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REVIEW

Critical Review of Analytical Methods for Determination of Inorganic Mercury and Methylmercury Compounds

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This review describes determinations of mercury compounds under three categories: total mercury; separate determinations of inorganic mercury(II) and organomercury compounds by selective reduction; and speciation of inorganic mercury(II), monomethylmercury cation, and dimethylmercury. Topics described for each category include sample treatment, separation, detection, and limit of detection. Finally, we note that most methods would not detect dimethylmercury if it were present.

Keywords: Analytical methods, mercury, monomethylmercury, dimethylmercury

NOTATION

AA	Atomic absorption
AF	Atomic fluorescence
APDC	Ammonium pyrrolidine dithiocarbamate
Carbo trap	Graphitized carbon-black column
CC	Column chromatography
Conc	Concentrated
Cry-PC	Cryogenic packed column
CVAA	Cold vapor atomic absorption
CVAF	Cold vapor atomic fluorescence
DER	Derivatization
DIG	Digestion
DME	Dropping mercury electrode
DMF	Dimethylformamide
ECD	Electron capture detector
Et_2Hg	Diethylmercury
ETAA	Electrothermally heated atomic absorption
EXT	Extraction
GC	Gas chromatography
GFAA	Graphite furnace atomic absorption
HCL	Hollow-cathode lamp
Hg^0	Elemental mercury
Hg(II)	Mercury(II)
Hg_{tot}	Total mercury
HOM	Homogenization
HPLC	High-performance liquid chromatography
ICP	Inductively coupled plasma
LOD	Limit of detection
MeHg	Monomethylmercury cation
Me_2Hg	Dimethylmercury
MIP	Microwave-induced plasma detector
OX	Oxidation
PRE	Pretreatment
RED	Reduction
RHg	Organomercury (R = Me or Me_2)
RSD	Relative standard deviation
SAMP	Sample
STOR	Sample storage

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GENERAL INTRODUCTION

Long-term and increasing interest in the speciation of inorganic mercury [Hg(II)], monomethylmercury cation (MeHg), and occasionally dimethylmercury (Me_2Hg) in environmental and biological samples has resulted in a large number of published analytical methods. A recent interlaboratory study on the determination of methylmercury (MeHg) in fish and mussels[1] clearly shows the importance of a methods review. The

Table 1 Scheme for the determination of mercury compounds.

Sample treatment	Separation	Detection
Homogenization	Gold	CVAA
Digestion	GC	CVAF
Oxidation	HPLC	ECD
Extraction	Cry-PC	GFAA
Reduction	Carbo trap	MIP
Derivatization	CC	ETAA
		DME

results were a relative standard deviation between laboratories in the range of 20–25%, indicating a lack of reproducibility of existing methods and the urgent need for improvements in MeHg determinations.

It is clearly impossible for us in a short review to describe hundreds of publications using dozens of analytical methods and their variations. We will summarize only major themes and organize existing methods into three major categories: (1) determination of total mercury (Hg_{tot}), (2) separate determination of Hg(II) and organomercury compounds (RHg) by selective reduction; and (3) speciation of Hg(II), MeHg, and Me_2Hg. Within each category we emphasize originators of methods and newest applications.

Most environmental samples require a sequence of three analytical steps (Table 1) namely sample treatment, separation and detection.[2,3] Each step is futher divided into one or more specific techniques depending on the mercury compound(s) of interest. Tables 2–4 list analytical methods for determining Hg(II) and methylmercury compounds. They include sample type and treatment, separation method, detection method, and limit of detection (LOD). LOD is the lowest concentration that is statistically different from the blank.[4,5] The tables list LOD based on the mass of mercury per sample weight (fresh weight or dry weight are not always mentioned) or volume. Missing information in some papers made it impossible to calculate LOD as the absolute mass of mercury in samples.

The first entry in Table 2 exemplifies the interpretation of Tables 2–4. Hatch and Ott[6] determined Hg_{tot} in metal, rock, or soil by a sample treatment of digestion and reduction followed by detection by cold vapor atomic absorption (CVAA). Their method has an LOD of 1 ng Hg g^{-1}.

DETERMINATION OF TOTAL MERCURY

Introduction

Determination of Hg_{tot} (Table 2) requires conversion of all forms of mercury to Hg(II). Since samples may contain Hg(II) bound to other molecules such as proteins or humic matter, it must be liberated from ligands present. In addition, sample treatment must convert bound or free MeHg and Me_2Hg to free Hg(II). Researchers usually convert all mercury compounds to free Hg(II) by an acidic, oxidative digestion (Eqns [1] and [2]).

$$\text{Bound Hg(II)} \xrightarrow{\text{DIG/OX}} \text{Free Hg(II)} \xrightarrow{\text{RED}} Hg^0 \quad [1]$$

$$\text{MeHg(or } Me_2Hg) \xrightarrow{\text{DIG/OX}} \text{Free Hg(II)} \xrightarrow{\text{RED}} Hg^0 \quad [2]$$

The final two steps are reduction of Hg(II) to Hg^0 by Sn(II) or $NaBH_4$ and detection of Hg^0, typically by atomic absorption (AA) or atomic fluorescence (AF).

Sample treatment

Researchers have digested and oxidized samples in various ways to release mercury compounds from binding substances, or have sometimes omitted this step.[7,8] Bricker[9] omitted the digestion and storage steps by using a field method for reduction and volatilization of mercury and purging Hg^0 onto a gold column. Hatch and Ott[6] digested samples with the oxidizing acid HNO_3. Other researchers used acid digestion and oxidation,[10–16] with or without heating.

The digestion procedure (if any) is followed by reduction of Hg(II) with tin(II)[13,14] (Eqn [3]).

$$Hg(II) + Sn(II) \rightarrow Hg^0 + Sn(IV) \quad [3]$$

Hatch and Ott,[6] Rezende *et al.*,[12] Bloom and Crecelius[10,11] and Robinson and Shuman[15] added hydroxlyamine (NH_2OH) as a preliminary reducing agent before adding the tin(II) solution.

$NaBH_4$ also reduces Hg(II) to Hg^0 (Eqn [4]).

$$Hg(II) + 2NaBH_4 + 6H_2O \rightarrow Hg^0 + 7H_2 + 2H_3BO_3 + 2Na^+ \quad [4]$$

Bricker[9] and Tsalev *et al.*[16] used $NaBH_4$ alone. Two groups[7,8] used a transition-metal catalyst with $NaBH_4$.

Table 2 Method summary for the determination of total mercury (Hg_{tot})

Sample type and treatment		Separation	Detection	LOD	Reference
SAMP:	Metal, rock, soil	None	CVAA	1 ng g^{-1}	6
DIG:	7 M HNO_3/4.5 M H_2SO_4				
RED:	NH_2OH/NaCl/Sn(II)				
	Air purge				
SAMP:	Urine	None	ETAA	1–2 ng ml^{-1}	7
DIG:	None				
RED:	$NaBH_4$/Cu(II)/pH 6.5 buffer				
	Ar purge				
SAMP:	River water, rainwater, pond water, sewage effluent	Gold	Helium–dc plasma emission	0.0005 ng ml^{-1}	9
DIG:	None				
RED:	$NaBH_4$ (in the field)				
	Air purge				
SAMP:	Water, waste water	Gold	CVAA	0.003–0.015 ng ml^{-1}	8
DIG:	None				
RED:	$NaBH_4$/Fe(III)/5 M HCl				
	Ar purge				
SAMP:	Fish	Gold	CVAF	1.0 ng g^{-1}	13, 14
DIG:	Hot conc HNO_3/H_2SO_4 (reflux)				
OX:	0.2 M BrCl				
RED:	Sn(II)				
	He purge				
SAMP:	Urine, river, lake water, rain water	Gold or without Gold	CVAA	0.01 ng ml^{-1} (with gold)	16
DIG/OX:	Microwave (50–90 °C) $KBrO_3$/KBr/HCl			0.2 ng ml^{-1} (without gold)	
RED:	$NaBH_4$/0.1 M HCl				
	Ar purge				
SAMP:	Seawater, sediment, sewage effluent	Gold	CVAA	0.0001 ng ml^{-1}	10, 11
STOR:	2% HNO_3				
DIG:	Conc HNO_3/H_2SO_4 (sediment only)				
OX:	0.2 M BrCl				
RED:	NH_2OH/Sn(II)				
	N_2 purge				
SAMP:	Stream water, river water	Gold	CVAA	0.02 ng ml^{-1}	15
STOR:	$HNO_3/K_2Cr_2O_7$/cysteine				
DIG:	Hot (60 °C) H_2SO_4/HNO_3				
OX:	$KMnO_4/K_2S_2O_8$				
RED:	NH_2OH/Sn(II)				
	N_2 purge				
SAMP:	Fish	None	CVAA	25 ng g^{-1}	12
DIG:	HNO_3/H_2SO_4 (4.5 M)				
OX:	$KMnO_4$				
RED:	NH_2OH.HCl/Sn(II) in 15% HCl				
	Air purge				

Table 3 Method summary for the determination of (Hg(II) and RHg by selective reduction

Sample type and treatment		Separation	Detection	LOD	Reference
Hg(II) + RHg = Hg_{tot}					
SAMP:	Fish, misc. biological samples	None	CVAA	10 ng ml^{-1}	22
DIG:	45% NaOH/1% cysteine/ 20% NaCl/100 °C				
Hg(II)					
RED:	Sn(II)/8 M H_2SO_4/cysteine/NaCl Air purge (NaOH added)				
RHg					
RED:	Sn(II)–Cd(II)/8 M H_2SO_4/cysteine/NaCl Air purge (NaOH added)				
Hg(II) + RHg = Hg_{tot}					
SAMP:	*Tap water, tuna, hair, urine*	None	CVAA	0.003–0.005 ng ml^{-1}	21
DIG:	10 M KOH (90 °C)				
OX:	0.24 M HNO_3/0.01% $K_2Cr_2O_7$/1% NaCl				
Hg(II)					
RED:	Sn(II)/HNO_3/$K_2Cr_2O_7$ N_2 purge				
RHg					
RED:	$NaBH_4$/HNO_3/$K_2Cr_2O_7$ N_2 purge				
Hg(II) + RHg = Hg_{tot}					
SAMP:	fish	None	CVAA	25 ng g^{-1}	12
DIG:	water/4.5 M H_2SO_4/KBr				
Hg(II)					
RED:	water phase after extraction with $CHCl_3$/$NaBH_4$ Air purge				
RHg					
EXTR:	as MeHgBr into $CHCl_3$				
RED:	$NaBH_4$/DMF/HNO_3 Air purge				
Hg_{tot} – Hg(II) = RHg					
SAMP:	Freshwater lakes and rivers	Gold	CVAF	Sn(II): 0.048 ng ml^{-1}	26
STOR:	0.05 M HCl				
Hg(II)					
RED:	Sn(II)/0.05 M HCL			$NaBH_4$: 0.192 ng ml^{-1}	
Hg_{tot}					
OX:	BrCl				
RED:	$NaBH_4$/0.05 M HCl or Sn/0.05 M HCl He purge				

Table 3 *continued*

Sample type and treatment		Separation	Detection	LOD	Reference
Hg(II)[a]					
SAMP:	standards, tap water, river water	None	CVAA	0.001 ng ml^{-1}	25
OX:	0.16 M HNO_3/$KMnO_4$				
RED:	Sn(II)/0.12 M HCl				
	Air purge				
Hg(II)[a]					
SAMP:	seawater, rain water, estuarine water, river water	Gold	CVAA	0.042 ng ml^{-1}	24
DIG:	None				
STOR:	0.06 M HNO_3				
RED:	Sn(II)				
	N_2 purge				

[a] Hg_{tot} – Hg(II) = MeHg: this Hg(II) method is used with a Hg_{tot} method in Table 1 to determine MeHg by difference.

Separation/concentration

The high 1.2×10^{-3} mm Hg vapor pressure of Hg^0 at 20 °C simplifies its detection by AA. Hg^0 formed during the reduction step is often concentrated on a gold column[8–11, 13–16] and then thermally desorbed prior to detection. Water, volatile organic compounds, sulfides or Cl_2 can sometimes interfere with the amalgamation of Hg^0.[17, 18] Concentration of Hg^0 on the gold column can decrease LOD by 20-fold. For example, Tsalev *et al.*[16] had an LOD of 0.2 ng ml^{-1} without a gold column and of 0.01 ng ml^{-1} with it.

Detection

Many groups[6, 8, 10, 12, 15, 16] used CVAA for the detection of Hg^0. CVAA avoids problems with nebulization and atomization that occur in classical flame AA.[19] Cold vapor atomic fluorescence (CVAF) detection for Hg^0 often has improved the LOD relative to AA detection.[13] Other types of detection include a electrothermally heated atomic absorption cell (ETAA)[7] and helium–dc plasma emission.[9]

DETERMINATION OF Hg(II) AND RHg BY SELECTIVE REDUCTION

Introduction

Separate determinations of Hg(II) and RHg (Table 3) combine two reactions that are carried out sequentially on one or more sample aliquots. The first reaction is typically reduction by the mild reducing agent tin(II) that reduces free Hg(II) to Hg^0 (Eqn [3]), but not C–Hg bonds in RHg. After complete purging of the resulting Hg^0, the same aliquot is treated under acid and oxidizing conditions to break C–Hg bonds in RHg and form Hg(II) which is reduced to Hg^0 (Eqn [2]). The separation and detection steps are similar to those described above.

A disadvantage of selective reduction techniques is the impossibility of confirming the identity of RHg. For example, the selective reduction method does not permit researchers to distinguish MeHg from Me_2Hg. The typical assumption is that RHg is predominant MeHg since it is the nearly exclusive form of RHg in fish.[14] Researchers have used selective reduction on samples such as fish,[12, 20–22] hair and urine,[21] animals[22] and blood.[23]

Sample treatment for mercury(II)

The sample treatment used to determine Hg(II) should separate free Hg(II) from any chemical that binds it without breaking C–Hg bonds. Digestion with NaOH and cysteine[22] or KOH[21] leaves the C–Hg bond intact but frees any bound Hg(II). Determination of Hg(II) in aquatic matrices involves sample treatment with tin(II) in aqueous dilute hydrochloric acid (HCl) to reduce Hg(II) to Hg^0.[24, 25] HCl prevents adsorption of mercury compounds on the sample container prior to reduction. Rezende *et al.*[12] used $NaBH_4$ rather than tin(II) with air purging to reduce the Hg(II) in the aqueous phase to Hg^0.

Table 4 Method summary for speciating Hg(II), M eHg and Me_2Hg

Sample type and treatment		Separation	Detection	LOD	Reference
MeHg					
SAMP:	Fish, eggs, meat, liver	GC	ECD	70–400 ng g^{-1}	27, 28
DIG:	None				
HOM:	Water/HCl				
EXT:	Benzene, cysteine, HCl, benzene				
MeHg					
SAMP:	Fish, biological tissue	GC	MIP	20 ng g^{-1}	36
DIG:	Conc H_2SO_4				
DER:	Iodoacetic acid				
MeHg					
SAMP:	Fish	HPLC	Heat/CVAA	0.37–0.6 ng g^{-1}	33
HOM:	Water/6 M HCl/ Celite 545		or DME		
EXT:	Elute with CCl_4, $Na_2S_2O_3$ (to eluate) Air or N_2 purge				
MeHg, Me_2Hg					
SAMP:	Fish	Carbo trap/	CVAF	MeHg: 0.5 ng g^{-1}	13, 14
DIG:	KOH/MeOH (70 °C)/neutralize	Cry-PC		Me_2Hg: 0.1 ng g^{-1}	
RED:	$NaBEt_4$/pH 4.5 acetate buffer N_2 or air purge to Carbo trap He purge to Cry-PC				
MeHg					
SAMP:	Fish, eggs, meat, liver	GC	ECD	70–400 ng g^{-1}	27, 28
DIG:	None				
HOM:	Water/HCl				
EXT:	Benzene, cysteine, HCl, benzene				
Hg(II), MeHg					
SAMP:	Fish, biological materials		GFAA	3.0 ng mL^{-1}	34
HOM:	Water/NaCl/1 M HCl				
Hg(II)					
DER/EXT:	Me_4Sn/MeOH (100 °C) Benzene/$Na_2S_2O_3$/benzene				
MeHg					
EXT:	Benzene, $Na_2S_2O_3$/Cu(II)/benzene				
Hg(II), MeHg					
SAMP:	Standards, tap water	HPLC	$NaBH_4$/CVAA	MeHg: 0.5 ng ml^{-1}	43
DER:	Hg–APDC complex formed on column Elute with APDC		(on eluted sample)	Hg(II): 0.015 ng ml^{-1}	
RED:	Eluent with $NaBH_4$				

Table 4 *continued*

Sample type and treatment		Separation	Detection	LOD	Reference
Hg(II), MeHg					
SAMP:	River water, tap water	CC	CVAF	6 ng g^{-1}	35
STOR:	0.08 M HNO_3				
Hg(II)					
Pre:	Pass through sulfhydryl cotton column with 0.01 M HCl				
OX:	$KBr/KBrO_3$				
RED:	Eluate with Sn(II)/HCl				
MeHg					
PRE:	Elute column with 3 M HCl				
OX:	$KBr/KBrO_3$				
RED:	Sn(II)/HCl				
Me_2Hg					
SAMP:	Seawater	Carbo trap/Cry-PC	Heat/CVAF		13
Hg(II), MeHg, Me_2Hg					
SAMP:	Fish, seawater	Gold/Carbo trap/ Cry-PC	Heat/CVAF	Seawater: 0.2 ng l^{-1} (Hg(II), 0.003 ng l^{-1} (MeHg and Me_2Hg)	13, 14
HOM:	KOH/MeOH				
RED:	$NaBEt_4$/pH 4.5 acetate buffer				
	He purge			Fish: 0.5 ng g^{-1} (MeHg), 0.1 ng g^{-1} (Me_2Hg)	
MeHg, Me_2Hg					
SAMP:	Sediment	Cry-PC	H_2/O_2/ETAA		39
EXT:	Acetic acid				
DER:	$NaBH_4$/acetic acid (pH 3.5)				
	He purge				
Hg(II), MeHg					
SAMP:	Fish, lobster	Cry-PC	ETAA	MeHg: 4 ng g^{-1}	44
DIG:	KOH/MeOH			Hg(II): 75 ng g^{-1}	
DER:	$NaBEt_4$/pH 4.5 acetate buffer				
	He purge				
Hg(II), MeHg, Me_2Hg					
SAMP:	*S. alterniflora*, eelgrass	Cry-PC	ETAA	Hg(II): 0.11 ng g^{-1}	42
EXT:	0.1 M HCl, MeOH				
DER/RED:	$NaBH_4$/0.01 M HCl			MeHg: 0.05 ng g^{-1}	
	He purge				

Sample treatment for RHg

Under most conditions, $NaBH_4$ does not reduce MeHg. However, $NaBH_4$ and air purge in the presence of dimethylformamide,[12] $NaBH_4$ and nitric acid,[21] or tin(II) plus metal-ion catalysts[22] reduce RHg left in the sample aliquot after the removal of Hg(II).

Separation and detection

A separation using a gold trap is generally unnecessary since both Hg(II) and RHg are separately reduced to volatile Hg^0.[12, 21, 22] However, Gill and Bruland[26] and Gill and Fitzgerald[24] did use a gold trap. The usual detectors for Hg^0 are CVAA[12, 21, 22, 24, 25] and CVAF.[26]

SPECIATION OF Hg(II), MeHg AND Me_2Hg

Introduction

Speciation of Hg(II), MeHg, and Me_2Hg (Table 4) generally requires extraction and derivatization (not all methods), separation and concentration (not all methods), and detection. This speciation section differs from the selective reduction section (Table 3) by identifying RHg compounds and confirming that the organomercury compound most commonly observed in the environment is MeHg.

Sample treatment

Extraction

Hundreds of papers on the determination of MeHg in the environment have appeared during the past 25 years. Most researchers use a variation of the original extraction method reported by Westöö.[27,28] Researchers have applied the method to a wide variety of sample types including fish, food, seawater, sediment, blood and urine. One goal of these extraction methods is to separate Hg(II) from MeHg. A second goal is to concentrate MeHg and separate it from chemicals such as proteins and humic matter to avoid interferences during the detection step. Extraction methods are commonly used before separation and detection by gas chromatography (GC).[28,29]

In the Westöö[27,28] method samples are typically homogenized in water, acidified with hydrochloric acid and treated with benzene to extract MeHgCl from the aqueous phase into benzene. After extraction of MeHgCl from the benzene phase with aqueous cysteine, the intitial benzene layer is discarded. The aqueous solution is acidified to break up the cysteine–MeHg complex and MeHg is again extracted into benzene.

Many determinations of MeHg in environmental samples are performed by variations of the Westöö extraction method in which bound Hg(II) and MeHg are converted to free forms using HCl or HBr.[30,31] Free MeHg halide is extracted into an organic solvent such as benzene,[28] toluene,[29,32] dichloromethane[13,32] or CCl_4.[33] MeHg halide is extracted from the organic phase by aqueous thiosulfate ion[33,34] or cysteine.[28,29] Other sample treatments requiring separation have been accomplished on microcolumns of sulfhydryl cotton,[35] which binds MeHg but not Hg(II). The eluted Hg(II) is treated with an oxidizing agent and reduced to Hg^0 with tin(II). MeHg is eluted from the column with 3 M HCl, an oxidizing agent is added to the solution, and Hg(II) is reduced to Hg^0 with tin(II) before its detection.

Derivatization

Some researchers have emphasized methods of volatizing MeHg to avoid extractions. For example, Lansens and Baeyens[36] and Decadt *et al.*[37] separated MeHg from biological tissue by treatment with concentrated sulfuric acid in a closed vial and conversion of MeHg into volatile MeHgI by addition of iodoacetic acid.

Bloom[13] developed based on ethylation of Hg(II) and MeHg to produce volatile compounds. The digested sample is reacted with sodium tetraethylborate ($NaBEt_4$) to convert MeHg to methylethylmercury (MeEtHg) (Eqn [5]) and Hg(II) into diethylmercury (Et_2Hg) (Eqn [6]).

$$MeHg^+ + NaBEt_4 \rightarrow MeEtHg + \text{'}BEt_3\text{'} + Na^+ \quad [5]$$

$$Hg(II)^{2+} + 2NaBEt_4 \rightarrow Et_2Hg + 2\,\text{'}BEt_3\text{'} + 2Na^+ \quad [6]$$

In both equations 'BEt_3' represents unstable BEt_3 which reacts with air and water.

More recently two groups[38–41] reported a hydride derivatization method in which $NaBH_4$ converts MeHg into volatile MeHgH (Eqn [7]).

$$MeHg^+ + NaBH_4 + 3H_2O \rightarrow MeHgH + 3H_2 + H_3BO_3 + Na^+ \quad [7]$$

$NaBH_4$ also reduces Hg(II) to Hg^0 (Eqn [4]) and Me_2Hg is purged unchanged. Quevauviller *et al.*[39] used this hydride generation method for detection of Me_2Hg in sediment samples. Puk and Weber[42] further developed the method for determinations of Hg(II), MeHg, Me_2Hg and Et_2Hg.

Separation by GC, HPLC or cryogenic packed column (Cry-PC)

GC[28,29,34] or derivatization followed by GC[36] is often used for separation of MeHg after extraction. HPLC has an advantage over GC in that formation of volatile derivatives is not necessary.[33,43]

The volatile products formed by reactions with $NaBEt_4$ or $NaBH_4$ can be separated in several ways. Hg^0, Me_2Hg, MeEtHg (Eqn [5]) and Et_2Hg (Eqn [6]) are separated sequentially with a gra-

phite carbon column, gold column and Cry-PC[13,14] or Cry-PC alone.[44] Hg^0 (Eqn [4]), MeHgH (Eqn [7]), and Me_2Hg from the $NaBH_4$ reaction can be separated on a Cry-PC.[39,42]

Detection

MeHg from an extracted sample can be separated by GC and detected by an electron capture detector (ECD)[28,29,45,46], helium microwave induced plasma emission spectrometry,[36,47,48] mass spectrometry,[49] inductively coupled plasma–mass spectometry[50] or graphite furnace atomic absorption (GFAA).[34]

Hg^0 can be detected after Cry-PC separation by atomic spectrometry either by CVAF[13] or by ETAA.[42,44] CVAA is a sensitive enough method for determining MeHg in environmental samples, provided it is converted into Hg^0 before detection.

The eluate from a high-performance liquid chromatography (HPLC) separation[33,43] must be reduced by $NaBH_4$[43] or atomized by thermal decomposition[33] for determination of MeHg and/or Me_2Hg as Hg^0.

Hg^0 is detected after HPLC by atomic spectrometry using CVAA,[33,43] atomic emission spectrometry[51,52] or CVAF after separation on a microcolumn.[35]

Critique of the possible presence of Me_2Hg

Recently Baldi *et al.*[53] reported formation of Me_2Hg from MeHg by sulfate-reducing *Desulfovibrio desulfuricans* strains. This result suggests that Me_2Hg may be more common in the aquatic environment that was generally believed. Despite this possibility, only Mason and Fitzgerald,[54] Quevauviller *et al.*,[39] Puk and Weber[42] and Bloom[13] have observed Me_2Hg in environmental samples. Virtually all known procedures for speciating RH_g in environmental and biological matrices have emphasized MeHg because MeHg was considered the sole RHg synthesized by bacteria in the aquatic environment. In this section we will attempt to convince the reader that with many common analytical methods for speciation of mercury compounds, Me_2Hg would not be observed even if it were present.

There for several reasons for non-observance of Me_2Hg in environmental samples:

(1) Volatilization of Me_2Hg may occur during storage, homogenization, hot digestion or other means of sample preparation.

(2) Me_2Hg may be lost during extraction of toluene or benene phases with aqueous cysteine or $S_2O_3^{2-}$. We confirmed (unpublished results) that Me_2Hg sometimes remains in the original organic phase which is usually discarded.

(3) Me_2Hg may not be detected when GC–ECD is used. The ECD is very sensitive to compounds like MeHgCl that contain at least one electronegative element, but it is not very sensitive to Me_2Hg. In addition, the absence of a retention time from Me_2Hg standards would accentuate the difficulties of identifying it.

(4) Me_2Hg may not be seen because of its high density and low solubility in H_2O. We sometimes observed significant amounts of Me_2Hg after extraction of plant material with 0.1 M HCl, and sometimes saw none in the same extract. The reason was that Me_2Hg was insoluble and at the bottom of the water layer. Addition of MeOH (1:1) to the 0.1 M HCl solubilized Me_2Hg and allowed its determination.[42]

(5) Determination of Me_2Hg during extractions requires sufficient acidity to free it from ligands in the matrix, but not enough to convert it to MeHg or Hg(II). Papers have estimated the maximum concentration of acid that leaves C–Hg bonds intact[13,53,55] but the results are inconsistent. Our unpublished work tested the stability of Me_2Hg in aqueous HCl solutions while sonicating 1 h at 40 °C. Under these conditions Me_2Hg is stable in 0.1 M HCl, partially decomposed in 1 M and 3 M HCl, and unstable in 6 M HCl. Many researchers used sufficiently strong acidic solutions for extractions, etc., to decompose Me_2Hg.

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