the influence of moisture on mercury emission.

After six hours the samples were cooled down and fluxes measured for two hours at room temperature. Mercury fluxes at room temperature were 3 to 10-fold lower, showing no significant difference when the two one-hour intervals were compared. The sudden flux decrease in comparison with fluxes measured at 70 °C indicated the importance of temperature on mercury emission. To confirm the influence of both, moisture and temperature on mercury emission, samples were remoisted (sample weight to water volume was 1 to 1), heated at 70 °C once again and mercury fluxes measured for another six hours. The trend observed in the first six hours of the experiment was repeated (with a correlation coefficient R^2=0.94). Once again, the highes fluxes were measured in the first two hours (during the eighth and tenth hour respectively), then a gradual decrease followed until the fluxes become constant. A very strong correlation (R^2=0.93) between the sum of 14-hours fluxes and total Hg indicates the importance of total Hg concentrations on mercury volatilization.

Application of the sequential extraction scheme. The results obtained from homogenized samples differ from the fresh ones (Fig. 4). Evidently there must be some kind of alteration of Hg during homogenisation, drying and sieving of the samples, particularly in the case of fractions F1, F2 and F3. That is why we discuss here the results obtained from fresh samples, representing the actual situation in nature.

Hg was principally distributed between the cinnabar (F5) and elemental (F4) fraction. Although the percentage of first three fractions is rather small (the lowest quantities of Hg were extracted during the second extraction step at pH 2), absolute values of these mobile Hg fractions are quite high due to very high total Hg values in these samples (9 to 369 mg Hg kg^{-1}). In general, samples can be divided into two groups: samples of flood plains and others. Samples of flood plains (S4-S7) contain more cinnabar and less water soluble and elemental Hg when compared to others.

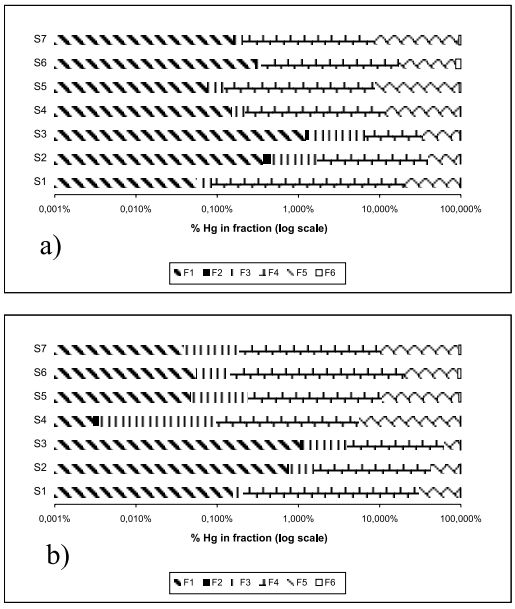

Figure 4. Sequential extraction results. a) homogenized samples, b) fresh samples

The third, organo-chelated Hg fraction, is presumably the most important one, as it is most strongly correlated with methylation potential.[1] The expectation was that fraction F3 would be more abundant in samples with a higher amount of organic matter, as Hg that appears in this fraction is associated mostly with humic organic matter. On the contrary, the results showed a decline in the amount of organo-chelated Hg with increasing percentage of organic matter. Thus, the only significant fraction F3 was measured in samples S2-S4 (between 0.3 and 0.46 mg kg^{-1}), containing less than 4 % of organic matter. The measurements of the Hg after fourth extraction step may be interpreted as an estimate of total Hg^0. This assumption was also confirmed by the very high correlation (R^2=0.81) between the relative amount of fraction F4 and relative amount of Hg evaporated during the volatilization experiments described above.

Grain size effect, relations between fractions and the amount of evaporated mercury. Cinnabar is especially concentrated in coarse-grained alluvial samples, where it constitutes on average more than 73 % of total Hg. In contrast, noncinnabar fractions were found to be enriched in areas where fine grained material was deposited, reaching up to 62 % of total Hg. An increased amount of any one fraction F1, F2, F3 or F4 lead to an increase of the remaining three fractions (R^2=0.71-0.99). On the other hand, an increased amount of fraction F5 resulted in decreased amounts of fractions F1 to F4 (R^2=0.71-0.98). This suggested that most chemical processes involved in mercury cycling in the soil occur within the noncinnabar mercury forms (F1-F4), as cinnabar (F5) is a very resistant insoluble form of mercury that does not enter in the mercury cycle. The relative amount of volatile (mainly Hg^0) mercury obtained during the emission simulation experiment increased when the relative amount of the F1, F2, F3 and F4 fractions increased, and decreased when the percentage of F5 fraction increased. The suggestion is that Hg bound in the fractions F1 to F4 is mobile and potentialy bioavailable, while Hg bound in fraction F5 is not, and therefore less harmful to the environment.

CONCLUSIONS

The simulation of the mercury vaporization from soil revealed that soil temperature and to a less extent added moisture are the main factors affecting the evaporation of mercury. Since a constant evaporation rate is obtained after 6 hours, we recommend that the procedure to assess the potential for mercury volatilization from soils should be completed after this period of time. We suggest that further investigations need to be performed to optimize the selected temperature. This is supported by the fact that bacteria may also be responsible for Hg reduction and volatilization, and the selected temperature should not kill the bacterial activity, as may be the case at 70 °C.

Sequential extraction of soils revealed that cinabarite and elementary mercury prevail. Biogeochemical conversion between noncinnabar mercury forms provides the basis for mercury's complex distribution pattern in the soil, for its biological enrichment, and its atmospheric enrichment as well. Our results suggest that data on the amount of the mobile fraction of mercury are more relevant than data on total mercury content. The total mercury concentrations are high due to high contents of cinabarite, which is not soluble and does not enter the processes of mercury transformation. One of the important conclusions of this work is also related to the effect of the sample preparation procedure and unspecific leaching on the results obtained by the sequential extraction. This suggest that further development and standardization of the method is of paramount importance to obtain results comparable with other studies.

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Mercury Speciation by Hydride Generation Atomic Absorption Spectrometry after Ion Exchange Separation in a FIA System (FIA-IE-HG-AAS)

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Abstract: Ion exchange is presented as a simple, non-expensive technique for the effective separation of inorganic mercury (Hg^{2+}) and methylmercury ($MeHg^{+}$) in hydrochloric media. Preliminary experiments using Pasteur pipettes packed with different resins were carried out in batch mode to define the best anionic exchanger and elution agent in terms of separation and elution efficiency. An Omnifit microcolumn packed with the selected resin was then implemented in a commercial FIA manifold to measure total mercury by cold vapor atomic absorption spectrometry. The geometry of the microcolumn (length and diameter) was optimised to get quantitative retention of Hg^{2+} and simultaneous maximum sensitivity in the analysis of $MeHg^{+}$. The concentration of the elution agent (cysteine) was then also investigated to optimise the sensitivity in the Hg^{2+} analysis. Finally, the weakly anionic exchanger Dowex M-41, a 10 cm lenght and 6.6 mm i. d. microcolumn and a 0.1 $mol \cdot dm^{-3}$ cysteine solution were selected as the best conditions to perform the analysis. The FIA system proposed allows the consecutive analysis of $MeHg^{+}$ and Hg^{2+} in a single injection of sample. Analysis of estuarine water samples spiked with both analytes was carried out following the described methodology.

Key words: ion exchange, mercury speciation, flow injection, cold vapor atomic absorption spectrometry

INTRODUCTION

The presence of mercury in natural systems is getting increasingly higher from the Industrial Revolution, mainly due to emission processes derived from combustion of coal and other fossil fuels[1]. Mercury occurs in different physical and chemical forms with a wide range of properties, being the inorganic mercury (Hg^{2+}) and methylmercury ($MeHg^{+}$) the two main species in natural aqueous systems[2]. The analysis of both species in environmental samples has been an object of great concern during the last 30-40 years. A large array of analytical methods has been proposed to distinguish between $MeHg^{+}$ and Hg^{2+}[3]. Most methods use a combination between a chromatographic separation and an atomic or mass detector. Ion exchange is a relatively cheap alternative to separate chemical species. A large offer in ion exchangers makes it especially versatile. In specific applications, its use may also result in an important clean up of the sample and a remarkable preconcentration of the analyte. In addition, it can be easily implemented in flow injection systems, resulting in automated and very reproducible procedures.

Despite these characteristics, the potentiality of ion exchange in mercury speciation analysis has been scarcely investigated by now. In a chloride medium, the anionic $HgCl_4^{2-}$ and the neutral MeHgCl are the most important Hg^{2+} and $MeHg^+$ species, respectively[4]. At these conditions, an anionic resin should retain Hg^{2+} and let CH_3Hg^+ freely pass through it with negligible retention. In this work, we propose a method for the sequential analysis (single injection of sample) of CH_3Hg^+ and Hg^{2+} in an aqueous sample. The analysis is preformed by quartz furnace atomic absorption spectrometry, after separation of the analytes in a microcolumn packed with an anionic resin, which has been inserted immediately after the injection port of a FIA system (FIA-IE-HG-QFAAS).

RESULTS AND DISCUSSION

Several experiments were first carried out in batch mode using the system shown in Fig. 1 in order to select the best resin. The Pasteur pipette was packed with about 2 g of wet resin and the outlet of the syringe was connected to the top of the pipette. In the retention experiments for Hg^{2+}, two fractions of water were first passed through the pipette. Then, four (Lewatit MP-64 and Amberlist A-21) or six (Dowex M-41 and Purolite A-100) fractions of Hg^{2+} solution (about 10 ppb) were propelled through the pipette. Finally, four (Lewatit MP-64 and Amberlist A-21) or six (Dowex M-41 and Purolite A-100) fractions of water were used to rinse the pipette. A similar procedure was followed in the retention experiments for $MeHg^+$. This time, two fractions of water, then six fractions of $MeHg^+$ solution (about 20 ppb) and finally five (Lewatit MP-64) or six (rest of the resins) fractions of water were successively passed through the resin. In the elution experiments, two fractions of water were first passed through the resin, and then, successively, two fractions of Hg^{2+} solution (about 10 ppb), two more fractions of water,

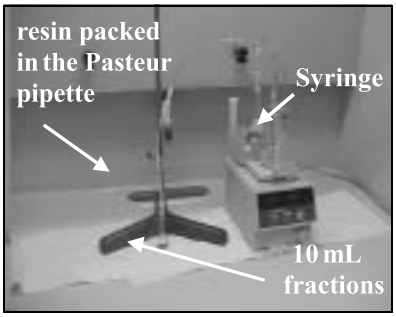

Figure 1. Experimental set-up used in the experiments in batch mode.

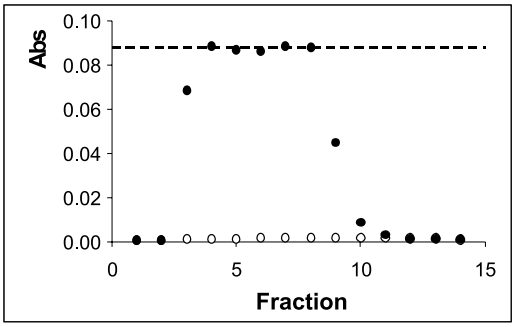

Figure 2. Results obtained in the retention experiments using the Dowex M-41 resin

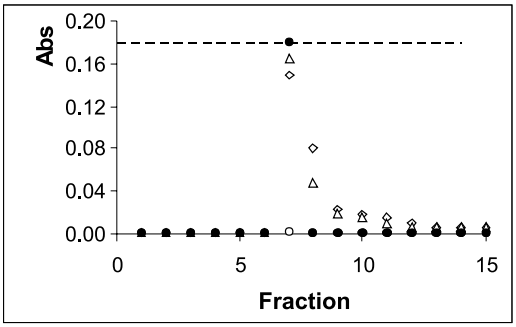

Figure 3. Results obtained in the elution experiments using the Dowex M-41 resin

six fractions of a solution of the elution agent investigated (0.01 mol·dm^{-3} cysteine, 2 mol·dm^{-3} NaCl, 0.1 mol·dm^{-3} $Na_2S_2O_3$, 0.1 mol·dm^{-3} Na_2EDTA, 0.1 mol·dm^{-3} Na_2S, 0.1 mol·dm^{-3} KSCN, 8 mol·dm^{-3} HCl and 2, 6, 8 and 10 mol·dm^{-3} HNO_3) and, finally, three more fractions of water. The fractions were of 10 mL in all the cases and the flow rate of the syringe was always fixed at 1 mL·min^{-1}. All the fractions were collected in separate flasks and analysed for total mercury by FIA-HG-QFAAS. The results obtained in the retention and elution experiments with the resin that was finally selected (Dowex M-41) are summarised in Fig. 2 (empty circles for Hg^{2+} and full circles for $MeHg^+$) and Fig. 3 (full circles: cysteine 0.01 mol·dm^{-3}; diamonds: HNO_3 8 mol·dm^{-3}; triangles: HNO_3 10 mol·dm^{-3}; empty circles: HCl 8 mol·dm^{-3}), respectively.

The sequential analysis of the $MeHg^+$ and Hg^{2+} in a single injection of sample by FIA-IE-HG-QFAAS was performed in two consecutive steps using the system shown in Fig. 3. In the first step (the $MeHg^+$ mode), 500 µL of sample (PP1 pump at 100 rev·min^{-1}) were injected in the flow of carrier (HCl 3 %), pumped by PP2 at 120 rev·min^{-1}. The Hg^{2+} got retained in the microcolumn (10 cm length, 6.6 mm i. d.), while the $MeHg^+$ freely passed through it, was converted into MeHgH, reached the quartz furnace and its absorbance was monitored and stored. In the second step (the Hg^{2+} mode), a 0.1 mol·dm^{-3} cysteine solution in HCl 3 % took the place of the HCl 3 % as carrier and the pumps started working (the PP1 pump at 120 rev·min^{-1} and the PP1 pump at 100 rev·min^{-1}). The Hg^{2+} retained in the microcolumn during the previous step was then eluted in the flow of cysteine, reduced to elemental mercury and its signal monitored and stored. The absorbance was measured in both cases at the 253.7 nm line with a slit of 0.7 nm. The quartz furnace was always kept constant at 900 °C. At this temperature, the sensitivity for Hg^{2+} is lower, but still high enough to determine the analyte in the samples considered in this work. In this way, the analysis time was considerably reduced, because the system needs about 90 minutes to cool down from 900 °C to 100 °C. In the optimisation experiments, the speed of the carrier pump, the concentration of the cysteine solution and/or the geometry of the column varied according to the experimental design.

Good calibration graphs, with correlation coefficients always over 0.99, were obtained for both analytes using the best conditions

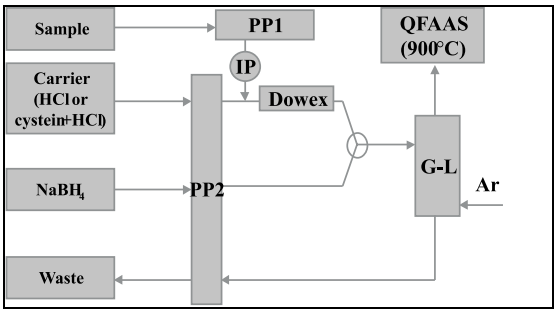

Figure 4. Scheme of the FIA system proposed for the sequential analysis of $MeHg^+$ and Hg^{2+} by FIA-IE-HG-QFAAS

described before. Absolute detection limits of 0.8 ng of $MeHg^+$ and 1.9 ng of Hg^{2+} were estimated for a sample volume of 500 μL (based on three times the standard deviation of the blank). The reproducibility of the system (5.4 % for $MeHg^+$ and 7.4 % for Hg^{2+}) was calculated as the relative standard deviation of the slope of seven calibration lines constructed in different and consecutive days. The accuracy was checked analyzing synthetic mixtures of $MeHg^+$ and Hg^{2+} of varying composition by the proposed method and another independent method (Eth-GC-MIP/AED). This method comprises the ethylation of the sample, the extraction and preconcentration of the obtained volatile compounds in an hexane phase, and the analysis of the organic phase by capillary gas chromatography with microwave induced plasma-atomic emission detection[5]. The results obtained by both methods did not differ significantly at a 95 % confidence level.

Estuarine water samples collected in different points of the Nerbioi-Ibaizabal estuary (Bilbao, Basque Country) were filtered (45 μm), acidified with HCl and spiked with $MeHg^+$ and Hg^{2+} to a final concentration of 15 ppb each. Before spiking the samples, they were analyzed for total mercury by cold vapor atomic absorption spectrometry. In all the cases the concentration was below the detection limit of the technique. The spiked samples were analyzed for $MeHg^+$ and Hg^{2+} following the procedure proposed in this work. The results are shown in Table 1. As it can be observed, the recoveries obtained were always satisfactory, both in samples with high and low salinity.

Table 1. Analysis of estuarine water samples spiked with $MeHg^+$ and Hg^{2+} (15 ppb) by FIA-IE-HG-QFAAS

Sample*	Conductivity ($mS \cdot cm^{-1}$)	$MeHg^+$ (ppb)	Hg^{+2} (ppb)	Recoveries (%)	
				$MeHg^+$	Hg^{+2}
1	24.2	14.39 ± 1.30	14.23 ± 1.05	96	95
2	5.3	14.39 ± 1.32	14.13 ± 1.14	96	94
3	0.4	14.56 ± 1.24	15.91 ± 0.99	97	106
4	0.3	14.48 ± 1.21	15.07 ± 1.00	97	101

CONCLUSIONS

Ion exchange is presented as an appropriate, easy-to-use and cheap alternative to other more expensive instrumental separation techniques for mercury speciation. Its easy implementation in a flow injection system has also been demonstrated, which carries a further potential of automation and reproducibility to the technique. The analytical method proposed here has demonstrated its potential utility in the analysis of water samples, both fresh and saline waters. The detection limit of the method does not allow by now, however, the direct analysis of real samples due to the low concentrations usually found in natural waters. This problem can be easily solved anyway by the inclusion on-line of any preconcentration method in the FIA system and/or the use of any other more sensitive detection technique. We are currently working in those two directions. Although

not checked here, the system as presented is susceptible to be used in the analysis of extracts from solid environmental samples, such as sediments or biota, which usually show considerably higher concentrations of both $MeHg^{+}$ and Hg^{2+}.

Acknowledgements

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Occurrence of Dimethyl Mercury ($(CH_3)_2Hg$) in Organic Solvents

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Abstract: A highly volatile and toxic mercury species, $(CH_3)_2Hg$, was found in a newly opened 4 L methanol reagent bottle. The compound was identified using three technically independent methods, independent standards, and quantified to be 75 µg/L (as Hg in $(CH_3)_2Hg$). Some commonly used organic solvents such as toluene, methylene dichloride, isopropanal, and many crude oil samples have been found to contain Hg fractions with behavior similar to the volatilization of $(CH_3)_2Hg$. This finding raises the questions "Is the occurrence of $(CH_3)_2Hg$ rare or common?" and "In addition to man-made, is $(CH_3)_2Hg$ naturally occurring in natural gases and/or crude oils?"

Key words: $(CH_3)_2Hg$, identification, quantification, organic solvents, crude oils

INTRODUCTION

Since the death of Dr. Karen Wetterhahn in 1997 was attributed to a few drops of $(CH_3)_2Hg$ that easily penetrated the latex gloves she wore and absorbed through the skin[(1)], this mercury species has received significant public attention[(1)]. However, $(CH_3)_2Hg$ is generally considered to be a man-made compound that is rare and not commonly used in laboratory operations. Lindberg and his co-researchers have identified and reported $(CH_3)_2Hg$ in municipal waste landfill gas[(2)]. They found the concentration of $(CH_3)_2Hg$ in the gas collected to be higher, by a factor of 30 or 40, than concentrations of total mercury in ambient air, and at least 1,000 times that of any $(CH_3)_2Hg$ concentration ever recorded in open air. This indicates that waste landfill gas is a source of atmospheric emissions of DMHg and that $(CH_3)_2Hg$ is not rare; everyone is exposed to this compound to some degree.

In the process of analyzing Hg in oil, results obtained from the first opening of a bottle were frequently found to be higher than subsequent openings. This suggests that there might be some Hg fractions that are even more volatile than elemental Hg (Hg^0). These fractions may escape when the bottles are opened, especially when the bottles are heated prior to opening. Generally, the results were found to become stable after several openings. It is possible that $(CH_3)_2Hg$ is one of these volatile fractions. If so, $(CH_3)_2Hg$ is not rare and is not necessarily man-made. Further identification and quan-

tification of this compound in natural gases and crude oils, as well as their byproducts are necessary. Recently, $(CH_3)_2Hg$ was identified and quantified in methanol of a newly opened reagent bottle. The concentration was found to be 75 μg/L. In this paper, detailed information associated with this finding is described.

RESULTS

The 4 L bottle of methanol was purchased two years ago, and stored together with other organic solvents in a cabinet in Cebam's laboratory. The bottle was tightly closed and never opened until the recent use. Because the reagent was to be used for dilution of a DMHg standard, the blank was pre-analyzed for total Hg (THg) by the combustion/trap method[3]. Unexpectedly, the THg concentration was found to be high. Another 500 mL bottle of methanol from a different supplier was analyzed and the blank value was found to be acceptable. This 500 mL bottle of reagent was opened a year ago, and about 300 mL of the reagent was left in the bottle before this use. It was used for dilution of the $(CH_3)_2Hg$ standard, while the methanol in the newly opened 4L bottle was further analyzed for $(CH_3)_2Hg$. The three methods used for identification and quantification of $(CH_3)_2Hg$ in methanol are listed below.

Method 1: Aliquots of the methanol solvent in pre-purged DDW in bubblers were purged onto gold traps that were then analyzed for THg by CVAFS. The concentrations were calibrated against Hg^0 that was generated by reduction of Hg^{2+} with $SnCl_2$, and collected on gold sand traps[4]. The working standard solution was prepared by a series of dilutions of $HgCl_2$ stock solution. The standard was traceable to a NIST standard.

Method 2: Aliquots of the methanol solvent were analyzed by combustion / trap technique for THg, and calibrated against a MeHg standard in CH_2Cl_2. A certified oil sample was also analyzed as the lab control sample.

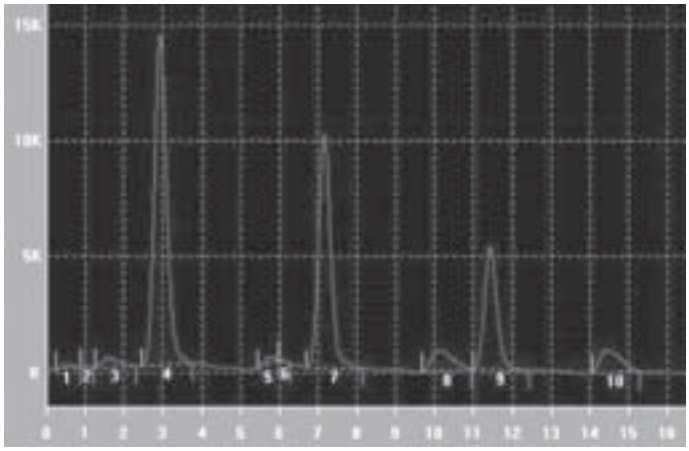
Method 3: The methanol solvent was analyzed by a GC/CVAFS system for $(CH_3)_2Hg$ [5]. Aliquots of the solvent in pre-purged DDW in bubblers were purged onto Tenax traps. The traps were then heated to release $(CH_3)_2Hg$ into the GC/CVAF system for separation and detection. Concentrations were calibrated against two standards from independent sources: (a) a carefully calibrated $(CH_3)_2Hg$ working standard was analyzed using exactly the same procedure as for the samples loaded on Tenax traps; (b) Hg^0 was generated by reduction of Hg^{2+} with $SnCl_2$, and collected on gold sand traps, but analyzed by heating the traps to release Hg^0 into the GC/CVAFS system for detection under the same GC conditions as for samples loaded on Tenax traps. Note that the Hg^0 standard can only be used for calibration of $(CH_3)_2Hg$ in the GC/CVAFS system when the peak area is used for signal measurements.

Concentrations of $(CH_3)_2Hg$ in the methanol sample generated using the above methods are listed below.

	Method 1	Method 2	Method 3	
Function	Quantification	Quantification	Identification and Quantification	
Analyzed for	THg	THg	(CH3)2Hg	
Standard used for calibration	$HgCl_2$	CH_3HgCl	(a) $(CH_3)_2Hg$	(b) $HgCl_2$
Results, µg/L as Hg	74.6±3.1 (n=6)	76.4±2.8 (n=6)	75.9±3.7 (n=6)	75.1±3.5 (n=6)

Certified reference materials including NIST 1641d and an oil sample were analyzed as lab QC control samples. Results of QC measurements were close to certified values.

Typical chromatograms of 141, 94, 47, and 0 pg of $(CH_3)_2Hg$ standards using method 3 are shown in the following figure.



Time (minutes)

Except for the blank that only appears in a Hg^0 peak (peak 10), each standard appears in two peaks. The first peak is Hg^0, and the second peak is $(CH_3)_2Hg$. The retention times were around 1.7 and 2.9 min for Hg^0 and $(CH_3)_2Hg$ respectively under the GC conditions used. The peaks 4, 7, and 9 in the figure are $(CH_3)_2Hg$ peaks of 3 non-zero standards with their area values of 3120, 2199, and 1188 respectively. The blank has no $(CH_3)_2Hg$ peak. The Hg^0 peak appears for all standards and samples. Area values of Hg^0 peaks were found to be irregular (sometimes higher, and sometimes lower), but independent of $(CH_3)_2Hg$ peaks and to not affect the results. This indicates that the Hg^0 peak is not a product of $(CH_3)_2Hg$ decomposition. When carbotraps were used, Hg^0 peaks were generally found to be smaller than those using Tenax traps.

An aliquot of 10 mL of the methanol solvent was transferred from the newly opened 4 L glass bottle to a 40 mL glass vial with a Teflon lined cap. After about 20 openings (each opening took about one min.) over 10 days at 20C, the sample was analyzed for $(CH_3)_2Hg$, and found not to be detectable. The sample was then analyzed for THg after oxidation with BrCl, and found not to be detectable. This indicates that all 750 ng of $(CH_3)_2Hg$ in the 10 mL of methanol evaporated and no degradation occurred. Another 200 mL of the methanol solvent was transferred into a 250 mL small mouth bottle, and purged with a N_2 flow of 160 ml/min for 10 hours. The methanol was then analyzed for $(CH_3)_2Hg$ and THg. The concentration of THg was found to be 27 ng/mL and all in $(CH_3)_2Hg$ form. About 15 mL of methanol evaporated during the 10 hours of purging. The standard solution of 10 ng/mL $(CH_3)_2Hg$ stored in a refrigerator was found to be very stable. This behavior is similar to that frequently observed in oil samples, but the loss of Hg in some crude oils via evaporation seems even faster. The evaporation rate is apparently dependent on temperature, and also seems related to the nature of the matrices.

Where and how does $(CH_3)_2Hg$ get into the bottle? The bottle was tightly closed until it's first opening and the lab air was found not to contain detectable $(CH_3)_2Hg$ so contamination at the Cebam lab could be ruled out. Two other possibilities might be: the compound was formed in the production process of methanol or; it might come from the original materials from which methanol was produced. Since $(CH_3)_2Hg$ is highly volatile, organic solvents as low temperature products of natural gases and crude oils may contain the compound. Therefore screening these organic solvents for $(CH_3)_2Hg$ is thought to be necessary.

Acknowledgement

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Mercury Speciation in Contaminated Soils Assessed by Parallel Extraction

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Abstract: The mercury in contaminated soil from two chlor-alkali sites (Bengtfors and Bohus, Sweden, (total load of 180 and 80 mg/kg, respectively) has been characterized by extraction. Two procedures have been compared: Sequential extraction (6 steps in sequence) and parallel extraction (4 parallel steps). The mercury was predominantly associated with organic matter in both soils. There were differences in performance between the two procedures. The sequential extraction procedure led to large losses of mercury. The parallel extraction appears to be more suitable for assessment of mercury speciation than the sequential extraction procedure.

Key words: speciation, sequential extraction, parallel extraction, leaching

INTRODUCTION

Mercury in contaminated soil is associated with the various soil constituents. Crucial information in risk assessments of the site is the mobility and bioavailability and not solely the total concentration of the mercury. Metal mobility in soils is controlled by the physical transport of a mobile phase (water) and the distribution of the metal between stationary solid components and the mobile phase. The solid components represent discrete minerals, as well as non-stoichiometric, poorly defined precipitates, organic debris etc. The solids can arbitrarily be divided into categories reflecting their composition and properties, e.g., primary and secondary minerals, precipitates, organic matter, etc. Sequential extraction schemes have been designed that would distinguish the fractions of a metal associated with different categories of soil constituents in at least a semi-quantitative manner. The most frequently used extraction scheme is the one by TESSIER (1979), modified by KARLSSON (1987), ZHANG (1998), as well as others. However, sequential extraction will never provide precise information on the distribution or the potential mobility of the individual metals for several reasons. Element redistribution occurs during the extraction as a response to the conditions imposed by the extractant. The target element might form or be occluded in secondary precipitates. The extractants are not specific enough to distinguish the designated solid species, and new adsorption equilibria are established (BERMOND, 1992).

Mercury has a complex chemical behaviour. Of particular importance is its affinity for organicmatter and sulphur, as well as its ability to form volatile species like elemental and alkylated mercury. Only a few speciation procedures for mercury in soils have been published (e.g., REVIS, 1989; LECHLER, 1997; WALLSCHLÄGER, 1998).

The aim of this study was to compare the speciation of mercury in contaminated soils assessed from two different procedures: Sequential extraction according to the scheme by TESSIER (1979) slightly modified, and a parallel extraction scheme for mercury by LIFVERGREN (2001).

RESULTS AND DISCUSSION

Mercury contaminated soil from two industrial sites (Bengtfors, Bohus), both with chlor-alkali plants, were selected for comparison of the extraction procedures outlined in Fig. 1 and 2. The Bengtfors soil was dominated by a calcium rich clay and had an elemental composition (% d.w.) of Si 20, Fe 2.6, Al 2.2, Ca 6, K 1.3, S 0.03 and organic matter 5.2. Also the Bohus soil was dominated by clay and had an elemental composition (% d.w.) of Si 20, Fe 3.3, Al 2.2, Ca+K 2.9, S 0.4 and organic matter 2.5. The total mercury content was 180±5 and 80±2 mg/kg, respectively (from digestion in nitric acid).

The two extraction procedures gave different results, Table 1. Losses of volatile mercury was substantial during the reductive and the oxidative leaching in method A. None of the speciation methods indicated any easily soluble mercury species in the Bohus soil. Method B showed that 60 % of the mercury was associated with the stationary organic matter. The residual mercury was soluble only after extended boiling in concentrated acid, suggesting the presence of highly stable secondary sulphides. With method A, all mercury was dissolved in the oxidising treatment.

The sequential treatment of the samples had a negative impact on the stability of the residual fraction, resulting in increased extractability of mercury. Method B gave reproducible data for weakly adsorbed mercury, as well as the fractions associated with secondary precipitates and water-soluble organic matter. As much as 80-90 % of the mercury content was associated with organic matter. The results from method A were inconsistent. A large fraction of the mercury was vaporised in the reductive as well as in the oxidising treatments. Mercury associated with organic matter was also mobilised in the reductive step resulting in over-estimation of mercury bound to hydrous oxides.

Table 1. Comparison of sequential (A) and parallel (B) extraction of Bengtfors soil (left) and Bohus soil (right). (Concentrations in mg/kg; average of three samples). P1 would include S1-S2, P2 would include S1-S4, P3 would include S1-S5 and P4 would include all of S1-S6; see Fig. 1,2.

	Method A, sequential	Method B, parallel				
		P0	P1	P2	P3	P4
S1	0.4		+	+	+	+
S2	0.1		+	+	+	+
S3	6.4			+	+	+
S4	18			+	+	+
S5	82				+	+
S6	6.3					+
Tot	113	0	0.5	4.3	178	182

	Method A, sequential	Method B, parallel				
		P0	P1	P2	P3	P4
S1	0		+	+	+	+
S2	0		+	+	+	+
S3	0			+	+	+
S4	0			+	+	+
S5	50				+	+
S6	0.1					+
Tot	50	0	0	0	56	80

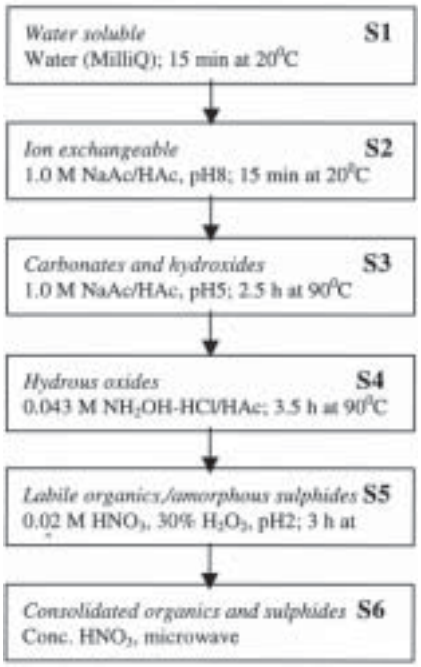

Figure 1. Sequential extraction scheme (modified from KARLSSON, 1987) Scheme A

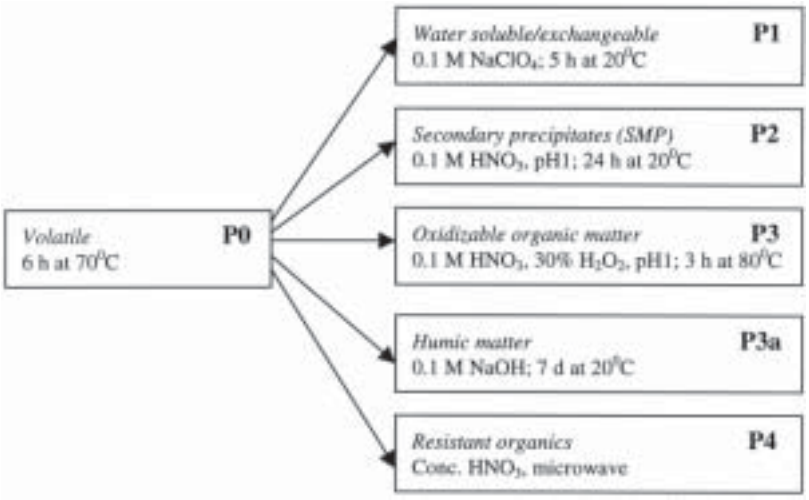

Figure 2: Parallel extraction scheme (LIFVERGREN, 2001) Scheme B

CONCLUSIONS

There are extensive chemical alterations and losses of mercury during the sequential extraction procedure. The parallel extraction appears to be more suitable for assessment of mercury speciation than the sequential extraction procedure.

Acknowledgements

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Determination of Ethyl Mercury and Methyl Mercury in Blood Samples

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Abstract: Thiomersal is a mercury-containing organic compound, commonly used as a preservative in topical pharmaceutical preparations, cosmetics, and biological products such as vaccines, as well as a disinfectant during dialysis treatment. The purpose of the present work was to develop a sensitive and accurate method for determination of ethyl mercury (EtHg) and methyl mercury (MeHg) in whole blood of dialysis patients.

Key words: ethyl mercury, methyl mercury, blood, speciation

INTRODUCTION

Current mercury investigations have focused primarily on MeHg from fish contamination and from rare occupational or catastrophic events. Recently, another source of exposure has been identified. Thiomersal, a preservative with both bactericidal and fungicidal action utilized in the production of biological and pharmaceutical products, contains 49.6 % EtHg by weight. [1] Because of an increasing awareness of the theoretical potential for neurotoxicity of even low levels of organomercurials, development of analytical techniques for determination of low concentrations of EtHg and MeHg is required.

RESULTS AND DISCUSSION

Metal speciation is impossible without the use of modern hyphenated techniques, in which highly sensitive and selective elemental detection systems are coupled to modern chromatographic separation systems. One of the most widely used separation method is gas chromatography which however requires volatile species. The main disadvantage of the commonly used derivatization reagent sodium tetraethylborate ($NaEt_4B$) is that the important ethylmercury species cannot be distinguished from inorganic Hg after ethylation. [2] In this work sodium tetra(n-propyl)borate ($NaPr_4B$) was tested for simultaneous determination of EtHg and MeHg in blood samples.

The method proposed is based on acid leaching (5 % H_2SO_4/18 % KBr/1M $CuSO_4$), extraction of EtHgBr and MeHgBr into an organic solvent (CH_2Cl_2), followed by back extraction into Milli-Q water, subsequent propylation with a 1 % solution of $NaPr_4B$, room temperature precollection on Tenax, isothermal gas chromatographic separation

(80 °C), pyrolysis (600 °C) and cold vapour atomic fluorescence spectrometric detection (CV AFS). [3,4]

Optimization of the method was performed on a number of different blood samples of patients before and after dialysis treatment. The concentrations of MeHg were comparable to concentrations of MeHg in the normal healthy population and showed similar values before and after dialysis. The concentration of EtHg were much elevated after treatment and reached up to 4 ng/g. Some of the results are shown in Table 1.

Table 1. MeHg and EtHg results in blood samples obtained using $NaPr_4B$ as a derivatization regent.

Sample		EtHg (as Hg) ng/g	MeHg (as Hg) ng/g
1	BT	0.09±0.00	0.36±0.04
	AT	1.74±0.07	0.33±0.05
2	BT	1.69±0.00	0.20±0.01
	AT	4.23±0.12	0.23±0.02
3	BT	0.05±0.01	0.15±0.02
	AT	1.54±0.14	0.11±0.01
4	BT	<0.01	0.18±0.01
	AT	1.06±0.08	0.17±0.01

BT- before dialysis treatment; AT - after dialysis treatment

The performance of $NaEt_4B$ and $NaPr_4B$ as derivatization reagents was checked. Comparison of the results in Table 2 shows that the values for MeHg obtained by the two derivatization reagents are in good agreement.

Table 2. Comparison of MeHg results obtained by $NaEt_4B$ and $NaPr_4B$ as derivatization reagents.

Sample	MeHg (as Hg) ng/g	
	$NaPr_4B$	$NaEt_4B$
1	0.45±0.01	0.47±0.01
2	1.13±0.04	0.92±0.05
CRM IAEA 405	5.26±0.49	5.02

IAEA 405 Estuarine sediment: certified value 4.96-6.02 ng/g

The limit of detection calculated on the basis of three times the standard deviation of the repeatability of the results was about 5-10 % for EtHg and 5-15 % for MeHg. Recoveries were between 90-110 % for both species. A certified reference material was tested to check the accuracy of MeHg determination, but for EtHg no CRM was available.

CONCLUSIONS

The analytical procedure developed was found to be a suitable and appropriate method for determination of low concentrations of EtHg and MeHg in blood samples. It also shows great potential for determination of both species in other biological samples influenced by thiomersal.

Acknowledgements

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Increased mercury load in protein A immunoadsorption

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Background. Immunoadsorption is an adsorption technique for extracorporeal removal of circulating autoantibodies in autoimmune diseases such as myasthenia gravis and Guillain-Barre syndrome. To prevent microbial growth during storage the protein A columns are primed with thiomersal containing toxic ethylmercury which could be released during the immunoadsorption treatment and potentially result to its accumulation and toxicity. To reduce a thiomersal-related mercury release during immunoadsorption treatment we introduced a modified rinsing solution containing N-acetylcysteine which is avid mercury scavenger.

Methods. Thirteen patients were treated by 17 protein A immunoadsorption treatments and 3 venous blood samples were collected immediately before and after each session. Whole blood mercury levels were measured by atomic absorption spectroscopy and ethylmercury levels by atomic fluorescent spectroscopy. According to the manufactrurer's recommendations we used 600 mg of N-acetylcysteine to rinse the mercury from protein-loaded columns before each immunoadsorption treatment.

Results. Following protein A immunoadsorption ethylmercury levels increased from 0.148 ± 0.402 ng/g to 2.026 ± 1.944 ng/g ($p < 0.001$) and whole blood mercury increased from 2.447 ± 3.065 ng/g to 14.613 ± 16.922 ng/g ($p = 0.01$). Post-treatment values of whole blood mercury exceeded upper safety level of 5 ng/g in all 17 immunoadsorption treatments but no patient developed clinical signs of mercury toxicity. In one patient immunoadsorption treatment was repeated within 7 days and the results of serial determinations of blood mercury levels are shown in the table:

	Ethylmercury (ng/g)		Whole blood mercury (ng/g)	
	Before IA	After IA	Before IA	After IA
Day 0	0.13 ± 0.03	1.35 ± 0.12	0.49 ± 0.06	76.8 ± 5.6
Day 1	0.17 ± 0.00	0.10 ± 0.02	8.14 ± 1.24	19.4 ± 0.6
Day 2	0.05 ± 0.00	0.09 ± 0.00	9.57 ± 0.80	11.8 ± 0.9
Day 3	0.03 ± 0.00	0.08 ± 0.01	6.96 ± 0.09	8.52 ± 0.39
Day 7	1.69 ± 0.00	4.23 ± 0.12	5.54 ± 0.32	9.04 ± 0.48

Data are presented as means ± standard deviation. IA – immunoadsorption.

Conclusions. The results of our study showed that whole blood mercury and ethylmercury levels were increased during the immunoadsorption treatments, suggesting mercury release from thiomersal-primed columns even with addition of N-acetylcysteine to the rinsing solution. Mercury release was more pronounced at the beginning of serial immunoadsorption treatments which indicates that mercury exposure might depend on the storage time of protein A columns containing thiomersal priming solution.

Mercury thermo-speciation in contaminated soils and sediments

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Abstract: Mercury species in contaminated soils and sediments show different properties and behavior both in biogeochemical cycling and in remediation processing, e.g. in thermal treatment. Therefore, it is important to know the dynamics of mercury evaporation from contaminated soils and sediments upon heating. We have investigated the thermo-spectra of mercury release from gradually heated samples of standard reference materials, non-polluted and contaminated soils and sediments using Lumex RA-915+ analyzer. Thermo-scanning enables to identify unique mercury species only in artificial mixtures. In real samples, however, the dynamics of mercury release strongly depends not only on speciation but also on bond strength of physical and chemical sorption on mineral matrix, mineral composition, and particle size. As a result of the investigations, the technique of mercury thermo-spectra data acquisition and processing was developed, and practical recommendation for thermal treatment of contaminated soils and sediments was worked out.

Key words: mercury thermo-speciation, soils and sediments, thermal treatment

INTRODUCTION

Mercury is one of the most hazardous pollutants of primary deponent media that are soils and sediments. Extremely heavy pollution is connected with industries, which use mercury, mercury compounds, or mercury containing raw materials in technological processes (smelters and gold mining, chlor-alkali and some chemical plants, etc.). The pollution is represented by different mercury species, which are stable under oxidation zone environment, such as elemental Hg, mercury oxides, chlorides and oxychlorides, mercury bound with organic material and silicate matrix. Mercury species show different properties and behavior both in biogeochemical cycling and in remediation processing. One of utilized remediation techniques is thermal treatment[1]. Therefore, it is important to know the dynamic of Hg evaporation from contaminated soils and sediments during their heating.

We have investigated the thermo-spectra of mercury release from gradually heated samples of standard reference materials (SRMs), artificial mixtures of minerals and SRMs, non-polluted and contaminated soils and sediments using Lumex RA-915+ analyzer with Zeeman background correction.

RESULTS AND DISCUSSION

The problem of direct selective mercury determination in samples with complex matrix is solved by using a Lumex analyser RA-915+, coupled with basic RP-91C attachment: a two-chamber pyrolytic catalyst atomizer[2]. The detection limit (DL) is 200 pg, if all Hg is released within a single peak. To provide thermo-scanning, we used the temperature gradient inside pyrolytic chamber of RP-91C (Fig. 1). Samples were gradually heated in a pyrolyser from ambient temperature up to 730 °C by step moving of a quarts boat from the inlet of pyrolyser (at the Fig.1 - position 7 cm) to "standard" position of the boat in the chamber (1 cm). The whole cycle of the measurement was 640 s., average temperature gradient - 1 centigrade per second. The behaviour of mercury release was monitored continuously through the heating cycle with the response time of 1 s. and recorded using an

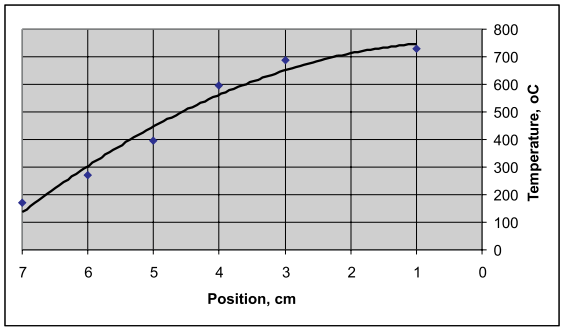

Figure 1. Sample temperature vs. its position inside pyrolyser. Air flow 1 L/min

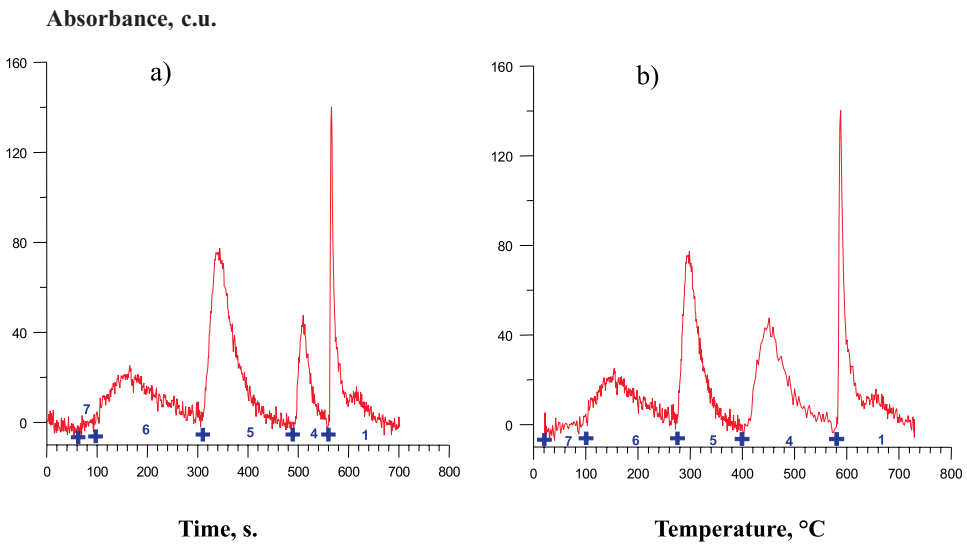

Figure 2. Thermo-scanning of standard reference sample SO-2 (soil; total Hg concentration 603 ppb, mass 60 mg). Dynamic of mercury release vs. time a), and temperature b). Changing of the sampling boat position is marked with crosses

external PC. The RA-919P software enables to record analytical signal in real time, determine total mercury concentration in a sample, and calculate portion of mercury released within any temperature range. The dynamic of analytical signal could be presented as a function of time or temperature of the sample (Fig. 2).

We have investigated the thermo-spectra of Hg release from gradually heated samples of different composition: standard reference materials (SRM), artificial mixtures of soils and SRMs; non-polluted and contaminated soils and sediments, such as: SRM RT-4, quarts sand (Qu) and HgO; SRM FeS; SRM SO-2, soil; Mix1, contaminated sediments from the Minamata Bay, etc. Some results are shown in the Table 1.

Different samples had various shapes of thermo-spectra, e.g., for pyrites and jasperoids 90 % of mercury released at a temperature above 400 °C, whereas in cases of contaminated soils and sediments, up to 87 % of mercury evaporated at a temperature below 400 °C.

In the initial investigations of mercury thermo-speciation (started in 1958), most of the researchers tried to identify each separate peak as a result of thermo-destruction of certain Hg compound. The release (destruction) temperature was studied for pure synthetic compounds, such as Hg^0 (sorbate), Hg oxide, chloride, sulphate, sulphides, etc. However, obtained dissimilarity between decomposition temperatures was rather big, even for synthetic compounds. It seems to be connected mainly with different measurement procedure techniques.

Thermo-scanning procedure makes possible to identify properly Hg species only in artificial mixtures. In real samples, this is much more complicated, because the dynamics of Hg evaporation depends not only on speciation but also on bond strength of physical and chemical sorption on mineral matrix, mineral composition, sample moisture, etc.

Table 1. Mercury release from samples within different temperature intervals

Sample	Hg release, %				
Position, cm	**7**	**6**	**5**	**4**	**1**
Interval of T, ^{O}C	**23 – 100**	**100 – 275**	**275 – 400**	**400 – 580**	**580 – 730**
SRM FeS 50 mg, 33 ppb	**0**	**0**	**10.3**	**69**	**20.7**
	10.3			**89.7**	
SRM RT-4 Qu + HgO 50 mg, 600 ppb	**8**	**46.5**	**45.5**	**0**	**0**
	100			**0**	
IDB-2 Soil + HgS 23 mg, 7000 ppb	**0**	**15.2**	**84.8**	**0**	**0**
	100			**0**	
SO-2 Soil 60 mg, 600 ppb	**0.6**	**26.8**	**42.7**	**10.1**	**19.7**
	70.1			**29.8**	
Mix1 + 50 uL H_2O 50 mg, 1650 ppb	**0.1**	**65.9**	**21.2**	**9.5**	**3.3**
	87.2			**12.8**	
Mix1 (dry) 54.6 mg, 1460 ppb	**0**	**50.2**	**36.2**	**9.1**	**4.5**
	86.4			**13.6**	

The size (thickness) of a sample, particle size, heating rate and sort of gas-carrier (air or inert atmosphere) affect the speed of Hg release and shape of peaks. These parameters determine difference between the temperature of the beginning and completion of thermo-peaks. As a result, thermo-forms of mercury in many cases cannot be identified as definite Hg compounds. It is possible to determine in natural samples the following mercury species: Hg^0; Hg physical sorption (adsorption); Hg chemical sorption, HgS, isomorphous Hg (and absorption).

Physical sorption is linking of Hg^0 mainly at the surface of particles – adsorption, or inside of particles - absorption. Adsorbed mercury can easily evaporate while heated. Temperature of evaporation for mercury absorbed in mineral matrix is much higher. Hg can escape to gas phase either due to diffusion through crystal matrix, or as a result of matrix destruction (as in the case of isomorphous Hg).

Definition of group of Hg species bounded as a result of chemical sorption is rather conditional. Chemical sorption can be considered as such position of chemical element, when it gets to bond with crystal matrix of mineral by due to dehydration, compaction, or recrystallization. In this case, mercury loses its individual properties, and can evaporate completely only after destruction of mineral-concentrator.

CONCLUSIONS

As a result of the investigations, the technique of mercury thermo-spectra data acquisition and processing was developed, and practical recommendation for thermal treatment of contaminated soils and sediments was worked out.

Acknowledgements

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A miniaturised sensor for gaseous mercury detection

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Abstract: A new microfabricated physical sensor for elemental gaseous mercury (Hg^0) determinations has been developed and experimentally tested by the Authors. The sensor is based on the technique of resistivity variation of thin gold film. The gold film surface and the sensor behaviour on different substrates have been investigated. The sensor design has been performed in observation of the minimum detection limit and power requirements. A study on thin film properties, sensor-substrate interaction and the characterization of the sensor in terms of performances and technical features has been performed. The use of Micro System Technologies (MST) have allowed to obtain a miniaturized system with the sensing element, the electrical routes and a temperature sensor integrated onto a small substrate with a SIM card shape.

Key words: mercury, sensor, gold, thin film, absorption.

INTRODUCTION

Mercury represents one of the main environmental pollutants of our planet. Studies on risk assessment and effects caused by mercury on human health drive the scientists and decision makers to consider this metal as a global pollutant. In this context, the Authors have developed a 'smart sensor' able to work in a low-cost portable mini-device and as a mini-dosimeter for the assessment of the personal exposition to mercury. This sensor is designed to measure elemental gaseous mercury (Hg^0) concentration, which represents 90 to 99 % of atmospheric mercury forms[1].

RESULTS AND DISCUSSION

The presented gaseous mercury sensor is based on the resistivity variation of thin gold films[2-4]. The sensor consists of four identical thin gold film resistors mounted in the Wheatstone bridge configuration. Two resistors work as sensitive elements, while the others work as reference. The absorption of mercury on the gold film produces a change in the resistivity of the film itself. Far from the saturation, this change is proportional to the amount of absorbed mercury. In order to reuse a saturated mercury sensor, desorption of accumulate mercury is required. The desorption process is obtained by the Joule effect, heating the gold resistors.

Many versions of the sensor have been developed[5] in order to obtain the best version of the system in terms of film shape (exposed surface, thickness), electrical layout, substrate (material and thickness) and micro fabrication process. The sensor fabrication has been performed by sputtering deposition

(Sputtering Sistec, model DCC 150) of thin gold film on different substrates[5].

The set-up used in the experimental activities is described. The fluidic circuit includes an air filter, a chamber containing the mercury sensor, and an air pump (KNF, NMP 05M; 0.5 l/min, 500 mbar in aspiration). The components are connected by silicon tubes. A National Instruments DAQ Card (model 6024E) and a dedicate software was used to control the excitation parameters of the sensor and to acquire the experimental data. A 500 µl sample of mercury saturated air is sucked from a thermos kept at controlled temperature and injected into the aspiration air using a precision manual syringe [5].

Adsorption experiment was performed on glass and Printed Circuit Board (PCB) substrates. The PCB substrate is a composite material covered with a layer of solder (epoxy resin, glass temperature about 300 °C) commonly used for the realization of integrated circuit. The experimental data showed a high readout variation and an evident linear trend. The detection limit can be estimated around 100 pg of mercury. A dedicated series of saturation tests have been carried out in order to assess the saturation limit. The experiments results showed that the sensor linear response limit (similar in PCB and glass substrates) is around 800 ng of injected mercury and the saturation limit is around 5000 ng of injected mercury.

Regeneration tests have been also performed. Different techniques can be used to heat the resistors. In order to reduce the power consumption, the most efficient way is the Joule effect self-heating, supplying a suitable regeneration voltage to the bridge. A significant sensor regeneration has been obtained at a temperature above 100 °C, as showed by experimental results.

Other experimental tests have been carried out in order to evaluate the 'sensor endurance' to regeneration, i.e. the minimum number of regeneration cycles that can be performed without inflicting any mechanical or electrical damages to the resistors: after more than 1300 regeneration cycles no damage was observed.

The results of the comparative tests allow us to conclude that the performance of the sensible element (detection limit, linear response limit, saturation limit and regeneration 'endurance') are the same for both substrates while the physical properties of the gold film (resistance, thickness and mechanical properties) change.

Because of the propensity of a thin film to reproduce the surface morphology and lattice structure of the substrate, there is a close correlation between the substrate choice and chemical, physical and mechanical properties of a thin film. For this reason, it is crucial to take into account this thin film characteristic in order to assure sensor performance and reproducibility.

The study of the morphology has been performed on tree types of substrate: glass, PCB and ceramic. The choice of these materials has been carried out in observation of compatibility system requirements for obtaining the highest level of integration.

The glass substrate (Borosilicate glass Corning 7059) presents a superficial roughness of about 80 nm. The PCB substrate is character-

ized by a superficial roughness of about 300 nm. The ceramic substrate (Coors 996 polished) offers a superficial roughness of about 160 nm.

The substrate choice influences the film adhesion acting on bond type and strength. The scratch and scotch tests performed on the three substrates showed an optimal film adhesion for the ceramic and PCB substrates but an unacceptable behaviour for the glass. The tests showed that the film interaction with the glass surface is very weak and the deposition of the adhesion layer does not avoid the gold film peeling.

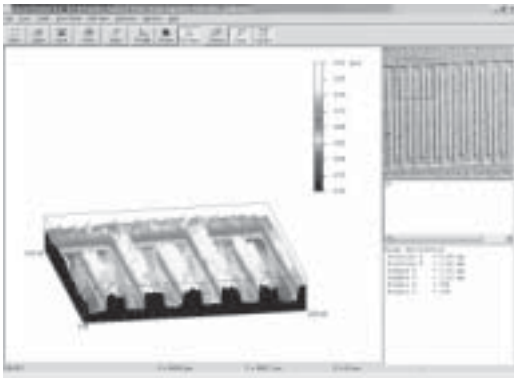

Figure 1a. Sensor on glass. Measured area in top view (Objective 20 x, Stitching 3 x 3). Height measurements for the selected profile.

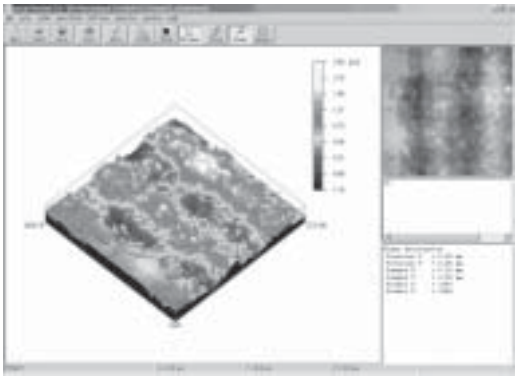

Figure 1b. Sensor on PCB. Measured area in top view (Objective 20 x, Stitching 3 x 3). Height measurements for the selected profile.

In the case of the glass substrate, the acquired images showed a very compact film with a fine grain structure. On the contrary, gold films deposited on PCB substrate are essentially grain boundaries free: during sputtering deposition, as the molecular mobility grows up for the local heating, the gold atoms diffuse inside the polymeric network. The close penetration between the gold film and the substrate avoids the nucleation and the growth of the crystallites. As the absorption of mercury atoms occurs at the grain boundary, a reduction of gold film sensitivity on PCB substrate is experimentally observed[5]. The experimental results showed that gold films on silica substrate present porous grain boundaries which act as active sites and catalyse the mercury atom adsorption: these films exhibit an optimum resistance change when these sites are occupied by mercury. The films deposited on glass and on PCB substrates are compared in Figure 1: the gold film follows the surface morphology of the substrate.

Summarizing, despite the poor adhesion, the glass confers to the gold film excellent surface properties improving some sensor features such as the adsorption capability. The PCB substrate, on the contrary, allows a very strong penetration of the thin film but with a decrease in the absorption rate and reproducibility of the sensor performance.

The best solution would be represented by a combination of the high superficial properties of the glass substrate with the adhesion capability of PCB substrate to obtain a stable and homogeneous film-substrate interface. The ceramic substrate, characterized by a very fine surface microporosity, satisfies these requirements and seems to have more

suitable characteristics for the development of the mercury 'smart' sensor.

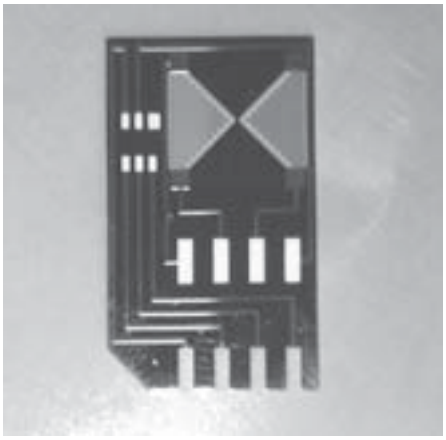

Figure 2. Picture of the sensor on ceramic substrate.

On the basis of this observation, a new sensor on ceramic substrate was designed. Figure 2 reports a sensor picture. The sensor has a SIM card shape, the pads are designed in order to be compatible with standard 8 SIM Card contact. The sensor fabrication was realized by lithography technologies. The electrical tracks are an Au/Ni/Au multilayer and the covering layer is in polyimide (PI). The sensor integrates on board a temperature sensor. The high-resolution micro fabrication process (resolution < 5 μm) allows obtaining reproducible sensors.

CONCLUSIONS

A microfabricated sensors for atmospheric mercury determinations have been described and experimentally tested. The sensors are based on the resistivity variation of thin gold film technique. The gold film surface and the sensor behaviour on different substrates have been investigated and the ceramic substrate seems to have more suitable characteristics for the development of the mercury 'smart' sensor.

The characterization of the sensor in terms of performances and technical features was performed. The sensors work in a large range of linearity and require a low power during the regeneration process. Sensors undergone numerous regeneration cycles do not show any mechanical or electrical damages to the resistors or change in the adsorption rate.

Acknowledgements

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A new Portable Atomic Gaseous Mercury Analyser with Network Capability for Environmental Monitoring

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Abstract: A new portable mini-analyser for the monitoring of atomic gaseous mercury concentration was designed and developed. The device is characterised by small dimensions, low power consumption, long operative time, autonomous operation, easy end-user interface and capability of wireless data transmission. The detection technique is based on the resistivity variation of a thin gold film. The device was tested in laboratory. The preliminary results show a good performance and a detection limit less then 1 ng of mercury sampled. In order to enlarge the measurement dynamic range, a preconcentration system is under development. The additional module will allow to improve the detection limit of the mini-analyser up to 100 times. This modular architecture makes possible the utilisation of the device both for industrial processes and environmental monitoring. Some features of the mini-analyser such as self data/hours/location updating by GPS embedded system and data transmission capability by GSM module have been implemented for applying the mini-analysers in a network configuration useful for environmental monitoring of large areas.

Key words: mercury analyser, sensor, gold, thin film, absorption

INTRODUCTION

Mercury represents one of the main environmental pollutants of our planet. Studies on risk assessment and effects caused by mercury on human health drive scientists and decision makers to consider this metal as a global pollutant. The present work has, as final goal, the development of a low cost mini-analyser for gaseous mercury detection. The analyser will be able to work in cooperative way, thus forming monitoring networks, which produce an enhanced knowledge on the dispersion of a pollutant, and which can be ultimately integrated in the health-oriented monitoring system.

Conventional methodologies for mercury detection are based on bulky and expensive devices. In order to develop a portable mini analyser, the technique of resistivity variation of thin gold film[1],[2],[3], characterized by absence of optical parts and low power requirements, has been chosen.

RESULTS AND DISCUSSION

Analyser

The core of the mini-analyser is a thin gold film sensor described in a previous work[4]. In Figure 1 a schematic representation of mini-analyser architecture is reported.

The mini-analyser comprises a fluidic module for air sampling and an electronic module for the control of the fluidic sub-system, for the acquisition the data and for the management of the user interface.

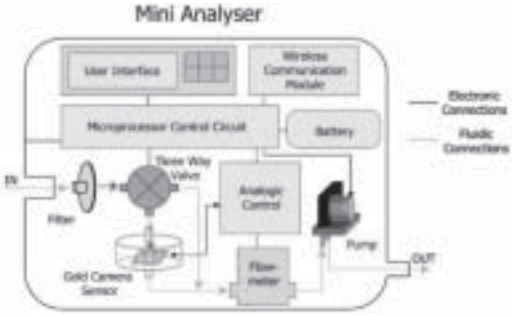

Figure 1. Schematic of the mini-analyser architecture.

The fluidic circuit includes a filters system, a three way valve (LHDA1231115H-LEE, 12 V, 15 psi), the sensor chamber, a flowmeter (AVM3300V -Honeywell, 5 V, 0-1000 cc/min) and an air pump (G12/01EB-ASF Thomas 12 V, 1.2 l max flow). All the components are interfaced with the analogic control. The filters system intercepts the raw impurities (e.g. dusts) and the contaminants (e.g. H_2S). The three way valve drives the sampling air into the sensor chamber (first way out) or directly into the flowmeter (second way out), bypassing the sensor chamber. During the first seconds of the sampling the first way out of the valve is open in order to clean the channel from residual mercury. Switching the ways out, the air sample is lead to the sensor chamber containing the mercury sensor[4] for the analysis. The opening and closing procedures of the valve are controlled by a microprocessor based electronic control system. The flow rate is about 0.9 liter/min and the sampling time is 1 minute.

The electronics of the mercury vapour analyser is based on a microcontroller module and a number of subsystems implemented on separate boards. In particular the following sub-systems are present: power supply/battery charger, bridge sensor signal conditioning, bridge sensor switching module, activation for pump, valve and flow meter, analog to digital converter board with signal pre-conditioning and GPS/GSM module for the system localization and remote connectivity. A user panel with a Liquid Crystal Display, push buttons and connectors are also present and they are controlled by the microcontroller module. The electronic analog subsystems are designed and carefully assembled together to achieve very low level of signal noise and to minimize power consumption in order to meet the user requirements in term of mercury sensitivity and measurement time. Thanks to its self calibration capability the instrument does not require any hardware intervention by qualified personnel for the calibration. With a 2000 mAh sealed lead acid battery and a cycle of 100 measurements the instrument is capable of 19 hours of continuous operation before re-charging the battery. The instrument is equipped with a GPS/GSM module (the instruments is actually identified in the GSM network by its SIM card telephone number) for self localization and data link with a remote host computer. The software running on the remote host PC will allow to

manage a network of several instruments spread over the territory. Each instrument can be automatically contacted at predefined time interval to download the available data. All the data downloaded from the instruments is then saved locally to the host PC for off-line data processing and analysis.

Experimental testing

A series of tests was carried out in order to evaluate the performance of the analyser prototype; in particular for the assessment of the electronic subsystem, the background signal and the mercury measurement.

The test of the electronic subsystem shows a good response of the conditioning circuit and the acquisition module. This test was performed using a "dummy" sensor (four precision resistors in Wheatstone bridge configuration) instead of the real thin gold film sensor. As results the electronic subsystem showed an electrical noise better then 1.5 mVV_{ex}^{-1} that in term of mercury corresponds to about 60 pg of Hg (considering a sensor sensitivity of 20 $mVV_{ex}^{-1}ng^{-1}$of adsorbed mercury).

The background signal test was carried out using the real sensors. The test was performed sampling pure air (without mercury) by using the analyser. The results show that the background is quite different from sensor to sensor and it depends on different factors as temperature and humidity. Typical background value are in the equivalent range 0.2 – 1 ng of Hg, depending from the sensor.

Measurement tests were performed by injection of a known quantity of mercury in the analyser during the sampling by using a manual syringe (200 ml precision syringe). The sample of mercury is obtained sucking saturated air from a thermos kept at controlled temperature. The results of some mercury measurement tests are reported in Figure 2. The calibration curves obtained by repeated measurements showed a very good linearity and reproducibility. The background is lower then 1 ng of mercury (in term of concentration less then 1 mg/m^3).

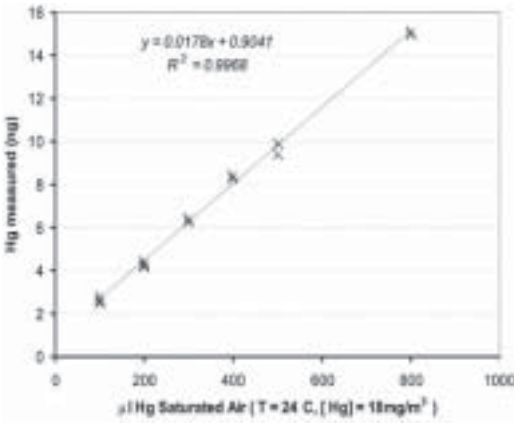

Figure 2. Calibration test: Hg measured vs. volume of mercury saturated air ([Hg^0] = 18 mg/m^3 at 24°C)

Preconcentration module

The mini-analyser is designed to detect high mercury concentration level (more then 1 mg/m^3). This limit can be enlarged by applying a Preconcentration External System (PEM). This system is composed by: a rechargeable lead battery; a flowmeter; a gold trap (gold-platinum alloy); an air pump (G12/01EB-ASF Thomas 12 V); a three way valve (LHDA1231115H-LEE, 12 V) and a heater system (a coil of nickel-chrome wire) and a stand alone control circuit (microprocessor based).

The air sample is sucked by the pump through the filtration system, as in the basic

instrument, and then it is lead to the gold trap where the mercury is captured. The three way valve is placed, in the flow line, after the gold trap and it is used to bypass the flowmeter and the pump when the mercury must be released. After the sampling the heater system in the preconcentration module is switched on and the gold trap, heated at about 600 °C, releases the captured mercury. The PEM is designed to operate with the mini-analyser but it can work also in stand-alone modality. The sample rate is 0.9 l/min (close-loop controlled) and the maximum sampling time is 100 minute. Using the module with the analyser is possible to detect mercury concentration up to 100 time lower.

CONCLUSIONS

A new mini-analyser for gaseous mercury detection have been presented and experimentally tested. The analyser is based on resistivity variation of thin gold film technique and use a solid state sensor ad hoc developed. The instrument is equipped with a GPS/GSM module for self localization and data link with a remote host computer.

A series of tests was carried out in order to evaluate the performance of the analyser prototype. The results of tests show good performance in terms of electrical noise, background level, linearity and sensitivity. In order to increase the sensitivity of the analyser a dedicated preconcentration module was designed and fabricated. The module allows to increase the sensitivity of the analyser up to 100 time.

Acknowledgements

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The use of Octanol Water Partitioning to Measure Hg Speciation in Natural Samples

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Abstract: The speciation of Hg in anoxic environments has been shown to control Hg methylation in laboratory studies but the Hg speciation has not been determine in anoxic environments. It is therefore not known if Hg speciation, predicted by thermodynamic modeling, truly reflects the in situ complexation of Hg in the environment. Octanol-water (Dow) extractions have been used to examine the speciation of inorganic mercury (Hg), but this method has only been utilized in laboratory studies with high concentrations or radioactive Hg in order to avoid detection limit and analytical difficulties. Analytical difficulties exist as a result of the slight solubility of octanol in water, which interferes with the detection of low levels of Hg. Modifications to currently used Dow extraction procedures have been made in order to remove the octanol from water samples so that in situ Hg speciation can be determined. Under oxic conditions, equilibrium calculations predict that dissolved organic matter dominates the Hg complexation. Dow extractions on oxic lake water support equilibrium calculations providing further evidence that Dow can be used as a tool to measure Hg speciation. Dow extractions were also used to measure Hg speciation under anoxic conditions to determine if Hg-sulfide complexes dominate and if equilibrium has been established and these results will be presented. Since the speciation of Hg in the presence of sulfide has been shown to control Hg methylation, in situ measurements of Hg speciation in anoxic environments is crucial in the understanding if the formation of methylmercury in the environment is controlled by Hg speciation or if other factors, such as kinetic effects, are important.

Key words: Hg speciation, octanol water partitioning

A double spike method for simultaneous inorganic and methyl-mercury isotope dilution analysis in environmental matrices

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Abstract: This study proposes a combined analytical and mathematical approach for double spike isotope dilution analysis for mercury species taking into account the reversible methylation/demethylation reaction. Equations have been applied to environmental matrices (biological tissue, water, sediment) exhibiting different mercury concentration levels and various methylmercury proportions. Results show the possible correction and the determination of transformation factors if degradations occur during the preparation step and show the interesting potential of this technique for the validation of the analytical procedures. Errors sources for calculations of transformation factors and concentrations have been also investigated. Limitations of the applicability of the double spike method are discussed as well as critical cases showing the restrictions of this technique.

Key words: mercury speciation, isotope dilution, environmental samples

INTRODUCTION

Accurate determination of mercury species in the different environmental matrices is critical to understand their biogeochemical cycle. Despite significant improvements in instrumentation, the quality of the results is mostly associated with sample pre-treatment stages. There are traditional problems related to non-quantitative recoveries and, more recently, questions have arisen about the artefact formation and the transformations of species during sample preparation[1]. To answer to the present problem of mercury speciation data validation, the use of isotope dilution techniques offers a great potential since quantitative recoveries are not necessary and rearrangement reactions can be easily detected[2]. For the case of mercury in environmental samples, inorganic mercury (II) (Hg^{2+}) and methylmercury (CH_3Hg^+) need to be determined taking into account the possible transformations by methylation, demethylation or reduction. The use of double isotope spikes methodology can allow to study and correct conversion reactions. Two different isotope enriched labelled species are needed, $^{199}Hg^{2+}$ and $CH_3{}^{201}Hg^+$. By measuring the different isotope ratios, it is thus possible to determine transformation factors and accurate concentrations.

Sample preparation

Sediments – 0.5 g of sediment is weighed is a glass tube with 10 ml of nitric acid 6N. The mixture is then placed in the open microwave system and submitted to irradiation (40W, 3 min.) For isotope dilution, 2 ml of extract is spiked with both $^{199}Hg^{2+}$ and $CH_3{}^{201}Hg^{+}$in order to get resulting ratios for each species around 1. The extract is buffered at pH 4 by addition of 5 ml of acetate buffer 0.1M and NH_3. 1 ml of $NaBEt_4$ is added with 1 ml of isooctane. The mixture is shaking for 5 min. and centrifuged. The organic phase is stocked in a GC vial in the freezer before analysis.
Biological tissues – 0.5 g of sample is weighed is a glass tube with 5 ml of TMAH 6N. The mixture is then placed in the open microwave system and submitted to irradiation (40W, 3 min.) For isotope dilution, 2 ml of extract is spiked with both $^{199}Hg^{2+}$ and $CH_3{}^{201}Hg^{+}$ in order to get resulting ratios for each species around 1. The extract is buffered at pH 4 by addition of 5 ml of acetate buffer 0.1M and HNO_3. 1 ml of $NaBEt_4$ is added with 1 ml of isooctane. The mixture is shaking for 5 min. and centrifuged. The organic phase is stocked in a GC vial in the freezer before analysis.

Mercury speciation analysis

The analysis is performed by GC-ICPMS both by external calibration and by species specific isotope dilution. For ID, ratios are corrected for mass bias by using Tl as internal standard. Each sample was extracted three times and each extract was injected three times.

RESULTS AND DISCUSSION

Isotope dilution equations for double spikes analysis

The high accuracy of isotope dilution analysis for trace metal speciation is based on the fact that, once isotope equilibration has taken place, decomposition of the species will not affect the final results. However, if the decomposition product of one species is another compound that also has to be determined, errors in the second species concentration will occur. For mercury compounds, possible transformations are summarized in Figure 1. According to this model, two simultaneous reactions are possible: CH_3Hg^+ can be degraded into Hg^{2+} whereas Hg^{2+} can be methylated.

To correct for species degradation, enriched mercury species labelled with different stable isotope can be used. Here $CH_3{}^{201}Hg^+$ is used and can be transformed into Hg^{2+} by a demethylation factor F1. $^{199}Hg^{2+}$ is used and can be methylated into CH_3Hg^+ by a factor F2. It is assumed than transformation of both species into Hg° will affect the same way all the isotopes and won't change isotope ratios. Moreover, transformation of Hg^0 into Hg^{2+} or CH_3Hg^+ is neglected. Then original concentra-

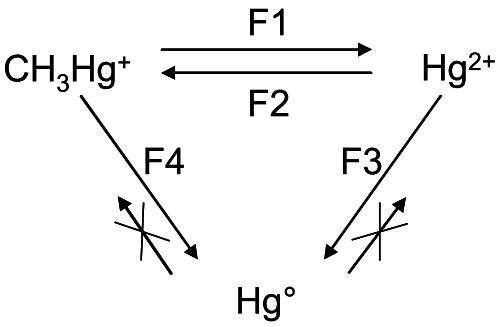

Figure 1. Degradation model.

tions and decomposition factors can be calculated by equations based on mass conservation.

Initial tests on standard solutions

First, to evaluate potential of this mathematical approach, equations for double spike methodology has been tested on standard solutions containing the same amount of the two species. A standard solution containing 10 ng.l^{-1} Hg^{2+} and 10 ng.l^{-1} CH_3Hg^+ was spiked with enriched $^{199}Hg^{2+}$ and $CH_3{}^{201}Hg^+$ and submitted to ethylation. Results after calculations using double spike equations, for five different solutions injected three times each, give accurate and precise results for concentrations with relative standard deviations of 2.5 and 3.3 % for CH_3Hg^+ and Hg^{2+} respectively. Regarding transformation factors calculated by these equations, results exhibit 1.1 and 2.4 % for methylation and demethylation respectively. These values represent the detection limits for transformation factors. Transformation factors lower than 2.5 % will be considered as negligible.

Tests on certified reference materials

Species specific isotope dilution was applied to certified reference material, a biological tissue (CRM710) and a sediment sample (IAEA405). Results are presented in Tables 1 and 2 with values found by external calibration (EE), isotope dilution for each species separately (SIDMS) and for double spike isotope dilution (DSIDMS).

Table 1. Results for the biological tissue CRM 710

Calibration method	CH_3Hg^+	Hg^{2+}
Certified values	115±9	
EE	154±25	136±11
SIDMS	117±7	144±4
DSIDMS	120±5	137±7

Regarding results for the CRM 710, values for CH_3Hg^+ agree with the certified value both by SIDMS and DSIMDS. Using external calibration, value is in good agreement but a higher precision compared to isotope dilution calibration. Using isotope dilution allows improving the precision on the results with relative standard deviation lower than 6 %. For Hg^{2+}, no certified value is available but values found with the three different calibration methods are in good agreement. Again precision on the results is improved using isotope dilution technique with relative standard deviation lower than 6 %.

Regarding results for the sediment IAEA 405, concentrations found for Hg^{2+} agree with the certified value for the three calibration method with better precision using isotope dilution methods. For the case of CH_3Hg^+, artefact from the methylation of Hg^{2+} during the sample preparation is observed when using external calibration. Improvement is observed using isotope dilution calibration but single spike method is not able to correct totally for the artifactual formation of CH_3Hg^+. Using double spike isotope dilution calculation allows generating a greater correction but the value found is lower than the certified value.

Table 2. Results for the sediment IAEA 405

Calibration method	CH_3Hg^+	Hg^{2+}
Certified values	5.49±0.53	810±40
EE	19.9±0.6	1095±122
SIDMS	9.2±0.4	864±40
DSIDMS	4.1±0.5	961±60

Limitations of the method

Double spike methodology allows obtaining accurate and precise results for water, biological tissues and sediments but some limitations have to be pointed out. Indeed, using uncertainty calculations proposed by KRAGTEN[3], it is possible to determine errors associated to calculated concentrations and factors. Regarding transformation factors found for the biological tissue (CRM710), no significant transformation has been found with 2 ± 2 % for demethylation factor and – 3 ± 1 % for methylation factors. But, in the case of sediment, mathematical calculations give inadequate results for transformations factors. A methylation factor of 0.2 ± 0.6 % and a demethylation factor of 67 ± 198 % are found. These wrong results are certainly caused by the great concentrations difference between CH_3Hg^+ and Hg^{2+}. Mathematical calculations do not provide correct results for transformation factors when the two species are not in the same concentration level. In addition, for sediment, methylation artefact is generally lower than 2 %, which is by now not detectable with this technique.

CONCLUSION

Double spike isotope dilution calibration provides additional degrees of information with accurate species concentrations and also degradation factors if transformations occur during the sample preparation. This technique offers an important diagnostic tool for the development and the validation of new analytical methods for speciation analysis.

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Quantum Chemical Studies on Interactions between Heavy Metal Species and Biomolecules

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Abstract: Interaction between heavy metal species (Hg^{2+}, $MeSHg^{+}$, Cd^{2+}, Zn^{2+}) and cysteine are examined with the B3LYP hybrid functional. In the most stable conformation of $HgCys^{2+}$ complex, the SH group is already deprotonated and followed by a strong binding with the metal ion. In $HgCys^{2+}$ complex, a cysteine complexs of Hg^{2+} without deprotonation of the SH group and mercury(II) carboxylate type structures are at least 80 and 116 kJ/mol less stable in energy than the most stable one (B3LYP/6-311++G(d,p)-SDD+d//B3LYP/6-31G(d)-SDD+d). In $MeSHgCys^{+}$, a thiolate structure is 17 kJ/mol more stable in energy than the structure bearing the SH group, in which the Hg atom binds to the NH_2 group. The natural bonding orbital analysis shows that the energy differences of bonding orbital energies and interaction integrals among metals reflect the energy difference between those isomeric structures.

Key words: mercury(II) ion, cysteine, interaction, quantum chemistry, B3LYP density functional method

INTRODUCTION

Mercury is one of the most important elements in the environment. The mercury(II) ion is known to act as a soft acid, and binds to SH groups of amino acids and proteins. [1] The X-ray structures of mercury-cysteine complexes, the SH group is already deprotonated. [2] An ethylmercurio protein system without deprotonation of the SH group is recently reported.[3] The same group element such as a zinc(II) ion exists as not only bound to SH group but also carboxyl groups of biomolecules in a body. The nature of interaction between heavy metal ions (e.g. Hg(II), Cd(II)) and biomolecules is yet to be scant. We examined the structures of conformers of $HgCys^{2+}$, $CdCys^{2+}$, $ZnCys^{2+}$, $MeSHgCys^{+}$, $Cu(I)Cys^{+}$ (which is already reported by Ohanessian[4]) and so on, using the high-precision B3LYP density functional method, and we compared the minimum structures and energetics.

COMPUTATIONAL METHODS

High-level quantum chemical methods such as the density functional theory have been very useful for not only physicists and chemists but also other scientists. We used the state-of-art B3LYP density functional method[5] in combination with the 6-31G(d) and 6-311+G(d,p) basis sets for C, H, N, O atoms[6] and with a quasi-relativistic SDD effective core potential[7] for Hg and S (with one d function) atoms. The calculations were performed with the Gaussian 98 program.[8] To examine orbital interactions, the natural

bond orbital (NBO) analysis is employed.[9] The effect of aqueous solution is examined with the COSMO polarized continuum method (CPCM). [10]

RESULTS AND DISCUSSION

The representative structures of $HgCys^{2+}$ were shown in Figure 1. The most stable structure **1** has a strong Hg-S bond and the carbonyl oxygen coordination to the mercury atom. In the second most stable mercury(II) thiolate structure **2**, the Hg-S bond is at the anti-position to the carbonyl oxygen. The most stable structure among those with the SH bond is the structure **3**, which possesses chelation with the carbonyl oxygen and the amino nitrogen. Mercury carboxylate **4** is ca.136 kJ/mol less stable than **1**.

Except for $Cu(I)Cys^{+}$, the most stable conformer possesses the deprotonation of SH group followed by protonation of amino group (detailed data will be published elsewhere). In $MeSHgCys^{+}$, which is a model of $Hg(Cys)^{2+}$, the energy difference of a mercury thiolate from mercurioamine and mercury carboxylate structures are lower to 16.5 and 14.6 kJ/mol, respectively, although the mercury thiolate structure is the most stable.

The analysis of second order interaction energy $E^{(2)}_{\sigma\sigma^*} = -2\dfrac{\langle\sigma|F|\sigma^*\rangle^2}{\varepsilon_{\sigma^*}-\varepsilon_{\sigma}}$ among filled and vacant NBOs for the most stable isomer and mercurioamine structure was carried out (Figure 2). Notice that σ/σ* and *F* refer filled/vacant NBO and Fock matrix, respectively. The NBO energy differences $\varepsilon_{\sigma^*}-\varepsilon_{\sigma}$ of Hg-S antibonding orbital and a lone pair of S or N are found to reflect its local hardness. The difference can be a clue of the chemical hardness. The larger value of the interaction energy in mercurioamine than that in mercury thiolate is due to the bigger size of a lone pair of S than that of N. The analysis also shows that the contribution of back-bonding from Hg d or Hg-S bonding orbital into the vacant orbitals of the S atom is small (only 5.6 kJ/mol).

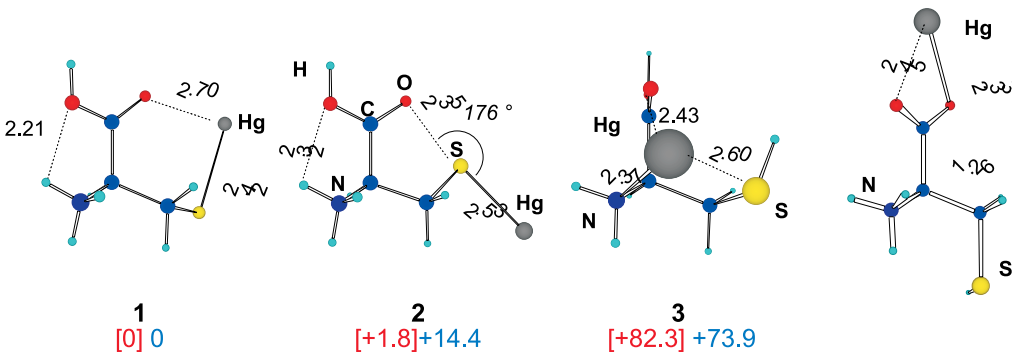

Figure 1. The representative conformers of $HgCys^{2+}$. Relative energies to the most stable conformer in kJ/mol are shown in bracket at the B3LYP/6-31++G(d,p)-SDD+d//B3LYP/6-31G(d)-SDD+d level, and Gibbs energies in aqueous solution are in italics at the B3LYP(CPCM)/6-31++G(d,p)-SDD+d//B3LYP/6-31G(d)-SDD+d level. Bond lengths are in angstrom and angles are in italic in degree at the B3LYP/6-31G(d)-SDD+d level.

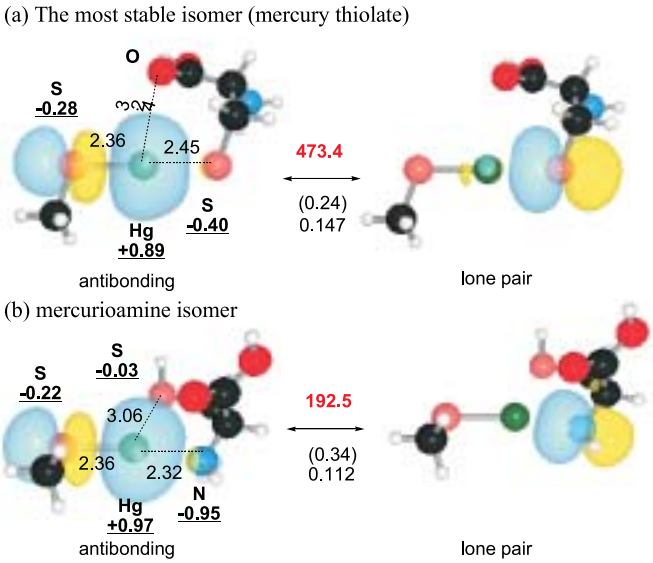

Figure 2. The strongest interactions between natural bonding orbitals of two isomers of MeSHgCys$^+$. Bond lengths are in angstrom and angles are in italic in degree at the B3LYP/6-31++G(d,p)-SDD+d//B3LYP/6-31G(d)-SDD+d level. Second order interaction energies in kJ/mol are shown in bold, and NBO energy differences in a.u. in parentheses, and interaction integrals in a.u. are in italics. Natural charges are shown in bold with underlines.

Table 1. Binding energies of M-Cys in kJ/mol.

M	B3LYP/II //B3LYP/I	B3LYP(CPCM) /II //B3LYP/I
Hg(II)	993	351
Cd(II)	836	270
Zn(II)	1027	309
Cu(II)	1156	367
Cu(I)	350	164

Basis I: 6-31G(d)-SDD+d
Basis II: 6-311++G(d,p)-SDD+d (S)

Finally, we examined the M-Cys^{2+} binding energies based on the most stable isomer of Cys and M-Cys^{2+} complexes (Table 1).

CONCLUSIONS

The most stable structure of M-Cys^{2+} bears a strong chelation between carbonyl oxygen and the sulfur atom, and on the other hand MeSHgCys$^+$ does little chelation between carbonyl oxygen and Hg. Hg favors to bind to S rather than N due to its softness and the atomic size of the counterpart. The order of the M-Cys^{2+} binding energies is shown in the following. In the gas phase, Cu(II) > Zn(II) > Hg(II) > Cd(II) >> Cu(I). In the aqueous phase, Cu(II) > Hg(II) > Zn(II) > Cd(II) >> Cu(I).

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Determination of total mercury and monomethylmercury in water samples, estuarine sediments and biological samples

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Abstract: The purpose of the present work was to compare the independent analytical techniques used by two different laboratories for determination of total mercury (Hg-T), and monomethylmercury mercury (MeHg) in seawater samples from the Atlantic Ocean (Adour Estuary), in sediments and biological samples from the Mediterranean Sea and Atlantic Ocean.

Key words: intercomparision, environmental samples, mercury speciation

INTRODUCTION

In studies investigating the fate of mercury in the natural environment is of essential importance to obtain reliable and precise data, which can be achieved by implementing adequate QA/QC protocols. Therefore, in the initial phase of the EU project »MERCYMS - An Integrated Approach to Assess the Mercury Cycling in the Mediterranean Basin« an interlaboratory testing programme was performed to assure the validity and comparability of results among the research teams. In this presentation the results from the interlaboratory study carried out between the Jožef Stefan Institute (JSI), Ljubljana, Slovenia and the Laboratoire de Chimie Analytique Bio-Inorganique et Environnement (LCABIE), Pau, France are presented. In this exercise different environmental samples were analysed for total mercury (Hg-T) and methylmercury (MeHg) including seawater, sediments and biological samples (zooplankton, oyster tissue, sea urchin, mussel tissue, golden grey mullet, anchovy) from the Mediterranean Sea and Atlantic Ocean. Analyses of the selected samples were performed using the various analytical techniques available in both laboratories (HORVAT ET AL., 1991, 1993A,B; LIANG ET AL., 1994; LOGAR ET AL., 2001; RODRIGUEZ MARTIN-DOIMEADIOS ET AL., 2002; STOICKEV ET AL., 2002, TSENG ET AL., 1999).

The accuracy of the results at JSI was checked by the use of the certified reference materials BCR 580 Polluted Marine Sediment; SRM 2976 Mussel tissue; SRM 1566b Oyster tissue and DOLT-1 Dogfish liver. At LCABIE IAEA 405 Estuarine Sediment; RM 278R Mussel Tissue; RM 710 Oyster Tissue were used.

RESULTS AND DISCUSSION

The results of the present study are summarized in Figure 1.

In spite of the fact that some deviations are observed on comparing results obtained by JSI and LCABIE in different samples, a good agreement is generally found on comparing all the results. It is evident from Figure 1 that all the data sets for both mercury species (Hg-T and MeHg) are well correlated. The results of this study confirmed that the methods used in the laboratories at LCABIE and IJS are suitable for determination of Hg-T and MeHg in biological samples using isotope dilution at LCABIE and simultaneous determination of inorganic Hg and MeHg at JSI.

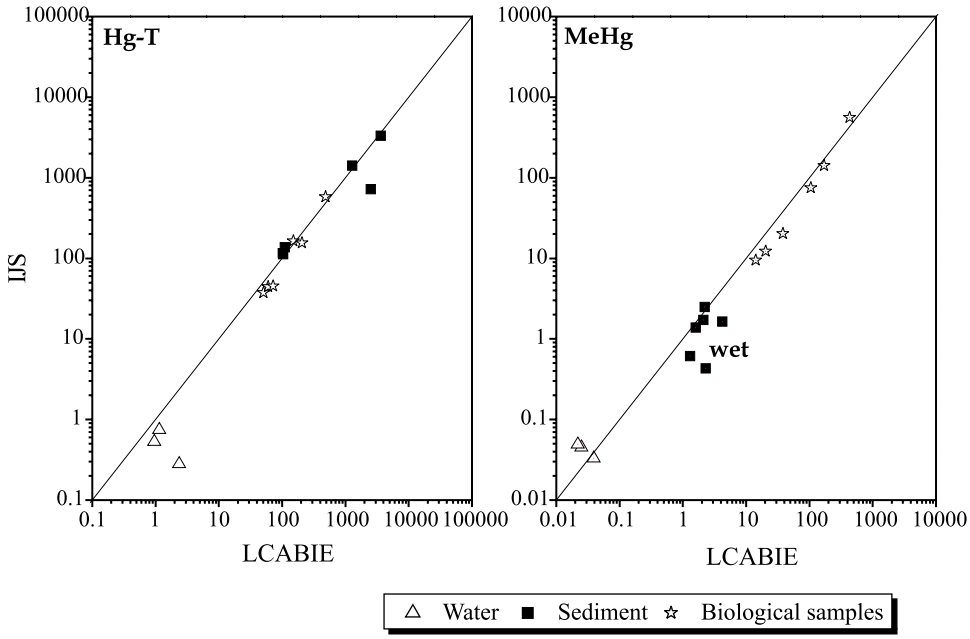

Figure 1. Comparison of the data for a) Hg-T and b) MeHg obtained by JSI and LCABIE in all investigated samples.

The differences found for MeHg concentrations in wet sediments compared to freeze dried sediments suggest that special care should be taken in the preparation procedure for MeHg determination in sediments. Therefore, further investigation is needed to establish a suitable protocol for the sampling procedure for determination of MeHg in sediment samples in both laboratories. The reason for the discrepancies observed for Hg-

T and MeHg in water samples is sample instability and/or contamination of Hg-T and MeHg in water samples. The intercomparison of water samples should be done on board ship during the sampling cruise immediately after sample collection.

Intercomparision on board ship: In this exercise the concentrations of two Hg species dissolved gaseous mercury (DGM) and Hg-T in water samples were determined immediately after sample collection during the sampling cruise performed in March, 2004: Additionally, an intercomparision of different samplers was performed.

For Hg-T in water samples a good agreement was obtained between both groups involved (JSI and Institut Français de Recherches pour l'Exploitation de la Mer - IFREMER). It was found that the concentrations in the acid cleaned teflon coated sampler (IFREMER) were systematically lower compared to the Urania samplers. Also, Hg-T concentrations measured by JSI were systematically lower than those of IFREMER, but not statistically different.

For DGM, a problem arose in the first intercomparison with a large discrepancy between the results obtained by LCABIE and those by Göteborg University (UGOT) and JSI. We could not explain it even after controlling and crosschecking the calibration procedures. Thus, a second and a third intercomparison were performed. In the second one we still found some discrepancies between groups, but to a lesser extent. In the third one, with a crosschecked purge and trap system and analysis system we obtained ideal results between the different groups. Therefore, a question concerning the two first intercomparisons still remains.

CONCLUSIONS

Good agreement of the results for Hg analysis and speciation was demonstrated in most of the samples, except those where mercury species are unstable (wet sediments and waters). Sample preparation and storage seem to be the most significant source of errors in mercury analysis in environmental samples. Therefore, it is recommended that water samples be analyzed as soon as possible after sampling. The same applies for sediments in which sampling and sample preparation may significantly influence the presence of mercury species.

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Preservation and Storage Techniques for Low-Level Mercury Speciation

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Abstract: Although researchers today generally employ appropriate techniques for the storage and preservation of aqueous samples for ambient-level Hg (ppb) speciation, these methods continue to be poorly documented. Numerous experiments were thus conducted to investigate the effects of acidification and bottle type on holding time for Hg species, as well as total Hg (THg). We documented that THg is stable for at least 300 days when stored at 0.4 to 0.5 % acidity in either Teflon or glass bottles. Polyethylene bottles allowed diffusion of Hg^0 through the bottle walls to or from the sample, depending on the Hg concentration of the sample and storage atmosphere. CH_3Hg in freshwater samples can be stored refrigerated and unacidified for days to weeks with no observed degradation of CH_3Hg. For long-term storage, samples should be acidified with 0.4 % HCl (v/v) and kept in the dark to avoid photodegradation. Preservation with 0.2 % (v/v) H_2SO_4 is preferred for salt water to avoid exceeding the optimal chloride concentration if the distillation procedure for CH_3Hg is used. For volatile species (Hg^0 and $(CH_3)_2Hg$), samples should be collected in completely full glass bottles with Teflon-lined caps, as these species are lost rapidly ($t_{1/2}$ = 10-20 hours) from Teflon and polyethylene bottles. Because acids can enhance the rapid oxidation of volatile species, these samples should be stored refrigerated and unacidified and processed within 1-2 days if they cannot be purged and trapped in the field.

Key words: mercury, methyl mercury, sample preservation, sample storage

INTRODUCTION

Researchers have been employing ultra-low level (pg L^{-1} to ng L^{-1}) Hg speciation techniques for more than 15 years; however, no comprehensive effort has been made to document the stability of Hg speciation under various storage and preservation regimes. The high cost of analysis for ambient level Hg speciation may have precluded systematic full-scale storage tests. Instead, several small-scale studies have been conducted by various researchers, which have resulted in an anecdotal literature on the subject. For example, most experienced researchers recognize the following: (1) low-level Hg samples should not be stored in polyethylene bottles (BOTHNER AND ROBERTSON, 1975; BLOOM, 1995) (2) methylated species are degraded by light (SELLERS ET AL., 1996); (3) volatile Hg speciation is too unstable to preserve, thus volatile species must be separated in the field (FITZGERALD 1986; MASON ET AL., 1991); (4) Teflon bottles are best for low-level Hg samples, and lids must be wrenched on tightly (GILL AND FITZGERALD, 1985); (5) freezing/thawing preserves monomethyl Hg (CH_3Hg), but may alter the inorganic spe-

ciation (J. RUDD AND R. FLETT, personal comm.); and (6) hydrochloric acid is a superior preservative to nitric acid because the chloride helps to complex the Hg(II). These beliefs are often in direct opposition to the guidance provided by regulatory agencies, leading to confusion for people new to the field. Thus, in this study we have attempted to verify and comprehensively present most of the important assertions regarding the storage and preservation of low-level Hg samples.

RESULTS AND DISCUSSION

In this study, we used several small-scale experiments to investigate reliable storage and preservation methods for Hg speciation, further details are provided in Parker and BLOOM (2004). When only THg is of interest, a simple procedure may be employed that allows long-term storage with full recovery, and little risk of contamination. The sample should be collected into a Teflon or glass bottle with Teflon-lined lid, and then preserved with a strong oxidizer such as acidic BrCl. This approach destroys all speciation information, but also disaggregates organic matter sufficiently to eliminate wall losses. If speciation information is desired, then the samples must be preserved less aggressively, at least until all other species have been determined. Once the other species have been determined, BrCl can then be added to the original sample bottle to ensure that any Hg on the walls is re-solubilized prior to analysis. In this study, THg was determined by $SnCl_2$ reduction and purging on to gold, with cold vapor atomic fluorescence detection (CVAFS). THg shown in Figure 1a (HCl acidified) and Figure 2 (unpreserved) was recovered by this preservation technique. Total Hg was recovered completely, even after 300 days of storage if Teflon or glass bottles were used.

We also investigated storage techniques for, where CH_3Hg was determined by aqueous phase ethylation and isothermal GC separation prior to CVAFS detection. CH_3Hg was extremely stable when preserved with 0.5 % (v/v) HCl and stored in the dark at 1-4 °C (Fig. 1b). Sulfuric acid (0.2 % v/v) is recommended in salt-water samples to reduce the volatilization of HCl, which at high

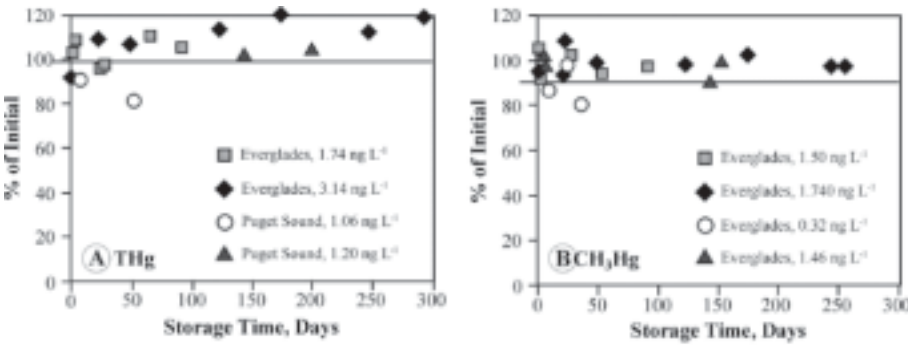

Figure 1. Stability of (A) THg and (B) CH_3Hg in preserved freshwater (Everglades, FL) and seawater (Puget Sound, WA). Samples were preserved with 0.5% (v/v) HCl, stored in Teflon bottles, refrigerated and kept in the dark. Data are presented in percentage of Hg remaining over time, and all points are the mean of 3-8 replicate bottles (error bars, ±10, left off for clarity).

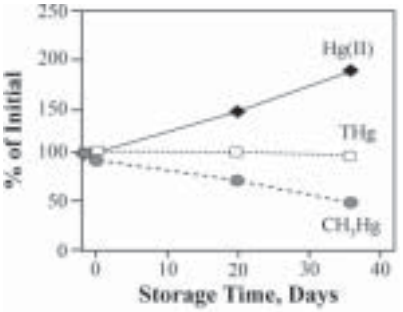

Figure 2. Stability of THg, CH_3Hg, and Hg(II) in unpreserved filtered water from Green Lake, WA (THg ≈1 ng L^{-1}). Samples were stored in Teflon bottles at room temperature.

concentrations (>0.4 % v/v) can co-distill and become an interference in the ethylation procedure. In filtered samples, CH_3Hg was stable for 1-2 weeks without preservation (Fig. 2), although in unfiltered, unpreserved waters the holding time is only a few days, and then only if stored in cold and dark conditions. This difference may be due to microbial demethylation in the unfiltered waters. Both Teflon bottles and glass bottles with Teflon-lined lids are acceptable for the storage of samples for CH_3Hg analysis.

$(CH_3)_2Hg$ and Hg^0 are clearly the most unstable of the Hg species, as shown in Figure 3. In order to accurately quantify these species, freshly collected unfiltered samples should ideally be purged onto appropriate trapping media in the field within hours of collection. If field purging of the samples is impossible, it is essentially futile to collect samples in plastic (Teflon and polyethylene) for $(CH_3)_2Hg$ and Hg^0, because losses are extremely rapid ($t_{1/2}$ ≈ 10-20 hours).

Labile Hg(II) appears to be relatively stable (days-weeks) in filtered, unpreserved samples (Fig. 3c). However, as was documented earlier (BLOOM, 1994), acidification quickly and dramatically alters the measured Hg(II) level in unpredictable ways. Acidification can lead either to desorption of Hg(II) from particulates, oxidation of Hg^0 to Hg(II), or coagulation of DOC with the concomitant adsorption and precipitation of Hg(II). Therefore, samples for Hg(II) should not be preserved.

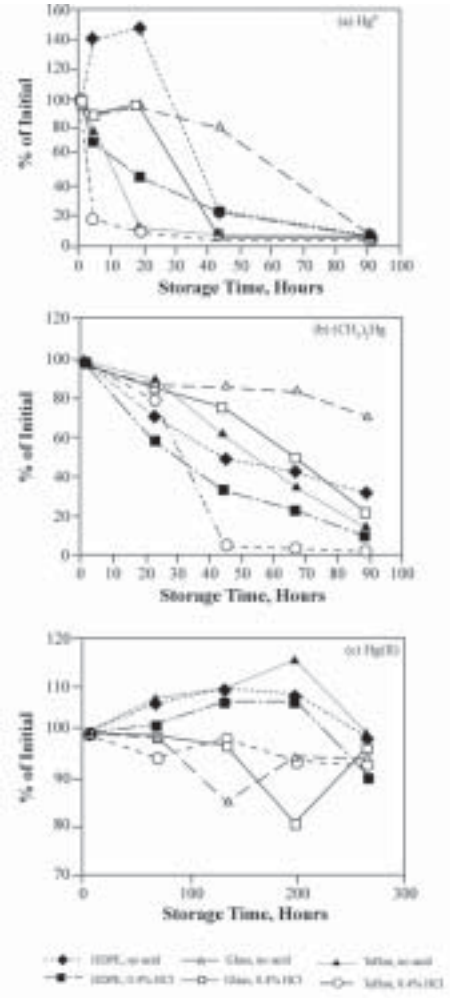

Figure 3. Stability of Hg^0, $(CH_3)_2Hg$, and Hg(II) in spiked deionized water stored in high-density polyethylene (HDPE), glass, and Teflon bottles. Acidified samples were stored on the lab bench in room light and room temperature, while unpreserved samples were stored refrigerated and in the dark.

CONCLUSIONS

We used several small-scale studies to investigate reliable storage and preservation methods, particularly for aqueous samples for Hg speciation at ambient concentrations (ng L^{-1}). Acidified samples in Teflon bottles had stable THg concentrations for 300 days. Similar stability was seen in shorter tests using glass bottles with and without preservation. In some cases, THg was adsorbed to the walls, but it was quantitatively recovered if BrCl was added to the original sample bottle at least 24 hours before analysis. When acidified samples were stored in polyethylene bottles, dramatic increases in THg were observed, due to diffusion of atmospheric Hg^0 through the bottle walls. This effect was greater for low-density polyethylene than for high-density polyethylene.

CH_3Hg was stable for at least 250 days when acidified to 0.5 % (v/v) with HCl and kept in the dark. However, samples that were exposed to light were found to slowly decrease in CH_3Hg over time ($t_{1/2}$ = 6 months). Overall, the recommended preservation technique for fresh water samples is acidification to 0.4 % (v/v) with 12 M HCl, kept dark and refrigerated (<5 °C). For salt water samples, 0.2 % (v/v) 9M H_2SO_4 is recommended, if CH_3Hg is to be determined using the distillation technique (HORVAT ET AL., 1993). For short periods (days-weeks), all types of water samples can be kept safely refrigerated and unacidified, allowing time for transportation to a laboratory for ultra-clean processing.

When measuring volatile species (Hg^0 and $(CH_3)_2Hg$ or labile Hg(II), samples should be collected into completely full glass bottles with Teflon-lined caps, and stored refrigerated and unacidified. For the best results, samples must be processed and analyzed within 1-2 days and then preserved for CH_3Hg and THg analysis. Both volatile species are rapidly lost from Teflon and polyethylene bottles ($t_{1/2}$ = 10-20 hours), presumably by diffusion into the walls.

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Direct Determination of Mercury in Samples with a Large Amount of Organic Compounds (Foodstuff, Oil, and Petroleum Hydrocarbons) using Zeeman AAS

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Abstract: Complex organic matrices of foodstuff and oil, as well as low mercury content therein, make such samples to be very difficult subjects of quantitative analysis. Effective monitoring of the mercury content is feasible only if a rapid analysis technique is used. Such a technique should not involve sample decomposition by acids and oxidants, which results in higher detection limit (DL) and longer time of analysis, and gives rise to errors.

We have developed a special-purpose two-section pyrolyzer PYRO-915 for analysis of organic-matrix samples. The sample is vaporized in its first section, and the organic compounds are catalytically oxidized in the second section. Downstream from the pyrolyzer the hot gas flow directly enters the measuring cell of an RA-915 mercury analyzer with the Zeeman correction for nonselective absorption (Lumex Ltd.). The effect of the residual compounds is eliminated due to the inherent selectivity of the analyzer. No false signals are detected even in the case of a large optical density of the nonselective absorption. This makes it possible to significantly increase the sample weight (without the use of mercury accumulation on a sorbent) and thereby to obtain a lower concentration DL. The absence of a cold duct between the pyrolyzer and measuring cell rules out the mercury sorbtion thereon; thereby enhancing the reproducibility and reliability of the analysis. This technique allows the use of weighed samples up to 100 mg, the DL for crude oil being not higher than 5 ppb and the analysis taking less than two minutes.

Table below presents a comparison of the results of determination of mercury in light petroleum fractions using an RA-915 analyzer with a PYRO-915 attachment and those obtained by neutron-activation analysis (NAA).

Key words: mercury, thermal decomposition, Zeeman AAS

RA-915	**NAA**	**%**
Ñ, ppb	**Ñ, ppb**	
15	16	+6
21	25	-16
25	28	-11
28	22	+27

Atmospheric mercury speciation measurements intercomparison at St.Anicet CAMNet site (Québec, Canada)

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Abstract: Numerous scientific and policy questions with respect to mercury as an environmental issue are internationally currently addressed. In 1996, Environment Canada initiated the Canadian Atmospheric Mercury Measurement Network (CAMNet). Major objectives of the CAMNet mercury measurement program, in progress, are: the current understanding of the atmospheric transport, transformation and removal processes of elemental mercury and its ecologically significant compounds released into the environment; and the identification of major point and/or regional (area/line) sources of atmospheric mercury emissions.

Reactive gaseous mercury and particulate mercury species are important components in the atmospheric mercury chemistry and remain to be addressed.

Recent technology innovation from a Canadian based company (Tekran inc.) with respect to mercury speciation measurements (Reactive mercury unit- model 1130 and Particulate mercury unit model 1135P) has been adopted and deployed in some CAMNet sites. In order to better assess the capability and capacity of this new technology to be currently used into CAMNet, a Canadian mercury speciation measurement intercomparison workshop has been achieved in the St. Anicet Atmospheric chemistry research station in Québec, Canada in winter 2004.

Five mercury speciation units have been run side by side in collocation for a 10 day period. The instruments were run independently under cold conditions (air temperature ~ minus 20 °C), and results compared. Measurements were for elemental mercury, reactive mercury and particulate mercury concentrations. Mercury speciation concentrations were compared to Total Gaseous Mercury measurements as well as Total particulate mercury concentrations along the intercomparison. This paper is presenting the main results from this intercomparison and addresses the main lines for developing a Standard Operating Procedure protocol.

Key words: Hg speciation, intercomparison, TEKRAN

A simple method development for the analysis of organic mercury in different environmental matrices

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Abstract: The presence of organic mercury in environmental and biological matrices deserves special attention, due to the extreme toxicity of these species (namely methylmercury) and ability to enter and biomagnify up in the trophic chain. Therefore, mercury speciation analysis has become an important issue of the present analytical research, with the specific purpose of finding simple and rapid methodologies. In the present work, the methodology proposed for the determination of organic mercury in fish, plant and sediment certified reference materials (CRM), it is based on an organic solvent extraction procedure followed by the quantitative determination by pyrolysis absorption atomic spectrometry (AAS). The results obtained assure the performance of the method, with recovery factors higher than 97 % for all certified reference materials and revealed a good precision of the methodology.

Key words: organic mercury, method development, environmental matrices.

INTRODUCTION

Mercury is a highly dangerous element because of its accumulative and persistent character in the environment and biota. It is well known that the toxicity, biogeochemical behavior and transportation of mercury in the environment are heavily dependent on its chemical forms[1], which includes elemental mercury, inorganic salts and organic compounds[2]. Conversion between these different forms provides the basis for mercury complex distribution pattern in local and global cycles and for its biological enrichment and effects. Changes in speciation from inorganic to methylated forms are the first step in the aquatic bioaccumulation processes. Once methylmercury is formed, it enters the food chain by rapid diffusion and binding to proteins in aquatic biota and attains its highest concentrations in the tissues of fish at the top of the aquatic food chain due to biomagnification through the trophic levels[3]. Therefore, the environmental monitoring of mercury and its related compounds, mostly organic that is the most toxic form of it, is a fundamental pre-requisite to human health[4].

Since the early 1960s, the growing awareness of environmental mercury pollution has stimulated the development of more efficient methods of determining mercury and its compounds in a wide variety of matrices[4]. A number of analytical methods have been described in the literature to measure organomercury species in samples of environmental significance, based on the combination of different analytical techniques. Most of them involve quite a few steps (quantitative extraction, derivatisation, preconcentration and quantification) in which random errors may multiply and give rise to low pre-

cision and lack of repeatability of the overall analysis[5]. Due to the complicated and time consuming procedures used to quantify organic mercury, simple analytical methodology still needed to be developed.

The main objective of the present work was to develop and establish a simple and rapid methodology for the determination of organic mercury in several matrices, able to produce accurate and precise results. To achieve this, organomercury species of certified reference materials (CRM) of fish, plant and sediment were extracted by a procedure proposed by CAI, TANG, JAFFÉ AND JONES[6] with slight modifications and analysed by pyrolysis absorption atomic spectrometry (AAS) using a LECO AMA-254 instrument.

RESULTS AND DISCUSSION

Quality control of results for organic mercury was performed by analysing certified reference material of several matrices. The extraction procedure was carried out using the following reference materials: CMR 464 (tuna fish) and CMR 580 (estuarine sediment) from the Community Bureau of Reference, IAEA-140 (sea plant homogenate) from de International Atomic Energy Agency and TORT-2 (lobster hepathopancreas) from the Institute for Environmental Research and Technology. Around 0.2 g of each reference materials of fish, plant and sediment samples were acidified using potassium bromide in sulphuric acid, copper sulphate and treated with toluene to extract organic mercury from the aqueous phase. The organic phase was separated by centrifugation and then decanted to glass vessels. This procedure was repeated, obtaining 8 mL volume of organic mercury in toluene[6]. The organomercury species remaining in the toluene were extracted into an aqueous sodium thiosulphate solution (5 mL) and finally directed analysed by absorption atomic spectrometry (AAS), using a LECO AMA-254 instrument.

An example of the calibration curve for mercury in LECO AMA-254 instrument is presented in figure 1 and the calibration data are given in table 1. Such a complete calibration is not required daily. Based on a work of HALL

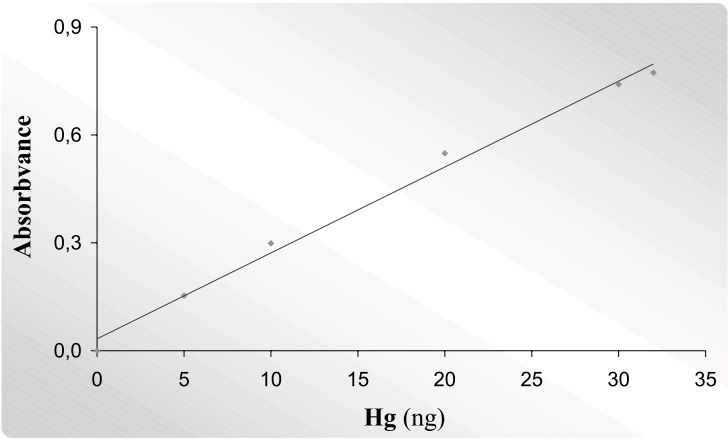

Figure 1. Calibration curve for mercury in LECO AMA-254 instrument.

AND PELCHAT[7] the change in curve slope over a period of a month is less than 2 %[7].

Table 1. Calibration data and detection limit (D.L.) for mercury in LECO AMA-254 instrument

Slope **(ng^{-1})**	***r*** (N=6)	**D.L. (ng)**
$2{,}39\times10^{-2}$	0.996	6.44×10^{-2}

The detection limit (D.L.) was calculated as the concentration corresponding to the blank signal plus three times the standard deviation of the blank for the determination of mercury[8].

The concentration of the extracted organomercury species in certified reference materials, expressed in μg g^{-1}, is calculated taking in account the concentration of the metal in the aqueous phase, the volume of aqueous phase (usually 5 mL), a dilution factor related with the several extraction volumes used and the mass of sample weighed. Blank signals are always subtracted from the sample one.

The results obtained for organic mercury in the certified reference materials are presented in Table 2.

Table 2. Organic mercury concentrations (μg g^{-1}) in certified reference materials. (N = number of replicates; RSD = relative standard deviation; Recovery was defined as the quotient between experimental and certified value * 100)

CERTIFIED REFERENCE MATERIAL	N	[Hg] (certified value in μg g^{-1})	[Hg] (experimental value in μg g^{-1})	Recovery (%)	RSD (%)
Tuna fish (CRM463)	12	2.82	2.82	100	2
Lobster hepathopancreas (TORT-2)	22	1.52×10^{-1}	1.52×10^{-1}	100	6
Estuarine sediment (CMR 580)	10	7.55×10^{-2}	7.38×10^{-2}	97.7	9
Sea plant homogenate (IAEA-140)	6	6.26×10^{-4}	6.17×10^{-4}	98.6	16

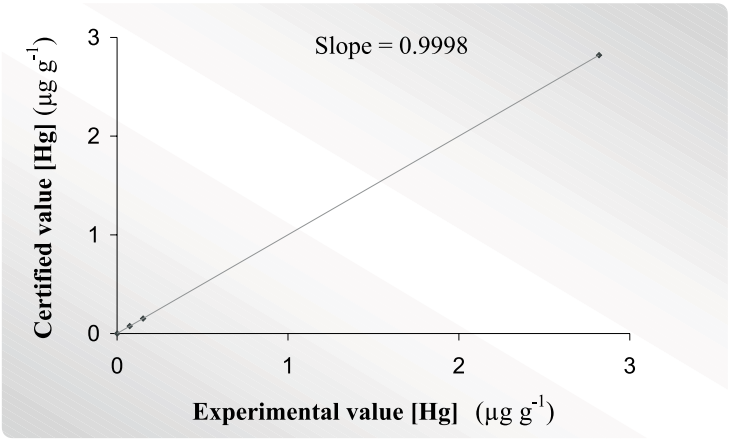

Figure 2. Certified and obtained organic mercury concentrations (μg g^{-1}) in certified reference materials.

The obtained results revealed a good agreement with the certified values in all cases, since the both values do not differ significantly at 95 % confidence level (Fig. 2; slope = 0,9998). The recovery factors were always higher than 97 %, which assure the performance and accuracy of the methodology, even though they differ depending on the matrix used.

The reproducibility of the methodology was evaluated by doing at least six independent analyses. The results indicate an RSD always lower than 10 % for certified materials of fish and sediments, however, for plant certified material RDS was 16 %. The high RSD for the IAEA-140 material was probably due to the low concentration of organic mercury on this material. The low RSD values demonstrate the good precision of the methodology.

CONCLUSIONS

The methodology proposed involves a simple extraction procedure of organic mercury compounds from the studied matrices and the analysis of the mercury by pyrolysis atomic absorption spectroscopy. The method is simple and relatively rapid to perform and showed good agreement with the certified values for two fish tissues, one estuarine sediment and one sea plant. The obtained results revealed that the developed methodology can be applied with success to different matrices, allowing several samples to be analysed in a single day.

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Direct determination of mercury concentration in natural hydrocarbon gases

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Abstract: The use of an atomic absorption spectrometer with the Zeeman background correction and a multi-path analytical cell provides very high selectivity and sensitivity of measurements. As a result, the Lumex RA-915+ mercury analyzer allows direct on-stream determination of mercury in natural hydrocarbon gases due to the elimination of preliminary precipitation and collection of mercury in absorption traps. Special measurement technique has been developed for high benzene concentrations in the gas. The results of concurrent measurements of mercury concentrations in natural gas are presented, they were obtained both by direct measurements using the RA-915+ instrument and by the cold vapour technique involving prolonged mercury accumulation in an acid solution.

Key words: mercury, natural gas, Zeeman atomic absorption analyzer, Lumex RA-915+

INTRODUCTION

The mercury vapors concentration in natural hydrocarbon gases from different gas fields may vary greatly from 0.001 up to 10 000 μg/m^3 (concentration of saturated vapor)[1]. The average Hg concentration in gas is about 2 μg/m^{3}over all 80 investigated deposits (Russia, Ukraine, and Central Asia). In 30 % of the studied sites the content of mercury in gas was below 0.2 μg/m^3, and in 28 % exceeded 2 μg/m^3 (Fig. 1).

For safety reasons, to avoid the electrochemical corrosion of equipment, gas producers often have to install Hg removal equipment before gas transportation or processing even if the mercury concentration is below environmental limit values. The residual Hg concentration in processed gas should not exceed extremely low level (0.005-0.01 μg/m^3), the ultimate level for tank gas being 1000 times higher (threshold limit value of the Hg concentration in tank gas is 28 μg/m^3 in EU states). Therefore, depending on a task, the

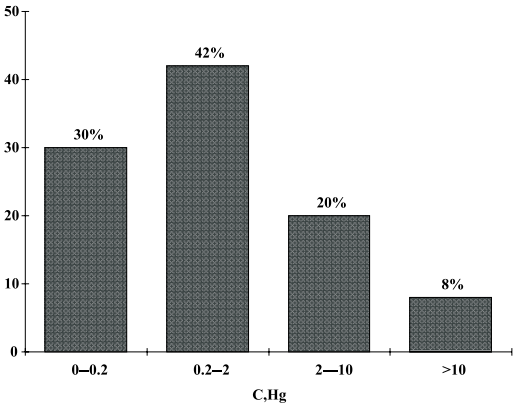

Figure 1. Distribution of the mercury concentration in hydrocarbon gases of 80 investigated gas, gas-condensate and oil deposits

Hg concentration should be measured in the following ranges:

- 0.005–1 μg/m^3: monitoring raw gas and treated gas with low and ultra-low Hg concentration;
- 1–100 μg/m^3: monitoring raw gas with prevailing Hg concentration and checking tank gas for regulations compliance;
- 50–10000 μg/m^3: monitoring raw and processed gas with high Hg concentration in gas treatment processes.

Direct mercury determination in gas by atomic absorption spectrometry (AAS) is complicated by strong background absorption of resonance radiation at 254 nm caused by impurity components in gas. The level of such absorption is variable and depends on the gas composition. That is why the determination of Hg in hydrocarbon gases is performed presently only after preliminary accumulation in an acid solution or on a gold sorbent[2]. Main drawbacks of this method are as follows:

- time-consuming and labor-intensive procedure,
- considerable measurement uncertainties due to impurity of chemicals,
- impossibility of continuous measurements.

Results and discussion

The RA-915+ mercury spectrometer is based on atomic absorption spectrometry (AAS) with Zeeman background correction. The combination of the very effective background correction with the high-frequency polarization modulation provides high selectivity: the attenuation of resonance radiation for 95 % caused by background absorption does not produce a false response. The analyzer is successfully used for detection of Hg in gas. The detection limit for mercury in gas is 0.2 μg/m^3 with a single-pass analytical cell and is 0.005 μg/m^3 with a multi-pass cell in direct continuous measurements in a gas flow without using any absorption traps. Combination of analytical cells with different optical lengths provides very broad dynamic range from 0.005 to 2000 μg/m^3.

In a measuring procedure, the analyzer is installed near a well or other sampling point, such as a pipeline, separator, etc. (Fig. 2). Continuous gas flow arrives into the analytical cell through a plastic hose downstream from a high- pressure valve. The flow rate (1–5 l/min) is set by a valve and is kept constant to the accuracy of 20%. A separator is installed upstream of the analyzer to separate the liquid phase (water, gas condensate, or oil). The zero signal is checked periodically by passing the gas through a special filter efficiently absorbing up to 98% Hg. The analytical signal is detected in real time (every second) and displayed on a built-in LCD or an external PC (Fig.3).

Figure 2. Mercury determination in a natural gas flow using RA-915+

The time of direct analysis is 100 to 200 times shorter than that with the methods used earlier. It is worth to remind that neither sam-

pling nor preliminary Hg accumulation are needed any longer, which allows the use of this method in field conditions.

Though the Zeeman background correction provides high selectivity of analysis, it should be pointed out that benzene (C_6H_6) has an absorption band with partially resolved vibrational-rotational structure at 254 nm. The very close spectral position of analytical and reference radiation in RA-915+ ($\Delta\lambda = 0.003$ nm) notwithstanding, the benzene molecules produce the differential absorption signal proportional to the concentration of the molecules. Since the differential absorption cross section of C_6H_6 molecules is low, the molecules can produce a considerable signal only when their concentration is relatively high (200 ppm of C_6H_6 generates a false response equivalent to about 1 μg/m^3 of Hg). To measure the mercury concentration in presence of a high concentration of C_6H_6 in hydrocarbon gases, a special filter, which blocks Hg and bypasses the C_6H_6, is used.

A comparison of concurrent measurements using the RA-915+ analyzer (direct determination of Hg) and Mercury 3000 analyzer (accumulation of Hg in an acid solution) are given in Table 1 below.

It is seen from the table that data obtained by different instruments are in a good agreement. It should be noted that the accumulation time according to ISO 6978 Method is 2 hours whereas the RA-915+ results are obtained within 5 min. As an example of an on-line Hg determination in gas, Fig. 3 shows results obtained using RA-915+ equipped with a single-pass cell.

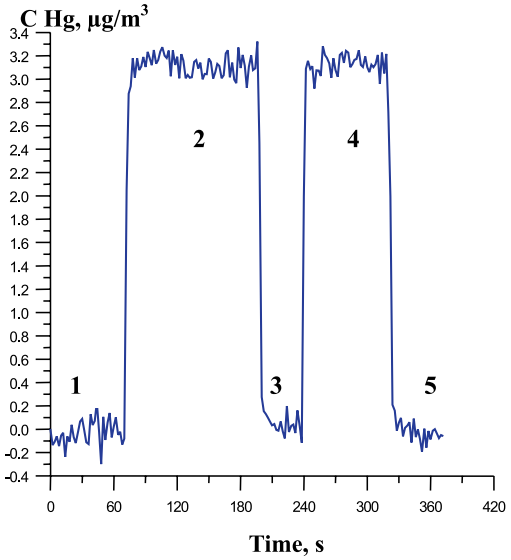

Figure 3. Determination of Hg in gas with RA-915+, single-pass cell: 1, 3, 5 – Zero control with mercury absorption filter, 2, 4 – mercury concentration in raw gas (3.1 μg/m^3, SD – 0.1 μg/m^3)

Table 1. Concurrent measurement of the Hg concentration in gas deposits before and after mercury removal from raw gas. October, 2002.

Sampling point	Hg in gas, μg/m^3		Δ, %
	RA-915+	Mercury 3000	
Gr-1, raw gas	110	93	+15
Ml-2, after absorber	34	39	–8
Ne-1, after absorber	24	23	+6
Pa-1, after absorber	19	21	–5
Sh-1, after absorber	9.8	12	–18
Bo-1, after absorber	1.7	2.5	–30
Uy-2, after absorber	< 0.5	Not detected	0
Bu-1, after absorber	< 0.5	Not detected	0
St-1, after absorber	< 0.5	Not detected	0

CONCLUSIONS

The proposed measuring method allows direct, rapid and on-stream determination of mercury in gas in field conditions[3]. Specific features of gas analysis with RA-915+ are as follows:

- no sample preparation is needed, hence reduced costs and better precision;
- wide dynamic range;
- visualization of continuous measurements;
- stability of calibration;
- measurement results independent of the gas flow rate in a wide range;
- field operation;
- PC is not necessary for measurements and data recording.

Acknowledgements

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Multifunctional Zeeman Mercury Analytical System RA-915+: Practical Experience and Future Trends

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Abstract: Zeeman mercury spectrometer RA-915+ is suitable for the direct determination (without the preconcentration step in the absorption trap) of mercury concentrations in various samples, such as air, water, soil, food, coal, oil, etc., at background levels of detection limits. The mercury concentrations were determined using a same RA-915+ spectrometer with different attachments to convert bound mercury to its atomic form. To determine mercury concentrations in samples with complex matrix without pre-treatment (whole blood, hair, crude oil, vegetation, and foodstuff), a two-chamber pyrolytic atomiser was developed. Its design allows separating the processes of evaporation and dissociation of mercury compounds as well as decomposing the matrix components in the gaseous phase in real time. Results of analyses of samples with simple and complex matrices are reported in the paper.

Key words: mercury, spectrometer RA915+, air, water, soil, food

INTRODUCTION

For effective monitoring of environment it is necessary to use such analytical techniques, which provide sample pre-treatment and mercury determination in real time. Many techniques exist for mercury determination in various samples, and almost all of them involve an intermediate stage of mercury preconcentration in absorption traps[1]. Multifunctional Zeeman atomic absorption mercury analyser RA-915+ (manufactured by Lumex Ltd, St. Petersburg, Russia) with dedicated attachments successfully substitutes for 3-5 high-quality special-purpose mercury analysers. Combination of the Zeeman background correction and a multipath analytical cell allows direct determination of mercury background concentration in air without mercury pre-concentration in absorption traps. The RP-91, RP-91C and PYRO-915 attachments are used for mercury determination in water, soils, foodstuff, and oil samples.

RESULTS AND DISCUSSION

Air. The range of detected mercury concentrations extends from as low as 0.3 ng/m^3 background concentrations in air to as high as up to 200 μg/m^3 concentrations in heavily contaminated areas. High throughput and the low detection limit provide effective mapping of the mercury contamination sources, monitoring of stack gases, and study of fluctua-

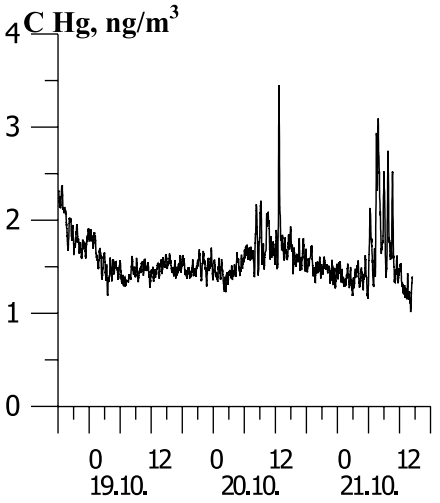

Figure 1. Mercury in ambient air. Thee-days monitoring. Averaging time 30 sec. 18-21.2002. Center of St. Petersburg Russia. –3+2 °C (rain and snow).

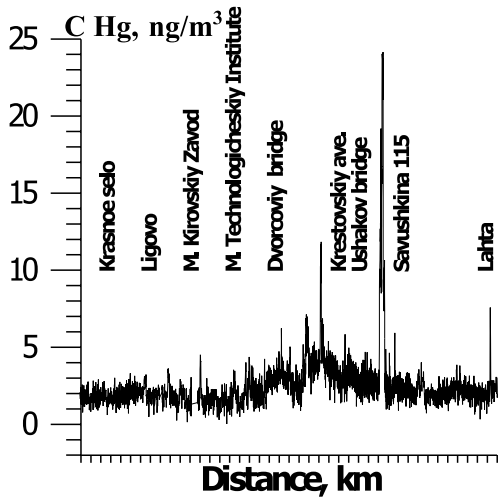

Figure 2. Mercury distribution in ambient air. Continuous car survey at a speed of 40-60 km/h, (07.06.2001, St. Petersburg, Russia.

tion of background mercury concentration. As an example, 3-days monitoring (18-21.02.2002) of the ambient air in the downtown of St. Petersburg, Russia, shows that the average and maximum concentrations were 1.8 ng/m^3 and 6 ng/m^3, respectively (Fig. 1). At the same time, very localized areas with relatively high mercury concentrations due to pollution of industrial enterprises were found during a car survey (Fig. 2).

Water. When the RA-915+ mercury analyser is used with the RP-91 attachment, a very low detection limit of 0.5 ng/l for mercury in water samples is attained, the sample volume being 10 ml and no mercury pre-concentration being used. The highest mercury concentration of 18 ng/l in natural water of St. Petersburg was found in the river Okhta.

Solids. The high selectivity of the RA-915+ provides, with the RP-91C attachment, direct mercury determination in such solid samples as sand, rocks, solids, and sediments without any sample pre-treatment. The analysis duration for an individual sample is one minute, 25 samples per hour can be manually processed during an 8-hour day with an average of 2.4 minutes per sample. The RA-915+/RP-91C combination was tested in field conditions[2]. Results of field determination of mercury in soil and sediment using Ra-915+ are illustrated in Fig. 3. The accuracy (95 % for SRM) and precision of the instrument was better than those for results obtained at a reference laboratory (the average RSD at reference laboratory was 22.3 %, whereas the average RSD for RA-915+ was 16.1 % or 7.6 % for SRM). EPA stated: "During the Demonstration, the RA-915+/RP-91C combination exhibited the following desirable characteristics of a field mercury measurement device: good accuracy compared to SRMs, good precision, good sensitivity, high sample throughput, low measurement costs, ease of use. The Demonstration findings collectively indicated that theRA-915+/RP-91C combination is a reliable field measurement device for mercury in soil and sediment".

A new attachment PYRO-915 was developed to determine mercury content in complex-matrix samples (foodstuff, crude oil and its products, biological materials) without sample pre-treatment. The attachment shows high efficiency of decomposition of the organic matrix. This method allows efficient testing of foodstuff for the compliance with Ultimate Tolerable Concentrations (see Table). In this case, a representative sample weight of more than 50 mg is ensured. The method is especially convenient for testing fish and seafood – in each sample we found appreciable mercury content.

Figure 3. Field test of EPA, Oak Ridge, USA May 2003

Table 1. Determination of total mercury in foodstuff using RA-915+ and PYRO-915.

Sample	Ultimate Tolerable Concentrations, ppb	Maximum sample weight, mg	Detection limit, ppb
Fish	300-700	300	0.5
Bread	10	>300	0.5
Cheese	30	120	2
Sausages	30	300	0.5
Tea	100	100	2
Sugar	10	40	5
Chocolate	100	100	2
Vegetables, (fruits)	20	>300	0.5

CONCLUSIONS

It should be noted that, in various samples (air, water, soil, food, coal, oil, etc.), the mercury concentrations were determined using a same RA-915+ spectrometer with different attachments to convert bound mercury to its atomic form. For all of the analyses of gaseous, liquid, or powder samples, the sample pre-treatment for the mercury determination was either absent at all (gaseous samples) or it was done in real time.

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Certification of total and methyl- mercury contents in tuna to provide reference values for international laboratory comparisons (IMEP-20 and CCQM P-39)

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Abstract: The Hg and CH_3Hg mass fractions were certified in a tuna material intended for distribution as a test sample for the Comité Consultatif pour la Quantité de Matière, CCQM, pilot study 39 and International Measurement Evaluation Programme, IMEP-20 laboratory inter-comparisons. Certification measurements were made by isotope dilution, ID, for Hg and by species-specific isotope dilution, SSID, by blending samples with ^{202}Hg enriched inorganic Hg and CH_3Hg isotope certified reference materials, ICRMs. Samples for total Hg were microwave digested and isotope ratios were detected by inductively coupled plasma mass spectrometry, ICP-MS. CH_3Hg was specifically detected by acid-leaching of the tuna, liquid-liquid extraction, derivatisation and separation by gas chromatography, GC, before ICP-MS. ID was applied as a primary method of measurement, for both analytes with the mass fractions traceable to the SI with uncertainties calculated according to ISO guidelines. The mass fraction of total Hg with expanded combined uncertainty, k=2, was 4.32 (16) x 10^{-6} g (Hg)·g^{-1}, which corresponds to a molar content of 21.53 (79) x 10^{-6} mol (Hg)·kg^{-1}. The mass fraction of Hg in the form of CH_3Hg, in the tuna sample, was 3.95 (25) x 10^{-6} g (Hg)·g^{-1}, which corresponds to a molar content of 19.7 (1.3) x 10^{-6} mol (Hg)·kg^{-1}.

Keywords: methylmercury, isotope dilution, certified reference material, SI-traceability, uncertainty budget

INTRODUCTION

The Comité Consultatif pour la Quantité de Matière, CCQM, (or International Committee for Weights and Measures), has the tasks to co-ordinate the activities of national metrology laboratories in establishing traceability of measurements to the SI and to stimulate understanding of the concept of uncertainty and assignment of uncertainty statements to measurements. CCQM working groups develop and execute international comparisons to establish the technical basis for the mutual recognition of measurement capabilities. In 2003, IRMM, the metrology institute of the European Commission, launched CCQM pilot study 39 on the measurement of pollutants including Hg and CH_3Hg in tuna. The tuna was also distributed for the inter-laboratory comparison 20 of the International Measurement Evaluation Programme, IMEP. IMEP studies offer to all interested laboratories the possibility to demonstrate their performance. The aims were to strengthen the comparability of measurements EU member states are obliged to make

under EC regulation 466/2001 (monitoring of contaminants in food) on the total element contents, and to evaluate the comparability of CH_3Hg measurement with new measurement techniques. The IRMM contribution to CCQM-P39 for the determination of the tuna's Hg and CH_3Hg amount contents was based on isotope dilution mass spectrometry, IDMS, applied as a primary method of measurement. The same values, with established traceability to the SI and adequately small uncertainty statements, were used as independent reference values for IMEP-20, thus allowing the participants to objectively picture their degree of equivalence and quality of chemical measurements.

Results and Discussion

For total Hg, isotope ratios were measured in microwave digested blends of tuna and IRMM-640 (a ^{202}Hg enriched isotopically certified reference material, ICRM) by an ICP-MS method optimised to eliminate Hg memory effects and maximise repeatability of measurements. For CH_3Hg, IRMM-670, a newly developed ^{202}Hg enriched CH_3Hg ICRM[1] was blended to the tuna sample from which Hg species were extracted and derivatised to non-polar forms. Gas chromatography inductively coupled plasma mass spectrometry, GC-ICP-MS, was used for Hg species separation and detection of the $n(^{200}Hg)/n(^{202}Hg)$ ratio in signals corresponding to CH_3Hg, of the blended material. The SI-traceable CH_3Hg amount content was then obtained through IDMS comparison with the IRMM-670 reference CH_3Hg amount content (including the isotopic compositions of natural Hg recommended by IUPAC, and certified for CH_3Hg in IRMM-670). In developing the CH_3Hg measurement method and the associated uncertainty budget, a number of parameters affecting measurements were studied, including the detector dead time correction and instrumental background correction of transient signals, and the degree to which the spike material equilibrated with incipient CH_3Hg in the tuna. IRMM-639, a natural-like Hg reference material with certified isotopic composition, was used to calibrate measurements by monitoring dilutions or extracts (derivatised for GC) of this material, between sample measurements.

The uncertainties associated with the results were estimated according to ISO/GUM. Budgets combined the individual uncertainty contributions attached to all identified experimental steps involved in the measurements. For the measurement of both analytes, it was necessary to assess the moisture content and hygroscopicity of the tuna. The moisture content was determined by an oven-drying gravimetric method, at a temperature optimised to preserve volatile components of the sample matrix (85 °C). Hygroscopicity of the tuna was estimated by opening bottles of the tuna, under the same environmental conditions, temperature and humidity, as sample weighing, and measuring the increase in mass of the bottles over time. A mathematical relation was used to relate the percentage mass gain to the time after opening so that the increased moisture contents of samples for blending could be calculated from the time after opening the sample bottle. Mass increases were between 0.01 and 0.03 % and were added to the water content for analyte mass fraction calculation.

For total Hg, the major contributions to the CCQM uncertainty budget were the uncertainties in the moisture content and the natural isotopic composition of the sample. The relative standard deviation of the ID-ICPMS measured Hg content was only 0.91 %, which lies within the calculated uncertainty. For CH_3Hg, the degree to which isotope equilibration could be established was found to be the most significant. This was assessed using comparing SSID measurement results for reference material BCR-464 (tuna) with the certified CH_3Hg content of the material. The relatively high uncertainty was therefore dependant on the ability to which our measurements could prove that isotope equilibration had occurred (with this material, which has a similar matrix to the sample tuna). As shown in the table, identification of the relative uncertainty contributions from each of the experimental processes allowed optimisation of the measurement procedure.

The 9 CCQM-P39 participants that measured CH_3Hg by SSID provided results with a standard deviation of 1.9 % (n=8, excluding 1, 2s outlier). Of these, 6 used IRMM-670 certified values, without re-characterisation of the material. The value submitted by IRMM lay 0.4 % from the mean, which provided an additional validation of the CH_3Hg measurement.

For the IMEP-20 study, the certified amount contents were required to be valid for all bottles distributed. The homogeneity of the Hg content was therefore independently assessed. As most of the Hg in the tuna was present as CH_3Hg, the uncertainty contributions from sample inhomogeneity were incorporated into the budgets for both analytes.

Table 1. Contributory factors to the uncertainty of the measured mass fractions

Contributory factor	*U on Hg, %*	*U on CH_3Hg, %*
$n(^{200}Hg)/n(^{202}Hg)$ IRMM-639	6.8	0.6
$n(^{200}Hg)/n(^{202}Hg)$ IRMM-670	*n/a*	1.0
Background correction	1.1	0.4
Blend ratio measurement	4.6	24.3
Deadtime correction	0.6	4.0
Isotope equilibration factor	*n/a*	51.1
IUPAC Hg isotope abundances	30.3	2.4
K-factor ratio measurement	1.3	4.1
Moisture content, oven-drying	36.1	3.3
Other factors	0.0	0.7
Spike concentration	18.4	8.1
Total expanded uncertainty (k = 2)	**1.7**	**5.6**

CONCLUSIONS

Hg and CH_3Hg amount contents were certified in a tuna material with low uncertainties. Investigations were made into all factors affecting the uncertainty of the experimental processes. IDMS and species-specific IDMS were used as primary methods of measurement, which together with the use of IRCMs with SI traceable values, allowed the certified Hg and CH_3Hg amount contents in the tuna to also be SI-traceable.

Acknowledgements

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A new ^{202}Hg isotopically enriched methylmercury spike material with SI-traceable reference values for isotope dilution measurements in biological and environmental samples

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Abstract: HgO enriched in ^{202}Hg was used for the preparation of a solution of ^{202}Hg enriched CH_3Hg. The CH_3HgCl was synthesised by reaction with a Grignard reagent and a subsequent comproportionation reaction between dimethylmercury, $(CH_3)_2Hg$, and $HgCl_2$, that was optimised to give a high yield of the product, pure from other Hg species and by-products of the synthesis reaction. To prepare the CH_3HgCl for use as an IDMS spike, it was dissolved in 2 % ethanol. Aliquots were sealed in quartz ampoules and a 1-year stability study was undertaken by storing a series of ampoules under different temperature conditions to all be measured on the same occasion (an isochronous study) and by retaining a portion of the solution in a closeable bottle under recommended storage conditions, with measurements at 3-month intervals. The Hg amount content in the form of CH_3Hg was obtained by subtraction of the inorganic Hg amount content (determined by gas chromatography inductively coupled plasma mass spectrometry, GC-ICP-MS) from the total Hg amount content (determined by blending with IRMM-639, a natural Hg isotopic certified reference material, ICRM, and isotope dilution mass spectrometry of the digested material). Only CH_3Hg and inorganic Hg were detectable in the reference material with inorganic Hg in <2 % of the total amount. GC-ICP-MS was also used to confirm that the isotopic composition of Hg in the form of CH_3Hg was identical to that of IRMM-640, an inorganic Hg ICRM prepared from the same ^{202}Hg enriched HgO, within enlarged uncertainty statements. These processes allowed the SI-traceable certification of both the amount content of CH_3Hg and its isotopic composition, accompanied by combined uncertainty statements estimated according to ISO/GUM.

Keywords: methylmercury, isotope dilution, certified reference material, SI-traceability, uncertainty

INTRODUCTION

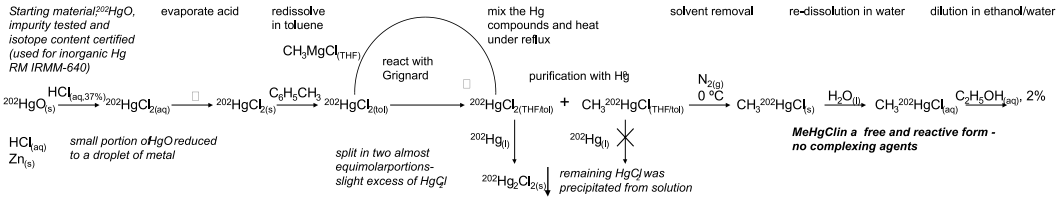
To be comparable measurement results must be traceable to the same units of the same system of reference. The Comité Consultatif pour la Quantité de Matière (CCQM)[1] recognised IDMS as a potentially primary method of measurement[2] in that its operation can be completely described and understood, and a complete uncertainty statement can be written down in term of SI units. IDMS rests on the principle of measuring the change in the isotopic composition of the element measured from the addition of some

isotopically enriched material to the sample of interest. For IDMS measurements to be species-specific, the species of the element in the added spike must be identical to that under scrutiny in the sample. Evidently, this material must be reliably characterised for the isotopic composition and the amount content of the element in (its particular chemical form) so that additional measurement biases and uncertainties associated to the characterisation step are eliminated.

A standard was certified for CH_3Hg amount content and isotope composition. A 1 year isochronous stability study was undertaken, the results of which permitted the estimation of an uncertainty contribution covering for potential changes over 2 years of shelf life. With this material the "Direct" IDMS model, based on the measurement of isotope amount ratios in a sample-spike blend can be applied.

Results and Discussion

The method for $CH_3{}^{202}HgCl$ synthesis was adapted from the one described by Snell *et.al.*[3] for milligram amounts of isotopically enriched methylmercury. After conversion to $HgCl_2$ with hydrochloric acid, evaporation of the acid and dissolution of the remaining solid in toluene, a portion of the solution is separated for reaction with $MgCH_3Cl$ to form $(CH_3)_2Hg$. A comproportionation reaction is utilised by mixing ^{202}Hg enriched $(CH_3)_2Hg$ and $HgCl_2$ to form CH_3HgCl. A slight molar excess of inorganic mercury was added to ensure that no $(CH_3)_2Hg$ would remain. To remove the inorganic Hg remaining in the material after the comproportionation step, the reaction of elemental Hg with $HgCl_2$ to form Hg_2Cl_2 was used, as this Hg species is effectively insoluble in both toluene (the reaction medium) and water. CH_3HgCl does not undergo an analogous reaction, but remains unchanged in the presence of Hg^0. After decantation to remove the inorganic Hg, toluene was evaporated and the solid residue was re-dissolved in water, as the ICRM was required to be in an aqueous form, to be miscible with biological matrices. The material was diluted in 2 % ethanol and aliquots were sealed in quartz ampoules. The ampoules measured for certification contained 1.95 % of the total Hg as inorganic Hg, which was highly enriched in ^{202}Hg indicating that no contamination with natural Hg had taken place.

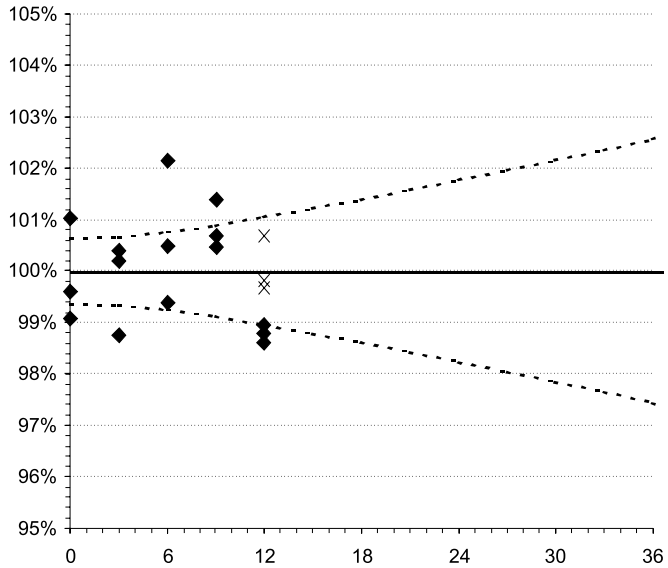


Two stability testing schemes were run concurrently over 12 months. In the first, 50 ml of the solution that remained after ampoulation was transferred to a screw cap glass bottle. This was stored at -20 °C and the CH_3Hg concentration of the contents was measured at 3, 6, 9 and 12 months by SSID. In this study the concentration did not change over the time period by more than the repeatability of measurement (0.66 %). Secondly, an isochronous study was undertaken in which 18 ampoules of the produced can-

didate reference material were stored under different temperature schemes After 12 months, relative CH_3Hg contents were measured in each of the 18 ampoules, in this way reducing the uncertainty on measurement that would otherwise be introduced by measuring samples on different occasions[4]. No difference in concentration was found between sets of ampoules stored under different conditions. The increase in uncertainty in the certified CH_3Hg content over time was predicted by calculation based on Linsinger, *et al*.[4] The degree to which the stability study proved that the CH_3Hg content is stable over time was taken as the uncertainty (k=1) of a unity factor, to be propagated to the CH_3Hg content. The figure depicts the extrapolation derived from reference to give the uncertainty component arising from a 24 month shelf life was obtained (r.s.u. = 1.65 %, k = 1).

The isotopic composition of Hg present as CH_3Hg in IRMM-670 was measured by GC-ICP-MS and was found to be the same as that of the inorganic Hg ICRM, IRMM-640, which was produced from the same enriched starting material, within the estimated uncertainty of measurement. To avoid assigning the relatively large uncertainties associated with transient signal measurement for the species-specific technique, IRMM-640 isotope ratios were assigned to IRMM-670, with enlarged uncertainty statements that more than covered any difference between the values.

The amount content of $CH_3{}^{202}Hg$ was given by the subtraction of the inorganic Hg content, measured by GC-ICP-MS with external calibration, from the total Hg content, measured by IDMS on digested samples. As



Diamonds represent CH_3Hg amount contents, relative to the average of samples stored at -20 °C for 12 months, of the ampoule sets for the isochronous study, stored at 4 °C for the periods indicated. Crosses are the relative CH_3Hg amount contents of an ampoule set stored at +20 °C for 12 months. Lines represent the predicted increase in uncertainty due to CH_3Hg content stability and include contributions (constant over time) from the uncertainty of measurement of the CH_3Hg content and the uncertainty due to between-ampoule homogeneity

the inorganic Hg content was less than 2 % of the total and no other species could be observed in IRMM-670, the CH_3Hg amount content could be certified with relatively low uncertainty. The final uncertainty on the amount content was 3.5 % (relative, k=2), which included the contribution covering a 2 year shelf-life.

Material : $CH_3{}^{202}HgCl$ in 2 % ethanol/water

amount content	Certified value	Uncertainty [1]
mol $(CH_3(^{202}Hg)Cl) \cdot g^{-1}$	$171.0 \cdot 10^{-9}$	$6.1 \cdot 10^{-9}$
mol $(CH_3HgCl) \cdot g^{-1}$	$175.1 \cdot 10^{-9}$	$6.2 \cdot 10^{-9}$

isotope amount ratios of Hg in the form of CH_3HgCl	Certified value	Uncertainty [1]
$n(^{196}Hg)/n(^{202}Hg)$	0.000 018	0.000 013
$n(^{198}Hg)/n(^{202}Hg)$	0.000 623	0.000 050
$n(^{199}Hg)/n(^{202}Hg)$	0.001 603	0.000 096
$n(^{200}Hg)/n(^{202}Hg)$	0.005 50	0.000 22
$n(^{201}Hg)/n(^{202}Hg)$	0.013 35	0.000 53
$n(^{204}Hg)/n(^{202}Hg)$	0.002 60	0.000 16

molar mass of Hg in the form of CH_3HgCl	Certified value	Uncertainty [1]
$g \cdot mol^{-1}$	201.944 66	0.000 76

1) All uncertainties are expanded uncertainties, with a coverage factor, k = 2

CONCLUSIONS

Ampoules of IRMM-670 are now available for distribution as an ICRM.

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Transfer of Know-how and Knowledge in the Area of Speciation Analysis from Research Institutions to Industry - The European Virtual Institute for Speciation Analysis (EVISA)

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Abstract: The Virtual Institute for Speciation Analysis (EVISA), a project funded by the EU for a maximum period of three years has started its operation. The Virtual institute acts as a provider of information, knowledge and know-how for the European industry and other clients seeking for information related to speciation. Available and foreseen services will be discussed.

Key words: speciation analysis, virtual institute, knowledge transfer, analytical services

INTRODUCTION

Today, there is little doubt that the role of speciation is crucial to answer the demanding questions about the activity and properties of trace metals and metalloids, such as their bioavailability, biological and chemical activity, toxicity or metabolism. Also it is clear that the environmental cycle of "elements", their transport, deposition, transformation and fate cannot be understood without the knowledge of the species involved. This is evident in the case of mercury, where the different occurring mercury species, e.g., elemental mercury, ionic mercury, methylmercury are present in different physical states (gaseous, liquid, solid) having totally different chemical properties. The important role of speciation analysis is well established within the scientific community and visible through the high publication rate in that area that has reached about 500 publications/year. However, despite all the developments in this area during the last decades, speciation is not yet well established in industrial analysis and other "real world" applications and is far away from being performed on a routine basis. Also, despite the fact that elemental information is not good enough to answer all questions about the activity of elemental species, few rules, regulations or laws require to get or use the necessary information about speciation. One of the reasons for this discrepancy is the lack of an efficient link be-

tween research scientists and potential users, regulators and policy makers resulting in insufficiently organized and synthesized information for their decision making process. Scientific publications and even more so scientific conferences are vehicles of a closed system with scientists informing each other. A first approach to break out of this closed system was made 1997-2000 by the thematic network "Speciation 21"[1-3] in which a link was created between scientists working in speciation method development and potential users from industry and of legislative agencies, in the field of environment, food and occupational health and hygiene. This link was established through a set of 8 meetings, 2 newsletters and a book about the state of the art and future perspectives in the field[4]. The Speciation 21 network has been very useful to establish the state-of-the art of speciation measurements and create links among the scientific community and representatives of different industrial sectors. But unfortunately, it has not been satisfactorily ensured a transfer of knowledge to industry nor developed awareness for speciation analyses and thus analytical servicing which could be of great benefit to various European industries and regulatory bodies.
In order to continue this initiative and to improve the mentioned interaction, a project supported by the European community has been launched, meant to combine the expertise of some of the most renowned research laboratories, industrial users, governmental facilities and manufacturers[5].

The principal aim of the project that manifests itself by the establishment of a European Virtual Institute for Speciation Analysis (EVISA) is to facilitate the transfer of the knowledge collected within the "Speciation scientific community" to potential users facing "real world" problems in industry, food and environmental issues and to facilitate its integration in far more effective legislative actions[6]. In order to fulfill its aims, EVISA is in the process to establish a bundle of services via its web portal that can be reached at http://www.speciation.net. Services provided are meant to enhance the information flow between scientists and potential "customers" and to improve the communication between scientists of different disciplines working in the field of speciation. All type of information related to speciation will be collected, discussed, evaluated and disseminated via appropriate tools, such as databases, a news section, link collections, discussion forums and a Speciation Newsletter.

It is estimated that in excess of 1 % of gross domestic product in the European Union is devoted to chemical measurement and testing. It is thus important that such measurements are highly informative, valid and cost-effective. Methods collected from the scientific world and made available through the Virtual Institute should be fit-for-purpose for the determination of chemical species in industrial products (both for product characterization and risk assessment studies). These methods should be robust and reliable to offer real benefits for industrial users. Open discussion of problems, pitfalls and artifacts of existing methodology combined with intercomparison exercises within the EVISA leading to Standard Operating Procedures will provide readily available solutions for the main species of concern. To enhance further the quality of speciation analysis, EVISA will organize and provide quality related training activities in different places in Europe and e-learning materials via its web

portal. Empowering young scientists for enhanced mobility through a network of research centers and laboratories being actively involved in the development of speciation related methodology is another way to enhance their education and knowledge.

Industry will find an effective and easy to use interface to place their questions, to discuss requirements and demands, and to order analytical services. The innovative Virtual Institute will finally interact and inform all major institutional European agencies of the current evolution of industrial demands, inform of the state-of-the-art of the current academic knowledge to help in the definition and promotion of most effective legislative regulation and action. By these combined activities EVISA will integrate European competence in the field into accessible and powerful tools supporting many industrial sectors.

EVISA has the ambition to become a Europe-wide well-known address where any customer can easily get answers to his element speciation related questions. Excellent working relationships shall be developed with European, other international or supranational bodies and also national instances that have a role in standardisation and regulation for the advancement of speciation related legislation. It is EVISA's objective to become an efficient network of partners, improving their cooperation, access to research projects, quality of education and visibility against politicians and the whole society.

Acknowledgements

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Testing of the total mercury content in the different samples of oil and gas condensate

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Abstract: With due respect to the high importance and interest for the problems of mercury content in oil industry, the objective of the present researches is the development, introduction and verification of the appropriate measurement methodology (identification and quantification) of the mercury in liquid carbohydrates. Towards this goal, the sampling of 8 oil and 2 condensate samples from oil and gas production plants in Croatia has been conducted. The researches were carried out by making use of the Mercury analyzer AMA 254 apparatus. In addition to the determination of the total mercury content, the comprehensive standard researches (determination of physical and chemical characteristics etc.) on all samples have been carried out.

INTRODUCTION

Mercury analyzer AMA 254 is an easily applicable atomic absorption spectrophotometer for determining the total mercury content in liquid and solid samples without the previous preparation of the sample. The technique of generating (collecting) the vapors are used, which has a high sensitivity and is independent from the sample matrix.

WORKING WITH THE APPARATUS

Liquid and solid samples can be analyzed, without any preparation. The known weight of the solid sample or the known volume of the liquid sample is placed in the vessel (10 µl - 1000 µl). In the case of petrol or condensate, which are explosive substances, the layer of Al_2O_3, is placed into the vessel – the quantity of the sample being 30-50 µl. By the corresponding software application running the whole process, the vessel is introduced into the catalytic tube. By the controlled heating of the decomposition furnace, the sample is first dried, and then thermically decomposed at 550 °C. The products of the decomposition are led to the amalgamator which selectively traps the mercury. The amalgamator and the measuring cuvettes are maintained at 120 °C in order to prevent the condensation of the water. The trapped mercury is released from the amalgamator by a short period of heating, and with the bearing gas, oxygen, which has a constant flow through the whole instrument, than led through the measuring cuvette to the detector. One part of the detector is the interference filter, isolating the spectrum line at 253.65 nm. All measured data are transferred to the personal computer and thus can be read directly.

The low pressure mercury lamp is used as the source of light.

Detection limit: 0,01ng Hg

There are two areas of measurement:

1) 0,05 - 40 ng Hg
2) 40 – 60 ng Hg

RESULTS AND DISCUSSION

Intention of the established program has been to determine the actual and real concentration of mercury in the produced gas condensate and crude oil (Figure 1.) before transporting for the treatment, Table 1. and Table 2. The main objective was to establish a database of hydrocarbons quality (total mercury measurements) at production site to assess worker and community exposure, and to provide guidance for processing activities.

Table 1. The results of the total mercury measurement in gas condensate

Sample reference code	Concentration Hg(ng/g)	Mean Value	Standard deviation SD	Relative standard deviation RSD (%)
1.PS Stari Gradec	425.57	432.05	8.29	1.92
	429.18			
	441.40			
2. PS IP Kalinovac	451.34	440.83	9.10	2.06
	435.34			
	435.81			

Table 2. The results of the total mercury measurement in oil

Sample reference code	Concentration Hg(ng/g)	Mean Value	Standard deviation SD	Relative standard deviation RSD (%)
1. Đeletovci	3.71	3.85	0.12	3.19
	3.90			
	3.94			
2. Benièanci	14.80	14.85	0.19	1.31
	14.68			
	15.06			
3. Lipovljani	2.96	2.86	0.10	3.50
	2.87			
	2.76			
4.Ferdinandovac	5.15	5.07	0.20	3.99
	4.99			
	5.07			
5. Šandrovac	2.90	2.77	0.15	5.27
	2.79			
	2.61			
6. Stružec	4.05	4.18	0.13	3.11
	4.18			
	4.31			
7. Kloštar*	6.38	6.61	0.23	3.41
	6.83			
	6.63			
8. Žutica	15.68	15.89	0.51	3.22
	15.51			
	16.47			

*The Kloštar oil contained free water that was subsequently separated.

The amount of the sample – condensate that was used for determining the total mercury is 50µl, and for oil it is from 50 – 100 mg. It can be found in the referential literature that the reproducibility is better than 1,5 % for a volume greater than 50 µl.

Figure 1. The oil and gas condensate samples

CONCLUSIONS

This research has confirmed that the reliability of the mercury measurement results in liquid hydrocarbons is a critical and essential stage for sampling the samples.

Further researches are necessary in order to introduce optimum sampling methods and confirm the reliability of the mercury measurement results in liquid hydrocarbons. It would reveal the appropriate steps to be taken in a timely manner to protect and enhance the working and living environment as well as to insure the safe operation of process plants.

Intercomparison of Manual and Automated Methods for determining RGM Concentrations over the Mediterranean Sea During the Summer 2003 and Spring 2004

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Abstract: Resent research on atmospheric mercury species in the troposphere have shown surprisingly high RGM concentrations compared to measurements from anthropogenic source areas suggesting that the marine boundary layer (MBL) may be a source of RGM. Ambient measurements of atmospheric mercury species were performed during two intensive cruise campaigns in summer 2003 and Spring 2004. An intercomparison for sampling and analysis of atmospheric gaseous divalent mercury species was held during the cruises.

Key words: mercury, Mediterranean, intercomparison, RGM.

INTRODUCTION

Mercury is found dispersed around the planet with uniform hemispherical background concentrations due to Hg^0 volatility, insolubility and its relatively low rate of oxidation by the major oxidants in the atmosphere. On the basis of the O_3 gas phase oxidation rate constant, the atmospheric Hg residence time has been estimated to be between six and twelve months (HALL, 1995, SHIA ET AL., 1999); therefore, Hg^0 is capable of being deposited anywhere around the globe including remote environments such as the Arctic and the Antarctic. In contrast, gas phase oxidised Hg compounds, commonly referred to as Reactive Gaseous Mercury (RGM), have an atmospheric residence time of days because of their lower volatility and higher solubility, therefore RGM is rapidly scavenged by fog or cloud droplets or by condensation onto atmospheric particles, influencing its dispersion from its source. Deposition fluxes of mercury species from the atmosphere to receptor bodies thus depend on the chemical and physical properties of the species involved and their cycling, from speciated emission via transport, deposition, interaction with biota and possible re-emission to the atmosphere. The discussion developed during the last couple of years among those involved in atmospheric mercury research, thus addresses the re-evaluation of the importance of mercury oxidation processes in order to estimate mercury deposition fluxes and re-emission to the atmosphere. Recently, with the improvement of RGM sampling techniques investigations of the atmospheric

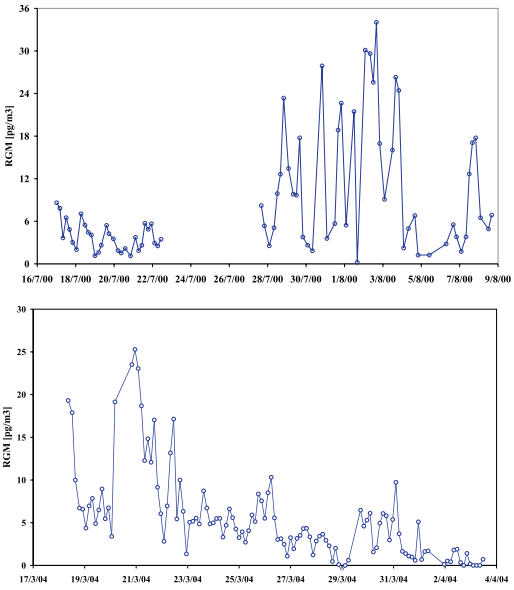
chemistry of Hg have been performed in Florida (STEVENS ET AL., 1999) and across Europe (MUNTHE ET AL., 2001; WANGBERG ET AL., 2001; PIRRONE ET AL. 2003), as well as in remote environments such as the Arctic and Antarctic (SPROVIERI ET AL., 2002). The aim of this paper is to present the RGM measurements performed during two intensive cruise campaigns over the Mediterranean Sea region and discuss, in particular, RGM results obtained from an intercomparison experiment performed on board the Italian Research Vessel (URANIA) in collaboration with the Swedish Environmental Research Institute (IVL) and Technion University using both manual and automatic techniques. The two sampling campaigns were performed along a 6000 km cruise path over the western and eastern sector of the Mediterranean Sea during summer 2003 and spring 2004 in the framework of the MED-OCEANOR project.

EXPERIMENTAL

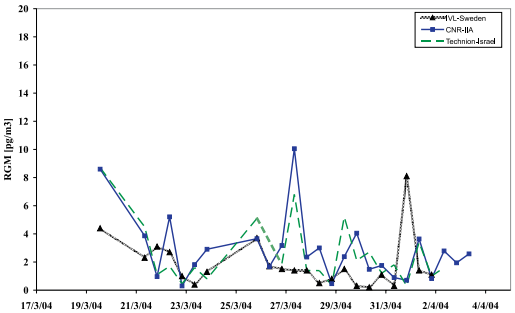
Ambient RGM concentrations were sampled by collection on KCl-coated annular denuders by both manual and automatic techniques. Annular denuders chemically pre-treated during the acid-cleaning step, were recoated by soaking in saturated KCl solution. During the campaign denuders were recoated and changed regularly in order to obtain a collection efficiency > 99 %. Automated sampling and analysis was performed using the Tekran Model 1130 Mercury Speciation Unit coupled to a mercury vapour analyser (Tekran 2537A). RGM collected at a flow rate of 10 Lpm, after 2 hours sampling time is desorbed at 500 ^{0}C to thermally decompose and reduce it to elemental mercury for analysis by a Tekran 2537A CVAFS downstream of the denuders. RGM was sampled manually with 12-hour time resolution at the same flow rate as the automatic sampling; the denuders were then purged with argon, desorbed at 500 ^{0}C and analysed by CVAFS using a Tekran 2537A analyser.

RESULTS AND DISCUSSION

One of the major findings of this study is that RGM observations suggest that there is a constant presence of oxidised Hg compounds in the MBL and thus a continual production of the most probable candidate which make up atmospheric RGM, $HgCl_2$. Figure 1 and Figure 2 show RGM concentration - time series collected during the two Med-oceanor campaigns. The RGM concentrations measured over the eastern sector of the Mediterranean Sea for both the cruises are lower than those obtained over the western sector of the basin. These results confirm the RGM behaviour observed during the 2000 cruise



campaign (SPROVIERI ET AL., 2003). There are, in fact, different RGM production processes: direct emission from anthropogenic sources, gas phase oxidation processes and out-gassing of $HgCl_2$ from deliquesced aerosol particles (HEDGECOCK AND PIRRONE, 2001).RGM is known to be emitted from industrial sources, but due to its chemical-physical properties it has an atmospheric lifetime of a few days therefore it can be transported only for short distances from its point of production thus high RGM concentrations are usually found close to emission sources. The anthropogenic contribution, in this case, could be negligible considering that RGM measurements were performed in open sea far from local sources. Moreover, the RGM concentration follows a diurnal cycle, increasing after sunrise and decreasing towards evening with the highest concentrations occurring around midday. The clear diurnal fluctuation in RGM concentrations in particular, the low nocturnal RGM concentrations could exclude the possibility that the high RGM values represent transport from anthropogenic sources (HEDGECOCK ET AL., 2003). The more probable sources of RGM, therefore, are the gas phase oxidation of Hg^0 and the out-gassing of $HgCl_2$ from aerosol particles. $HgCl_2$ may be indirectly produced by the gas phase oxidation of Hg^0 and OH (HEDGECOCK ET AL., 2001) which leads to the production of HgO; the latter due to its efficient scavenging by the aerosol particles is transferred to the aqueous phase where reacts with H^+ ions producing Hg^{2+} (HEDGECOCK ET AL., 2001; SPROVIERI ET AL., 2003). The RGM intercomparison employed during the two (MedOceanor 2003 and MedOceanor 2004) campaigns with the Swedish Environmental Research Institute (IVL) and Technion University showed that both methods produced very comparable results. Figure 3 gives the results from the experiment. The RGM results obtained during MedOceanor 2003 showed RGM concentrations higher than those measured during MedOceanor 2004 (see Fig 1 and 2) reflecting the potential influence of the meteorological factors on RGM. The 2004 campaign was performed during spring, from 17th of March to 5th of April and the meteorological condition in the Mediterranean region were quite different to those during the summer 2003 campaign (from 4th of August to 27th of August). The 2004 measurements were, in fact, characterised by rough seas and bad weather which caused high Liquid Water Content (LWC) in the troposphere over the sea and in particular at the height where the measurements were performed (10 m a.s.l.). Therefore, under these conditions, RGM scavenging was very efficient because of the high Henry's Law constant of both HgO and $HgCl_2$. Ambient concentrations of RGM are strongly affected by the LWC which is thought to influence the balance between scavenging and outgassing of Hg(II) from the aerosol. In order to improve our knowledge of the chemical-physical processes discussed above, our next step will be a third MED-OCEANOR campaign planned for October-November 2004 following the same route and performing more highly time-resolved RGM measurements in the MBL



along with measurements of other chemical species i. e. halogens and major ions. The RGM results will provide necessary data to support the development of chemical models to clarify the role played by the RGM in atmospheric mercury chemistry and its significance to the spatial distributions of Hg fluxes on hemispheric and global scales.

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Mercury in soils: Whether the accurate analysis is a guarantee of correct result

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Abstract: The attempt to quantify possible errors arising at mercury determinations in soils is undertaken. Changes of the mercury content in samples have been supervised on all analytical stages - sampling, storage, drying, sieving, milling, and analysis. The study of sampling and storage is based on periodical determinations of mercury concentration in soil samples and some reference materials. Wrong packing and bad storage conditions can result both in loss and infecting of samples. The study of sample preparation has been carried out in the specially designed chamber. The greatest losses of mercury occur at milling and can achieve 50 %. The losses depend on initial concentration of mercury, structure of soil, method and time of milling. The revealing of sources and quantitative rating of errors allow providing conditions for correct determination of mercury in soil.

Key words: accuracy, analysis, soil, reference materials.

INTRODUCTION

The correctness of analytical results has the great importance for assessment of an ecological situation. The unusual physical and chemical properties of mercury are responsible for its high mobility in nature and possibility to change one form to other under the action of various factors. Evaporation, sorption and desorption can result in distortion of mercury concentration in samples even before the analysis. The good agreement of analytical results with values for the certified reference materials is only proof of correctness of mercury determination in the prepared samples but not conformity of these data to concentrations in initial samples. The contribution of an analytical method to a total error of determination is least from all analytical procedures. Therefore there is not important what analytical method is used for determination of mercury in the prepared samples. The stages of the sampling, storage and sample preparation before this analysis are more important for correctness.

The attempt to quantify possible errors arising before mercury determinations in soils is undertaken. Study was carried out in specially designed chamber connected to AA mercury analyzer RA-915+. Soil was placed into the chamber and subjected to various actions (different stages of sample preparation) - drying under a quartz lamp, sieving, milling in agate mortar and sampling for the analysis. The concentration of mercury in air through the chamber measured in real time.

Changes in concentrations of mercury in soil and some certified reference materials as a result of long storage in various conditions have also been studied.

RESULTS AND DISCUSSION

Sampling of soil breaks the equilibrium in soil environment and part of mercury weakly bound with particles leaves the soil (soil gas). This process is difficult to check and evaluate quantitatively, but loss can be 10 % and more at small concentration. Use of the tools from different materials also can lead to changes in concentration (ZAICHIK, 1996).

Storage. The variations at storage depend on time and conditions of storage as well as packing material. Wrong packing and storage can result both in loss and infection of samples. The information about permeability of various packing materials to mercury vapor was reported in STAKHEEV (1976). To study influence of a storage time the concentration of mercury in some reference materials have been periodically determined from the end of 70s. Samples were packed into a tracing-paper, polyethylene bags and plastic cans (packing of the manufacturer). The results are contradictory because for different samples concentrations changed variously. Apparently it is necessary to find quantitative dependences between concentration of mercury and soil composition.

Other set of soil samples was collected during geochemical survey and has been analysed twice – on the next day after sampling and 10 years later. Results have shown smoothing (and sometimes disappearance) of mercury anomalies existing originally.

Sample preparation. *Drying.* The increase of sample's temperature raises volatility of sorbed Hg. Mercury can leave surface of particles and transfer to a gas phase. Desorption of mercury begins already at 80 °C. The losses of mercury can become appreciable at long drying and higher temperatures. *Sieving.* Up to 20 % of total Hg may be lost. Typically it is the mercury physically sorbed on a surface of particles of soil. *Milling.* The greatest losses of mercury occur at milling of samples from transition humus horizon and in mechanical mill. It can achieve 50 %. The least losses - at manual milling. The value of losses depends on initial concentration of mercury, structure of soil, method and time of milling.

CONCLUSIONS

The revealing of sources and rating of value of errors allow provide conditions for correct determination of mercury in soil.

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Repeatability and Reproducibility of Data from Different Groups and Locations in Ny-Ålesund During the Hg-Campaign 2003

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Abstract: Round robin test procedures and other statistically-based performance criteria were applied in order to investigate the reproducibility of measured concentration data obtained by different groups at different measurement spots during an international Arctic field study at Ny Ålesund, Spitsbergen. Gaseous elemental mercury concentrations were highly reproducible during background conditions. Concentrations of mercury species obtained with different procedures were only poorly reproducible.

Key words: atmospheric mercury, intercomparison, round robin test, precision, z-score

INTRODUCTION

Field intercomparisons are well established to determine the degree of comparability of sampling and analytical procedures for atmospheric mercury species (Gaseous Elemental Mercury = GEM, Reactive Gaseous Mercury = RGM and Particulate Mercury = PM) being used by different groups around the world and hence the comparability of measured results (e.g., EBINGHAUS ET AL., 1999).

In practice precision can vary when the replicates are performed in different laboratories or even in the same laboratory in different lapses of time. This also happens during field intercomparisons and it is necessary to distinguish between the repeatability and the reproducibility of the individual results.

In our work we present concentration data of different atmospheric mercury species, obtained by five different groups in three different measurement spots during an international Arctic field study in Ny Ålesund, Spitsbergen (78°55 N, 11°90 E) in April and May 2003. Several Atmospheric Mercury Depletion Events (AMDEs) were detected during this campaign (BERG ET AL., 2004). Different manual and automated techniques

for the determination of GEM, RGM, and PM concentrations were applied during the 4 weeks campaign from the participating groups (LANDIS ET AL., 2003). All procedures based on atomic fluorescence detection of the analytical species Hg^0 with a TEKRAN 2537A.

The trueness of the Hg^0 measurements was assured by manual injections of a known amount of gaseous Hg^0 into the analyser, at the beginning and at the end of the campaign.

The three different measurement spots were compared by parallel sampling and analysis of GEM concentrations with two TEKRAN 2537A.

In order to estimate the errors during this intercomparison, random samples of the final dataset were demanded from each group and evaluated according to round robin test procedures.

In Addition, method detection limits (MDLs) were calculated for each analytical method and compared with previous values.

RESULTS AND DISCUSSION

Parallel sampling with two different TEKRAN 2537A at three different measurement spots, all located in an area of about two square kilometres (Zeppelin-mountain, Italian station, Ny-FID Sund) was done for more than 10 hours in each case during typical meteorological conditions. One TEKRAN remained stationary and was operated at sea level (Ny-FID Sund, located outside the village) and compared with a second instrument, first at the same location and second at the other two measurement spots (1. Italian station, located in the village Ny Ĺlesund, 12 meter a.s.l.; 2. Zeppelin mountain, 474 meter a.s.l.). The mean GEM con-

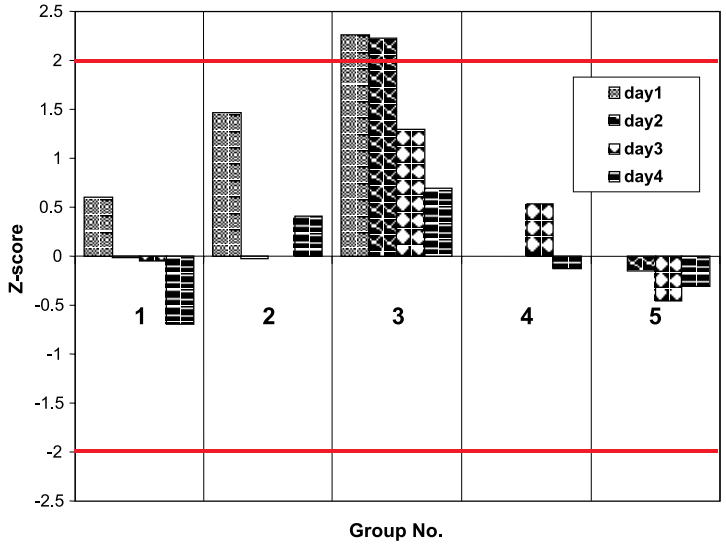

Figure 1. Z-scores for GEM concentration measurements of five participating groups at four different days (chronological) without AMDEs (mean concentrations were used). The relative reproducibility standard deviation was set to 10 % and the quality limit for the z-score was set to a value of 2 (probability = 95 %).

centrations revealed no significant differences between the three measurement spots.

The reproducibility between the five groups was assessed by round robin test procedures (e.g., DIN 38402-45). One example for the performance of GEM-measurements of the different groups is presented in Figure 1. Four days without AMDEs were randomly selected according to meteorological conditions, covering the complete period of the campaign. The mean GEM concentrations for each group and at each location were used for further calculations. The so-called z-score shows the harmonized parameter z which is calculated from the difference between the measured value and the best available estimate, divided by the standard deviation (UHLIG & LISCHER, 1998). We choose the median (= 1.58 ng/m^3) of the complete dataset from all four groups during the four days of non AMDEs as a robust approximation for the best available estimate. The relative reproducibility standard deviation was set to 10 %. Only one group exceeded the quality limit of z = 2 (the probability of the absolute value of z not exceeding the value 2 is 95 %) during the first two days. The performance of GEM measurements of group no. 3 advanced in the course of the campaign.

During background conditions (no AMDEs) Hg species concentrations (RGM and PM) were most of the time near the detection limit of the applied methods and could not be quantified. Due to generally high variances close to the MDL a comparison for these periods is not applicable. But even during AMDEs with significant higher concentrations (more than 20-fold of the background concentrations) the reproducibility for Hg species concentrations was only poor, sometimes with more than 100 % variations between different groups.

CONCLUSIONS

The results point out that the different measurement spots with different altitudes during the study are not necessarily the sole reason for significant variations in mercury concentrations of different groups. The precision of each individual group (within-laboratory precision) for measurements of GEM concentrations with a TEKRAN is consistently good (relative repeatability standard deviation of about 5 %).

The reproducibility (between-laboratory precision) for GEM measurements during typical background conditions without AMDEs was shown in z-scores for each group.

Most of the participating group meets the quality requirements z = 2 (probability = 95 %) for a given relative reproducibility standard deviation of 10 % during the entire campaign.

Comparison of Hg species concentrations at different measurement spots, obtained with different techniques, is more difficult than for GEM because of their strong ability to be deposited and influenced by small changes in meteorological conditions. According to our results, manual and automated sampling and analysis methods for RGM and PM are poorly reproducible not to mention the unknown composition of RGM and PM present during AMDEs. With state-of-the-art procedures for atmospheric mercury species we can only differentiate between “high” and “low” concentrations of “fractions” called RGM and PM. Based on our results we can-

not quantify the concentrations neither with sufficient accuracy nor within the details of the measurement uncertainty. Standard reference material for calibration and a validation of these methods are essential in the near future.

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Electrochemical Detection of Sub-ppb Levels of Ionic Mercury by Chemically Modified Electrodes

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Abstract: The determination of very low levels of mercury by fast, cheap and yet reliable means is still an open challenge in analytical chemistry. The essence of our approach has been to take advantage of the inherent sensitivity of voltammetry and add a selectivity factor at the solid-liquid interface.

Initially, we used a cryptand, i.e., Kryptofix 222 that was adsorbed on an activated glassy carbon electrode as a means of introducing the selectivity towards Hg^{2+}. More recently, we have replaced the adsorption process by the incorporation of the cryptand in a polymeric matrix. This has added stability to the system, which could be eventually integrated as part of a sequential injection stripping analysis (SISA) system. The flow system exhibited high flexibility since the range of concentrations of Hg^{2+} where it responded linearly could be controlled by diluting the sample.

At present we examine other approaches based on molecularly imprinted polymers whereby the Kryptofix is incorporated inside a matrix in the course of polymerization.

Key words: electrochemistry, voltammetry, modified electrodes.

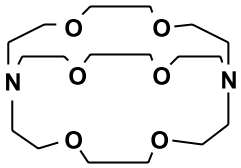
INTRODUCTION

Electrochemistry in general and voltammetry in particular have widely been used for the determination of low levels of heavy metals in aquatic systems. This stems from the inherent sensitivity that electrochemistry exhibits which makes it an ideal analytical approach for determining electroactive species such as metals. The major challenge is introducing a selectivity factor, which will differentiate between the different species and for example, will be responsible for extracting only mercury ions without affecting other ions such as cadmium(II).

We have developed during the years different approaches based on either self-assembled monolayers or thin organic and inorganic polymeric films for the selective recognition and extraction of heavy metals[1, 2].

Our efforts have also been directed toward developing a selective electrode for mercury ions. Initially, we adsorbed the selectivity factor, i.e., Kryptofix 222 (I), which is a macrocyclic ligand on an electrode surface. This resulted[3] in extremely high sensitivity, of the order of ppt (parts per trillion) towards Hg^{2+}. Nevertheless, the robustness of this electrode was not sufficient and therefore we have tried to embed the Kryptofix inside a polymeric matrix[4]. Such an approach made it possible to integrate the electrode for mercury in a flow system[5]. Yet, the polymeric film used is not ideal as it slows down the

diffusion across the interface. Therefore, we constantly seek for better methods for assembling the selectivity factor at the interface.



(I)

RESULTS AND DISCUSSION

Figure 1 shows a typical square wave voltammetry recorded with a Kryptofix-222 modified GCE, in a solution containing different concentrations ($1.51.10^{-12}$ M - $1.18.10^{-11}$ M) of mercury(II). The conditions for obtaining such high sensitivity were optimized (potential and time of deposition) and involve a deposition time of only 5 minutes under a constant potential of -0.5 V vs. Ag/AgCl.

A simple regeneration process was developed to eliminate the mercury without affecting the modified surface. The modified electrodes were electrochemically regenerated by soaking the electrodes after each experiment in a mercury-free solution for 1 min at 0.3 V or by cycling them between ±0.3 V.

The selectivity of the electrode was examined by the effect of the addition of 10^{-5} M Zn^{2+}, Cu^{2+}, Pb^{2+}, Cd^{2+}, Mn^{2+} and 10^{-7} M Ag^{+} to a 10^{-11} M solution of Hg^{2+}. We found that the stripping peak current was slightly decreased as a result of adding more than 10^{-6} M Cr^{3+}, however, other ions had no noticeable influence on the mercury stripping peak. Anions, such as acetate, chloride and thiocyanate had no influence on the electrochemical response of the modified electrode.

The extremely high sensitivity obtained by this simple method allowed determining

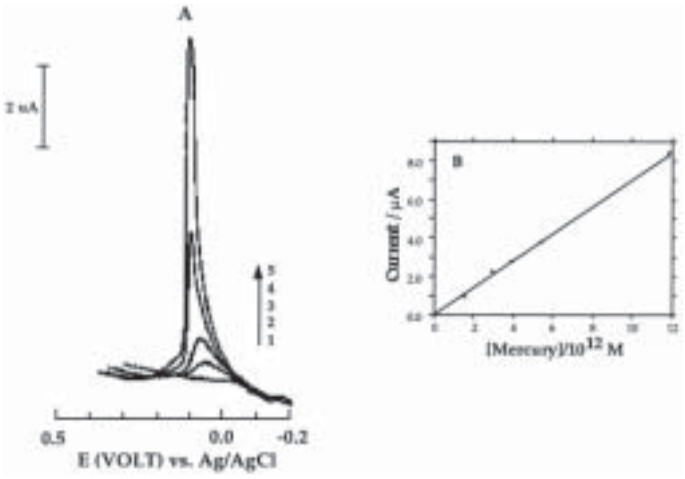


Figure 1. A- Anodic square wave stripping voltammograms of a GCE coated with Kryptofix-222 in a solution of 0.01 M acetate buffer (pH 4.0): (1)- Hg(II)-free; (2)- $1.51 \cdot 10^{-12}$; (3)- $2.89 \cdot 10^{-12}$; (4)- $5.34 \cdot 10^{-12}$ and (5)- $1.18 \cdot 10^{-11}$ M Hg(II). B- The stripping peak currents of mercury as a function of mercury(II) concentration.

mercury in different media, such as seawater as well as biological fluids, e.g., amniotic fluid and human saliva. Mercury was always determined by the single standard addition method. For example, the concentration of mercury in seawater was ca. $4.97 \pm 0.20 \cdot 10^{-11}$ M (9.9 ppt).

Better performance with respect to the robustness of the electrode was accomplished by incorporating the Kryptofix inside a polymeric matrix[4]. Recently, we reported on the application of such modified electrode, in which the Kryptofix was embedded inside polyvinylpyridine for the on-line analysis of mercury using sequential injection stripping analysis[5]. The latter is a powerful flow system technique, which offers significant advantages in electroanalytical chemistry.

Figure 2 shows the anodic differential pulse stripping voltammograms recorded with PVP-Kryptofix/GCE after different volumes of solution consisting of $1.2 \cdot 10^{-8}$ M Hg (II) and 0.025 M H_2SO_4, 0.1 M HCl were aspirated from the mixing chamber and transported through the cell. The dilution of mercury sample is performed in the mixing chamber. Changing the pumping time and/or flow rate can easily control the injected volume of the solution from the mixing chamber. The response increases with the injection volume up to 300 mL, thus providing higher sensitivity at increased injection volumes and showing a typical saturation behavior at injected volumes larger than 1800 μL (Figure 2B). Such saturation is expected and is due to mass transport limitations during the preconcentration step.

The ability to control precisely the injection volume enables manipulation of the amount of mercury that is deposited under specific conditions, i.e., preconcentration potential and time. This provides a convenient and flexible way to obtain a linear dependence between the current and mercury concentration. Namely, smaller volumes are to be injected

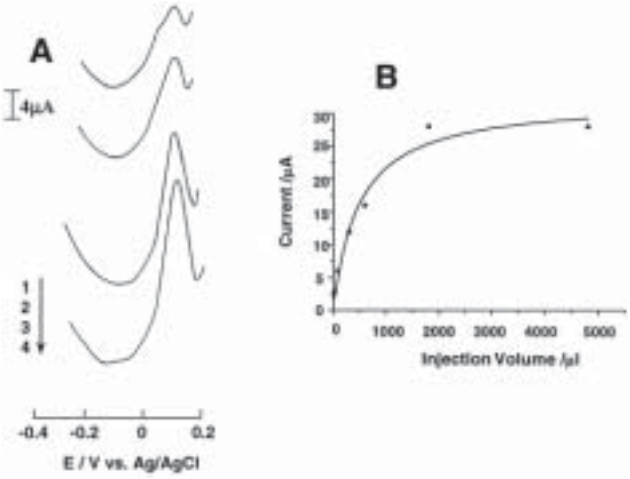


Figure 2. (A) Differential pulse anodic stripping voltammograms of poly(4-vinylpyridine)/Kryptofix GCE recorded for different injection volumes: (1) 30; (2) 90; (3) 300; and (4) 600 μL of $1.2 \cdot 10^{-8}$ M Hg(II) and 0.025 M H_2SO4, 0.1 M HCl. (B) Anodic stripping peak currents as a function of injection volume.

in the presence of relatively high Hg(II) concentrations, while the detection of very low concentrations of mercury can be accomplished by increasing the injected volumes.

Finally, we currently examine other and more sophisticated approaches that are based on molecularly imprinted polymers (MIP). The concept involves the polymerization of inorganic silica sol-gel thin films are where the selectivity factor is incorporated during the polymerization and therefore creates spaces that are accessible specifically to the analyte. The formation of film of the order of tens of nanometers allows fast diffusion and regeneration of the electrode surface.

CONCLUSIONS

It is evident from our work that Hg(II) can be detected electrochemically using an electrode that is either modified with a monolayer or a polymeric film in which the selectivity factor that recognizes the mercuric ions is embedded.

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An improved cold vapor atomic absorption method for the gaseous mercury monitoring

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Abstract: Cold vapor atomic absorption method (CVAAS) is an easy-to-use and cost-efficient alternative to cold vapor atomic fluorescence (CVAFS) for the total gaseous mercury (TGM) monitoring in the atmosphere and in other environments. It is sometimes suspected, however, that non-dispersive CVAAS might be more subjected to both positive and negative interference because of different compounds present in the atmospheric air.

Our recent investigation focuses on the quality of data obtained by CVAAS in various complex environments, as for example: hot and humid marine and terrestrial climate atmospheric air, containing low concentration of total gaseous mercury and high concentrations of both natural and antrophogenic interfering compounds.

An appropriate sampled air pre-filtering, modification of the gold traps design and modification of the desorption heating temperature profile are shown to substantially improve the UV light absorption response and to extend the lifetime of the gold traps/optic cells. The benefits of the use of the newly developed ultra-low-level automated Hg dosing device are also demonstrated.

Key words: atmospheric, CVAAS, interference, TGM

Determination of Mercury in Fish from the Atlantic Coast of Ghana by Cold Vapour Atomic Absorption Spectrometry using an Automatic Mercury Analyzer

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Abstract: The concentration of mercury in fish samples from the Altlantic coast of Ghana was determined using a simple, rapid and accurate method at levels as low as 0.5 ng. A mixture of HNO_3, $HClO_4$ and H_2SO_4 was used for complete oxidation of organic tissue. Mercury is determined by cold vapour atomic absorption spectrometry using a mercury analyzer developed at the National Institute for Minamata Disease (NIMD). In total 52 samples covering 12 species were analysed for total mercury. The concentration of mercury in the edible muscle tissue of these fish ranged from 0.004 to 0.122 μg g^{-1} wet weight. All fish species sampled had concentrations less than the WHO limit of 0.5 μg g^{-1} wet weight. The low concentrations of mercury detected in the samples are not a public concern.

Key words: fish, mercury, cold vapour atomic absorption spectrometry, mercury analyzer, atlantic coast of Ghana

INTRODUCTION

Mercury contamination of the marine environment has long been recognized as a serious environmental concern. It is widely recognized that human activities are artificially increasing mercury loads in the atmosphere on a local, regional and even hemispheric scale, leading to the contamination of the environment. A relative increase of 1.2 % to 1.5 % per year of mercury concentrations in the atmosphere over the Atlantic Ocean was reported recently, suggesting an increase of direct mercury load to this ocean[1]. This increase in the anthropogenic mercury load to the oceans may reflect in fish mercury concentrations[2].

Since the tragedy of Minamata Bay in Japan[3], most concern has centred on the presence of mercury in fish since seafood is a major source of this element. Fish accumulate substantial concentrations of mercury in their tissues and thus can represent a major source of this element to humans. This has been a matter of concern since its toxicity was clearly documented[4]. Mercury, particularly in the form of methylmercury, is extremely toxic to marine organisms, wildlife, and man. The main pathway for human exposure to methylmercury is through consumption of fishery products. The likelihood of mercury toxicity from fish consumption has been identified in Peru and some coastal regions of the Mediterranean[5, 6]. Consequently extensive surveys have been carried

out in a number of countries to evaluate the presence of mercury in the aquatic biota including fish. The establishment of maximum permissible mercury concentrations in fish for human consumption in the range of 0.5 to 1.0 μg g^{-1} wet weight by many countries, has triggered a process of surveying mercury concentrations in natural fish populations[7]. Recently, levels of mercury in fish have been widely reported[2, 7-11]. However, information on mercury levels in marine organisms from this region is unavailable. Consequently, no work has been undertaken in Africa to study human exposure to mercury through the consumption of fish.

This paper reports results of Hg concentrations in a variety of species from the coastal waters of Ghana obtained using a procedure, which was developed at the National Institute for Minamata disease in Japan (NIMD)[12] with slight modifications.

RESULTS AND DISCUSSION

The method described in this paper for the determination of mercury in fish provides a rapid, sensitive and accurate system that can be used for routine analysis of fish. It facilitates the relatively rapid (30 - 60 min) wet oxidation of samples (0.5-1 g). In addition, few reagents are required to carry out the wet oxidation. In this digestion procedure, a small amount of sample can be digested in a 50 ml volumetric flask (Pyrex) and the solution is diluted to volume (50 ml) in the volumetric flask reducing the amount of glassware and eliminating time consuming steps. Most digestion procedures for mercury determination employed condensers to prevent mercury losses during the heating. In this procedure a condenser was not used but excellent recoveries were obtained using an open digestion technique possibly because of the long neck of the volumetric flask allowing

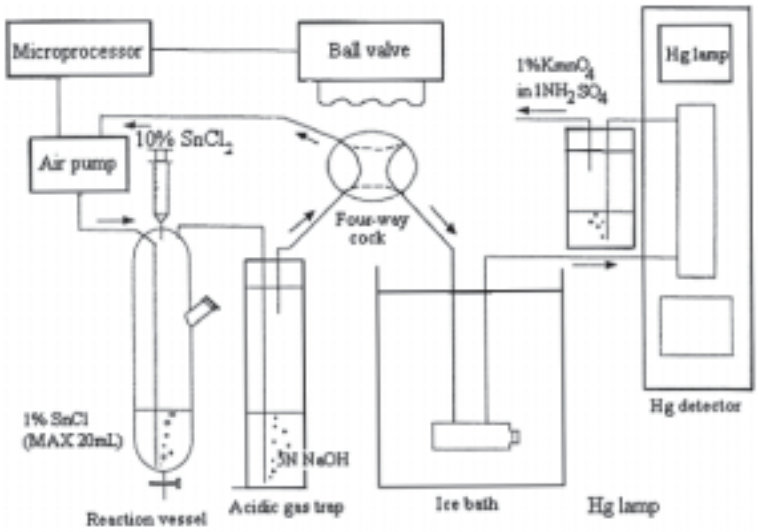

Figure 1. Schematic diagram of the mercury analyzer

Table 1. Mercury concentrations (μg g^{-1} wet weight) in fish from the Atlantic Coast of Ghana (N=no of samples, SD=standard deviation).

Species Name	N	Mean	SD
Stromatteus fiatola	4	0.004	0.003
Brachydeuterus curitus	5	0.037	0.017
Panulirus argus	5	0.035	0.015
Calappa rubroguthata	5	0.057	0.022
Gerres nigri	5	0.056	0.024
Decapterus rhonchus	5	0.043	0.020
Braehydentera aurita	3	0.122	0.030
Diplodus puntazzo	4	0.070	0.013
Parapristipoma humile	3	0.112	0.021
Selene dorsalis	5	0.034	0.023
Galeoides decadactylus	5	0.041	0.020
Pseudotolithus senegalensis	3	0.031	0.025

for reflux. Good recoveries (94-116 %) of spiked samples demonstrated the accuracy of the method used. The accuracy of the procedure has also been demonstrated at NIMD laboratory by the analysis of reference standards IAEA 085 and DORM-2. The use of micropipette (1-5 ml) for the introduction of the digests into the reaction vessel of the mercury analyzer coupled with the short digestion time makes it possible to analyse more than one hundred samples daily. Figure 1 shows the schematic diagram of the analyzer

All the fish species analysed in this study are consumed by humans. Total mercury in fish in μg g^{-1} on wet weight basis from the coastal waters of Ghana, which is part of the Atlantic Ocean, are presented in Table 1. Mercury levels were determined in a total of fifty-two samples, covering twelve fish species. Mercury concentration ranged from 0.004 to 0.122 μg g^{-1} wet weight. All the samples had concentration of mercury below the 0.5 μg g^{-1} wet weight limit recommended by the FAO/WHO[13] and adopted by many countries[14]. The concentration of mercury in fish has been the subject of intense study in recent years and the mercury content of marine fish has variously been reported[8]. Many of the reports indicated that mercury levels in most species of oceanic fish fall in the range of 0-0.5 μg g^{-1} wet weight with most values close to 0.15 μg g^{-1} wet weight within which our values fall.

Mercury content in fish is considered to be a good indicator of human exposure to organic or methylmercury contamination. That mercury in fish appears to be predominantly in the form of methylmercury has been reported by many researchers[8, 10, 15]. Therefore, diet consisting particularly of fish, could be the main source of exposure to methylmercury in the general population. The results of this study as such provide a basis for assessment of human exposure to methylmercury. The concentrations of mercury in the fish samples obtained in this study are not high when compared to some other areas of the world and

can be said to reflect background mercury concentrations that are even much lower than most published mercury concentrations in fish from non-polluted areas of the world. For example mercury in the edible portion of various fish species landed at Irish ports during 1993 are in the range of 0.1-0.39 with a mean of 0.1 within which our values fall. These levels are reported to be low and are well within the maximum limits set by the EC for mercury in fisheries products[9]. Mercury concentrations reported here are lower by an order of magnitude when compared to values reported for other tropical, less industrialized areas like Indonesia, Thailand and Papua New Guinea[14]. Though the estimation of maximum amounts of daily intake of mercury from the consumption of fish cannot be obtained due to lack of information on nutrition survey on the population, the results of this study indicate that mercury content of fish from the coastal waters of Ghana is unlikely to constitute a significant health threat to the public because of consumption of fish.

CONCLUSION

The proposed method offers a fast and simple approach to sample digestion, dilution and mercury determination as low as 0.5 ng in fish. Mercury levels determined in fifty-six samples covering thirteen species ranged from 0.004 to 0.122 μg g^{-1} wet weight. All the samples had concentrations of mercury below the FAO/WHO recommended limit of 0.5 μg g^{-1} wet weight. These levels do not therefore constitute any significant health hazard to the general population.

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Improvements and Quality Assurance Evaluation of Semi Quantitative Method for Mercury Determination in Fish

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Abstract: With the objective of lowering the operational cost of a semiquantitative method for mercury determination in fish, previously published by YALLOUZ, experiments were carried out to remove the magnetic stirring. The results showed no significant difference, thus stirring would be eliminated. Quality assurance of the analytical results has been confirmed through the comparison with the quantitative method and by regular participation in the Mercury Quality Assurance Program coordinated by the Canadian Food Inspection Agency (CFIA). The efficiency evaluation was accomplished in 2 ways: the first one, verifying the agreement between the average of the results and the interval which was determined by the semi quantitative method, and the second one is to verify the overlap level of the distribution around the medium values that were determined by the quantitative method and compared to the obtained interval with semi quantitative method. In the first case, it was possible to observe that 75 % of medium values were in the proposed interval by the semi quantitative method. On the other hand, we could observe that 40 % of the results showed an overlap level higher than 90 %, 40 % showed overlap level between 50 and 90 % and other 20 % showed overlap level lower than 50 %. We concluded, that the results are satisfactory for routine analysis, and proposed some further trials for improving the overlap level.

Key words: semiquantitative mercury determination, quality assurance, low cost, fish

INTRODUCTION

The environmental exposure of the human population to mercury around the world, has made this a chemical global concern. It is known that in Brazil, mercury has been used for small gold mining and many locations have been reported as having been potentially affected by mercury pollution. Many authors have already carried out risk evaluation for the exposure of the people living around these areas (SANTOS, 2000 and HACON, 1997) and the results confirmed the fact previously described where carnivorous fish accumulate more mercury. Due to the high biodiversity, the administration of the fishing activity should plan an action to protect the human health of the local population. A continuous evaluation of the mercury content in the fish most consumed by the population in general is recommended (YALLOUZ, 2002). The most usual analytical method to determine mercury level in biological samples is the cold vapor technique coupled to atomic absorption spectrometer(CVAAS) (HERBER, 1994). The huge extension on

which all these locations are located, the lack of laboratory infrastructure and the difficult access to these places associated to the high cost of analysis, has inspired the development of a semiquantitative (SMQ), low cost and easy operational method which attends the WHO recommendations (YALLOUZ, 2000). The present work reports improvements with the objective to lower costs and to assure quality tests for SMQ analytical results.

To perform the SMQ analysis, simple labwares are needed (Figures 1 and 2). In the first step, 10 g of the sample is heated at 95 ^{0}C with an acid oxidizing mixture (H_2SO_4/HNO_3/V_2O_5), followed by the addition of 25 mL of $KMnO_4$. The solution is transferred to a determination flask (Figure 2), and the ionic mercury is reduced to elemental mercury by the addition of 25 mL stannous chloride solution. The mercury vapour is forced to pass through a detecting paper covered with an emulsion containing cuprous iodide. A colored complex is formed (Equation 1), with a characteristic reddish color, where the intensity of the color is proportional to the mercury concentration in the sample (Figure 3).

Formerly, in the method previously described (YALLOUZ, 2000), magnetic stirring plate was used for each determination to carry mercury vapour. To evaluate this need stirring 20 independent aqueous solutions were analysed. The results with and without stirring were compared and no significant difference was observed. To calculate the recovery factor for each experiment, the detecting paper was

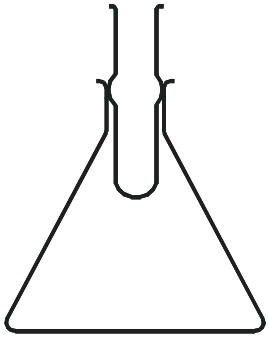

Figure 1. Digestion system Erlenmeyer with cold finger

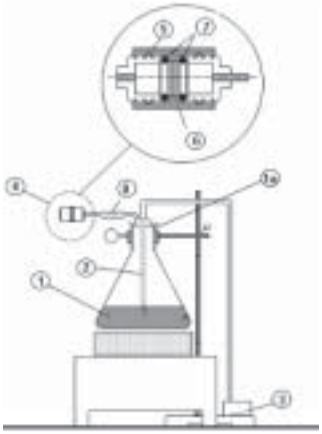

Figure2. Determination system
Glass made flasks and simple materials

Figure 3. Similar colors to those developed in the detecting papers, using standard solutions equivalent to 0, 100, 300 and 600 ng/g

digested with the oxidant solution and the mercury content analysed, using the same methodology previously described (YALLOUZ, 2000). The final solution was analysed using CVAAS. The % recovery calculated for both situations demonstrated that no significant difference could be observed. To confirm that the same behaviour would be observed with real samples, it was performed a similar experiment with real samples. No stirring was anymore used for method performing.

For quality assurance, the semi quantitative results method has been compared to CVAAS results. To check CVAAS performance Standard Reference Materials (SRM) of fish muscle and liver fish produced and distributed by National Research Council Canadá (DORM-1 and DOLT-2) and participation on the Mercury Quality Assurance Program (MQAP), coordinated by Canadian Food Inspection Agency were used. Some results are shown in Table 1 and Figure 4. The results confirmed the CVAAS method accuracy.

Table 1. Some results of SRM analysis, by CVAAS, used during method improvements

CRM	Dolt-2	Dorm-1
N	3	6
Found Value(ng/g)	2146±168	753±49
Reference value(ng/g)	1990±100	798±74

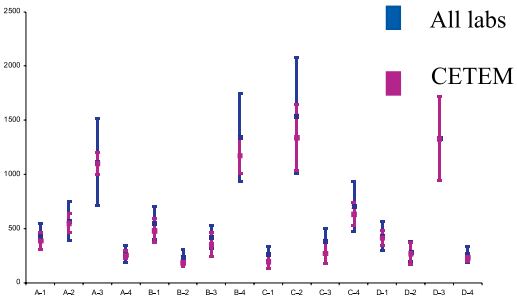

Figure 4. Quality assurance results for MQA the quantitative method (CV-AAS)

Table 2. Comparison of semiquantitative results by participation Mercury Quality Assurance Program (MQAP), coordinated by Canadian Food Inspection Agency

Sample	Found value ng/g (n=3)	Reference Value ng/g Average value ± δ	Confidence range (ng/g) (n)
MQAP 308	300-600	282 ± 46	190 - 374 (43)
MQAP 309	300-600	390 ± 52	286 - 494 (42)
MQAP 310	>1000	2204 ± 385,5	1433 - 2975 (43)
MQAP 311	300-600	289 ± 46	197 - 381 (42)
MQAP 312	300-600	391 ± 45	301 - 481 (42)
MQAP 313	600-1000	611 ± 73	465 - 757 (42)
MQAP 314	300-600	390 ± 42	306 - 474 (42)
MQAP 315	>1000	1101 ± 197	707 - 1495 (43)
MQAP 316	300-600	477 ± 64	349 - 605 (42)
MQAP 317	300-600	380 ± 49	282 - 478 (42)
MQAP 318	600-1000	1116 ± 161	794 -1438 (42)
MQAP 319	<300	202 ± 41,5	199 - 365 (42)
MQAP 320	<300	215 ± 34	147 - 283 (40)
MQAP 321	<300	405 ± 61	283 - 527 (39)
MQAP 322	300-600	438 ± 75	288 - 588 (39)
MQAP 323	300-600	630 ± 94	442 - 818 (40)
MQAP 324	300-600	525 ± 73	379 - 671 (49)
MQAP 325	600-1000	603 ± 81	441 - 765 (49)
MQAP 326	300-600	305 ± 40	225 - 385 (49)
MQAP 327	>1000	1236 ± 190	856 - 1616 (49)

At the semiquantitative level, Since February 2002 the semiquantitative results are being accompanied by quarterly performance evaluations coordinated by the Canadian Food Inspection Agency (Table 2). The semiquantitative results are reported in four concentration ranges: <300; 300-600; 600-100 and > 1000 ng/g.

The efficiency evaluation was accomplished in 2 ways: the first one, verifying the agreement between the average of the results and the interval which was determined by the semi quantitative method, and the second one is to verify the overlap level of the distribution around the medium values that were determined by the quantitative method and compared to the obtained interval with semi quantitative method. In the first case, it was possible to observe that 75 % of medium values were in the proposed interval by the semi quantitative method. On the other hand, we could observe that 40 % of the results showed an overlap level higher than 90 %, 40 % showed overlap level between 50 and 90 % and other 20 % showed overlap level lower than 50 %. It was observed that the overlapping is smaller in the samples, where the average of the results are very near the concentration limits (300, 600 e 1000), as was the case of the MQAP 308, 311, 323, 325 e 326 samples. The result obtained for the MQAP 321 samples is very different from the expected valued, which probably means an error in the experiment. The results whose overlap level was higher than 50 % were considered satisfactory.

CONCLUSIONS

We concluded, that the results are satisfactory for the proposed application. It is a good routine tool for detecting mercury, in a semi quantitative way, to be used in some places where the mercury concentration needs to be determined fast and with an acceptable effectiveness. However, one can notice an opportunity for improvement in the use of this method. Previous studies demonstrate that the minimum interval between the two concentrations should be 150ng/g color discrimination. Thus, in case necessary, the concentrations used in the systems of standardization could be 150, 300, 450 or any other combination that it would be suitable to the safe fish consumption of a specific community.

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Mercury semi quantitative determination in urine: a low cost alternative for preliminary intoxication diagnosis

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Abstract: A low cost and easy method was used for determining mercury in urine at a semi quantitative level. In this paper the method was described, and the analytical results compared with the ones from the quantitative CVAAS (cold vapour atomic absorption spectroscopy) method and a small application study using exposed workers urine. It was observed that it is possible to determine mercury at levels as low as 10 ng/mL, demonstrating that it is a good tool for preliminary diagnosis for elemental mercury intoxication.

Key words: semi quantitative, mercury determination, urine, low-cost

INTRODUCTION

Elemental mercury is used in different industrial activities, such as the ones in the chlor-alkali and fluorescent lamp plants, and for hand made activities as gold mining workers and dentists. It is known that the exposition to elemental mercury occurs mainly with workers chronically exposed to atmospheres with high mercury concentration (AZEVEDO, 2003).

As a preventive measure, in addition to periodical medical examinations, bio-indicators are useful and recommended as a complement for diagnosis. Urine is the best one to evaluate the exposure level to elemental mercury vapour. The usual methods for mercury determination are based on Cold Vapour Atomic Absorption Spectrometry or Cold Vapour Atomic Fluorescence Spectrometry (HERBER, 1994). Looking for alternative low cost method, it was chosen a semi quantitative method, formerly developed for mercury determination in fish samples (YALLOUZ, 2000). The chemical principle, on which the method is based, is the specific reaction of elemental mercury with cuprous iodide resulting in a red colourful complex (HgI_4^{2-}) (Equation 1).

$$Hg^0 + 2Cu_2I_2 \rightarrow 2Cu[HgI_4] + 2Cu^o \qquad (1)$$

In general, a safety index is the concentration up to 10 ng/mL that is adopted as health reference for non-exposed humans, while the range from 50 ng/mL to 150 ng/mL is considered as a warning level. (AZEVEDO, 2003).

The present work reports the results of the application studies of an alternative, semi-quantitative mercury determination method and a small application study performed with volunteers from a hand made fluorescence lamp recycling factory.

To evaluate the method efficiency, recovery tests were performed using artificial samples prepared by doping a homogeneous urine sample with different mercury concentrations. The expected final concentration for those samples would be equivalent to 0, 5, 10, 25 and 50 ng of Hg/mL of urine, giving samples U-0, U-5, U-10, U-25 e U-50 respectively. The samples were stored with 10 % nitric acid and in the freezer until the determination. Exposed workers and neighbours from a hand made fluorescent lamp recycling factory, located at the Metropolitan area of Rio de Janeiro, were volunteers for the application tests. Samples were collected in three dates: June and October 2003 and February 2004 and each one was analysed using two methods: cold vapour atomic absorption spectrometry and the SMQ one. The results were compared for quality assurance evaluation.

For quantitative mercury determination it was used an oxidant digestion (AKAGI, 1991). Sample was heated to 230-250 °C with HNO_3:$HClO_4$(1:1), H_2SO_4 and water, during 20 min. The determination was performed using spectrometer Automatic Mercury Analyser Hg-3500.

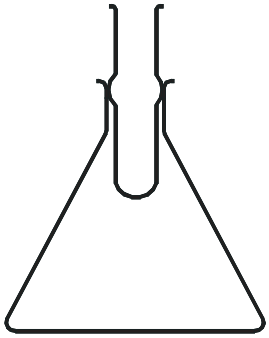

Figure 1. Digestion system (Erlenmeyer with cold finger)

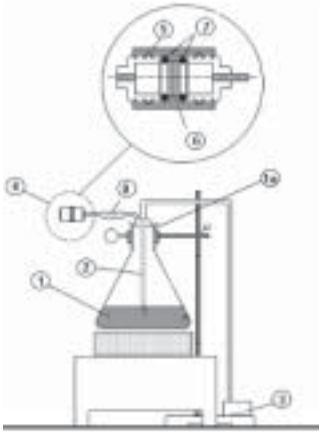

Figure 2. Determination system (Glass made flasks and simple materials)

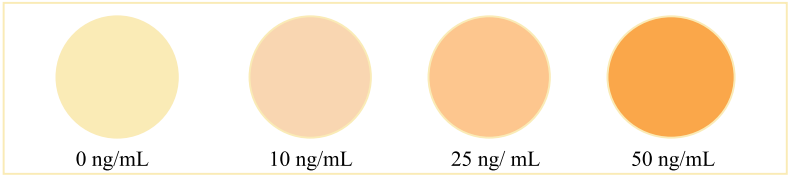

Figure 3. Similar colors to those developed in the detecting papers, using standard solutions equivalent to 0, 10, 25, 50 ng/mL

For semi quantitative determination, 100 mL of sample was heated to boiling temperature with 10 mL of HNO_3, as recommended by JUNGREIS (1984), during 15 min, using a reaction flask similar to the one shown in Figure 1. After cooling, the solution was transferred to a determination flask (Figure 2), and 10 mL of the reducing solution were added (50 % w/v of tin chloride in hydrochloric acid 50 %). The mercury vapour is forced to pass through a detecting paper covered with an emulsion containing cuprous iodide. A colourful complex is formed (Equation 1), with a characteristic reddish colour, whereas the colour intensity is proportional to the mercury concentration in the sample (Figure 3).

Simultaneously, standard solutions were prepared, with concentrations similar to the expected in the urine samples analysed (0, 5, 10, 25 and 50 ng $HgmL^{-1}$. At the end, a visual comparison was made of the colours generated on the paper discs of each one of the systems. The developed colours are similar to those shown in Figure 3.

It was observed that for samples with high turbidity, the addition of 15 ml $KMnO_4$ 5 % w/v, and heating more 5 min, was efficient to clarify the final solution. Just before the determination, some drops of hydroxylamine chloridrate solution are used, for eliminating excess of permanganate.

Table 1. Comparison of the quantitative and semi-quantitative results for spiked samples

Sample	Expected concentration	SMQ*(ng/mL)	QM**(ng/mL)
U- 0	0	Similar to O	1.93 ±0.63
U- 5	5	Similar to 5	5.33 ±0.55
U-10	10	Similar to 10	13,3 ±0.28
U-25	25	Similar to 25	22.93 ±1.48
U-50	50	Similar to 50	49.43 ±3.46

*SMQ= semi-quantitative method; **QM= quantitative method

Table 2. Comparison of the quantitative and semi-quantitative results for volunteer's urine samples.

Volunteer	SQM(ng/mL)	QM(ng/mL)
V01A	20-40*	37.7±5.6
V02A	10-20*	23.9±3.9
V03A	<10	3.13±1.81
V01B	≥50	58.1±2.08
V08B	<10	2.85±4.96
V09B	10-20*	16.24±2.02
V11B	10-20	14.7±2.89
V01C	50-100*	96.8 ±1.39
V05C	10-25	17.3±2.05
V12 C	<10	6.8±1.1
V13 C	<10	2.7±0
V14 C	10-25	20.6±0
V 15 C	0-10	6.8±1.10

Sampling A= June 2003; B= October 2003; C= February 2004
* closer to

RESULTS AND DISCUSSION

The results for the recovery tests are shown in Table 1, and for volunteers' urine in Table 2.

The results obtained for recovery tests confirmed that the alternative methodology is efficient and the results found were coherent with the expected values. For volunteers' urine, SMQ and QM results comparison demonstrated that the results obtained of the expected concentration are inside the concentration range predicted by the SMQ.

CONCLUSIONS AND FUTURE

The results obtained by the SMQ method are comparable with the quantitative results, even in a semi-quantitative level. As the SMQ method is simple and low-cost, it could be recommended, as an alternative method for screening programs of environmental health surveillance. In the near future this methodology will be included in training programs for new users of the SMQ method for mercury determination in fish that already started in August and September 2003 (YALLOUZ, 2004 a).

The volunteers' group are now being guiding to use individual protection equipment and will participate in the near future in a Health Surveillance Program from the Núcleo de Estudos da Saúde Coletiva (NESC), for medical assistance.

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Development of semi quantitative method for mercury determination in soils, sediments and small gold mining residues

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Abstract: A semi quantitative method for analysing mercury in soil, sediment and mining residues was developed and the results compared with the ones from the conventional quantitative methodology, the cold vapour atomic absorption spectrometry, demonstrated its efficiency. For this study, samples collected in Itaituba, Pará State, Brazil, with geochemical and mineralogical composition apparently different, were used. A small application study demonstrated that it is possible, using this method, to correlate the mercury concentration with the particle size. In conclusion, the developed alternative method, which is simple and with low-cost, can be used in regions where a preliminary diagnosis is necessary, as well as at programs of environmental surveillance.

Key words: semiquantitative mercury determination, soil, sediment and mining residues, low-cost.

INTRODUCTION

Since decade of 70, the mercury environmental contamination has worried the scientists due to the consequences to the human health caused by this pollutant. In Brazil, besides its use in industrial activities, the mercury is used in gold prospecting areas, generating residues from the amalgamation process, from the gold amalgam thermal decomposition by the miners and from the gold purification in the gold shops. Some authors attribute to this sort of human activity 80 % of the mercury pollution (LACERDA, 1992). The mercury released during those processes can be deposited in soils and sediments of the neighbourhood, which are considered as mercury reservoir and that are available for the pedological leaching, in charge of transporting this metal and the contamination of the hydrological net (LACERDA, 1999). Consequently, the mercury accumulation is observed in sediments and fishes.

The main analytical techniques used for mercury quantification in soils, sediments and mining residues are based on the so-called Cold Vapour Atomic Absorption Spectrometry (CVVAS), which demands qualified professionals and specific infrastructure, that disables the continuous management of

mercury pollution in critical areas of contamination. To attend this necessity, an alternative, low cost and easy-to- handle method for determining mercury semi-quantitatively (SMQ) was developed by YALLOUZ (2000). To perform the SMQ analysis, only simple lab wares are needed (Figures 1 and 2). In the first step, 10 g of the sample is heated with an acid oxidizing mixture. All mercury present in the sample forms ionic mercury. In the next step stannous chloride is added and ionic mercury forms elemental mercury that is forced to pass through a detecting paper containing cuprous iodide. A colourful complex is formed (Equation I) and the colour intensity is proportional to the mercury concentration in the original sample, therefore the results are obtained in concentrations ranges (Figure 3).

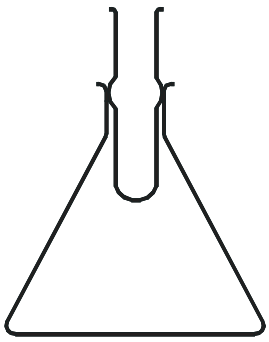

Figure 1. Digestion system Erlenmeyer with cold finger

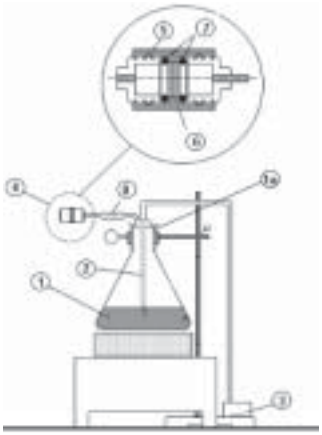

Figure2. Determination system
Glass made flasks and simple materials

$$Hg^{o} + 2Cu_2I_2 \rightarrow 2Cu[HgI_4] + 2Cu^{o} \qquad \text{Equation 1}$$

Figure 3. Similar colours to those developed in the detecting papers, using standard solutions equivalent to 0, 100, 300 and 600 ng/g

We are now presenting the results of application of the SMQ for mercury determination in soil, sediments and mining residues, as well as its use to evaluate different mercury distribution according size particle.

METHODOLOGY

Samples were collected at two different gold mining sites from Itaituba, Pará State, Brazil, as part of the Global Mercury Project

(GMP), under the general coordination of the United Nations Industrial Development Organization (UNIDO).

Twenty and two samples, with geochemical and mineralogical composition apparently different, were selected to certificate that a great variety is being used, looking for no further chemical interferences. For the application study, 9 samples were analysed, each one with 3 different particle size, so that it was possible to evaluate the adsorption in distinct grains size.

To perform quantitative analysis, 2 mL of an oxidant 1:1 acid mixture ($HClO_4$:HNO_3) were added drop wise into 0.5 g sample previously weight in a 50 mL volumetric flask. Then, 1 mL of water was added. The mixture was carefully heated to 230-250 ^{0}C, during 20 min. After cooling the solution diluted up to 50 ml and the determination made using Automatic Mercury Analyser Hg-3500 spectrometer. Each sample determination was performed in duplicate, and each set of 10 samples could be evaluated by a control sample.

For the semi quantitative method, 10 g of the selected sample was heated in the digestion flask (Figure 1), for two hours with an acid mixture composed by 3 parts of HCl and one part of HNO_3. Following this step, 20 mL of deionised water was added and the mixture was filtered. After cooling, the solution was transferred to a determination flask (figure 2), and 2 mL of the reducing agent solution were added (50 % w/v of tin chloride in hydrochloric acid 50 % v/v) and the aeration system turned on. The mercury from the samples was forced to pass through a detecting paper containing cuprous iodide. Simultaneously, standard solutions were prepared, with concentrations similar to the expected ones defined in preliminary tests.

RESULTS AND DISCUSSION

The table 1 shows the results for quantitative and semi-quantitative mercury determination.

The comparison of the semi-quantitative results with the quantitative ones showed that the quantitative average result is in the

Table 1. Comparison of the obtained results by the quantitative (QM) and semi-quantitative (SMQ) methods of the mercury concentration in environmental samples

Sample*	SMQ (ng/g)	QM (ng/g)	Sample	SMQ (ng/g)	QM (ng/g)
SD-01	300-600	544	SD-11	200**-400	308
SD-02	> 2000	2700	SD-12	200**-400	226
SD-03	>2000*	1930	SL-01	200-400**	387
SD-04	>2000	2490	SL-02	600**-1000	613
SD-05	> 2000	2390	SL-03	>2000	2370
SD-06	< 200	98,6	SL-04	200**-400	279
SD-07	< 200	127	MRS-01	>2000	4430
SD-07	200*	210	MRS-02	>2000	2015
SD-08	< 200	159	MRS-03	600-1200**	1008
SD-09	< 200	95	MRS-04	100-200**	239
SD-10	< 200*	258	MRS-05	200-400**	330

Notes: * SD-sediments; SL-Soils and MRS- mining residues ; ** Closer to

Table 2. Mercury concentration in different particle sizes of a same sample

Sample	<200#	100#	80 #	>48 #	Natura
SD-03	> 2000*	----	1200-2000*	100- 300	-----
SD-04	>2000	----	< 100	-----	600-1200*
SD-08	100-200	----	-----	< 100	100*-300
SD-12	200*-400	----	-----	< 100	< 100*
SL-01	200-400*	-----	-----	100-200	100-300
SL-02	600*-1000	----	-----	100-200	100-300*
SL-03	>2000	----	----	100-200	300-600*
SL-05	1200-2000*	----	----	<100	100- 300
MRS-01	>2000	600-1200	600*-1200	----	----

Note: * - Closer to

expected range in 100% of the tests, demonstrating the efficiency of the new methodology.

In Table 2, the results of an application study are shown, where for each sample, different size particles were analysed for mercury content.

The obtained results demonstrated that it is possible to identify a geo-chemical affinity between the particle size and the mercury concentration, confirming the behaviour previously described by the literature (RODRIGUES-FILHO, 1995). The mercury concentration increases for small grains size, when the specific surface area is also increased.

CONCLUSIONS AND FURTHER APPLICATIONS

The results obtained by the SMQ method are comparable with the quantitative results, even in a semi quantitative level. As the SMQ method is simple and with low-cost, it could be recommended, as an alternative method for screening programs of environmental surveillance. In the near future this methodology will be included in training programs for new users of the SMQ method for mercury determination in fish, that already started in August and September, 2003 (YALLOUZ, 2004 a).

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