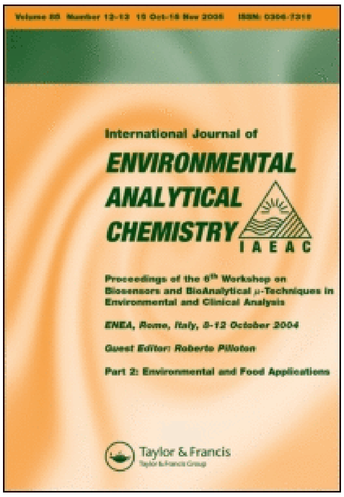

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Overview on the Environmental Analysis of mercury in china

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OVERVIEW ON THE ENVIRONMENTAL ANALYSIS OF MERCURY IN CHINA

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This paper summarizes some of the research and evaluation studies about mercury analysis in the environment during the past years in China. The main contents is as follows: 1) Determination of total mercury and speciation of mercury in air; 2) Storage and handling of water samples; 3) Pre-treatment of solid samples; 4) Determination of total mercury and speciation of mercury in water and solid samples; 5) Certified reference materials.

Keywords: Mercury; China; air; water; CRM

INTRODUCTION

Mercury was used in a wide variety of industrial and civil activities in China. The risk of mercury pollution was threatening the civil health and the sustainable development of economy due to the increasing amounts of emissions. The concentrations of Hg in air, water, and soil had increased since 80's when the GDP grew up. The increasing rate of Hg used was very high, especially in metallurgical industry, gold mining, electronic industry, household batteries and electric lights. Therefore, studies on monitoring methods for mercury compounds were greatly stressed. A large number of articles for the speciation of mercury in environmental samples had been published. This paper summarizes some of them.

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RESULTS

Determination of total mercury and speciation of mercury in air

Determination of total mercury

Normally, methods for determination of total mercury in the air employed a sampling train consisting of a filter to retain particulate phase mercury followed by an adsorbent trap which retains total gaseous mercury[1]. Cold vapour atomic fluorescence spectrometry (CVAFS) and cold vapour atomic absorption spectrometry (CVAAS) determination of mercury collected from ambient air on sulphhydryl cotton fiber or gold coated sand, respectively, were recommended by the China National Environmental Protection Agency in 1990. The former technique was more sensitive, however the operation was more complex. Absorption in a solution of potassium permanganate/sulfuric acid ($KMnO_4/H_2SO_4$) and further $SnCl_2$reduction followed by CVAAS was recommended for the determination of mercury in polluted areas. The method was sensitive (detection limit: 0.6 ng) with less interferences[1]. Dithizone-spectrophotomertry was an alternative method for high concentrations of mercury but the operation was tedious[1]. Pang Shuwei et al.[2,3] reported a method for the determination of total mercury in air by using silver wire and gold coated sand. They also determined dimethylmercury in air using selective absorption. The samples can be stored over 96h. Yu Guotai et al.[4,5] studied the pre-concentration and separation of inorganic and organic mercury in air using sulphhydryl cotton fiber. Jing Zhiyan et al.[6] made a systematic study on the emissions of mercury from coal combustion in Shenyang area. They trapped the gaseous phase of mercury from ambient air using a glass tube filled with super pure MnO_2-cotton, and the mercury from flue gases using a $KMnO_4/H_2SO_4$ solution, respectively. The mercury concentrations in air were measured during the heating and unheating periods in Shenyang area. In May 1989 (unheating time) the average concentration was 34 ng/m^3, whereas in January 1990 (heating time) was 290 ng/m^3. The background value in the countryside was around 3 ng/m^3.

Speciation of mercury

In general two approaches were used for the determination of mercury species in the atmosphere: (1) selective adsorption methods; (2) gas chromatography interfaced with atomic absorption spectrometry. Yuan Lan and Zhong Chonglin[7] collected airborne particulate mercury (PM), mercury chloride (MC), methylmercury chloride (MMC), elemental mercury (Hg^0) and dimethylmercury

(DMM), selectively or simultaneously, using porous filter, Chromosorb W-SE30-HCl, 420 resin (made in Shanghai), spiral silver wire and gold coated sand, successively. The amounts collected were in the range of 0.1–240ng of total mercury with relative standard deviations between 4.5–11.7% Pang Shuwei et al.[2] determined total gaseous mercury and DMM using gold coated sand and silver wire in series. The method was simple with a collection capacity in the range of 0–50ng of mercury and a relative standard deviation of 6%. The detection limit was 0.5ng of mercury for DMM. Jiang Guibin et al.[8] successfully separated DMM, DEM and MMC, EMC by GC that was interfaced to AAS for detection. The sensitivity of the method was 0.2ng of mercury for DMM and DEM and 0.5ng of mercury for MMC and EMC. The concentrations of mercury species measured in a residential area(Beijing) and in a mercury storage room were given in Table I.

TABLE I Concentration of organic mercurials in air (ng/m^3)[8]

Sampling site	*Sampling time*	*Volume of air*	*DMM*	*DEM*	*MMC*	*EMC*
Laboratory	28/04/88	900	ND*	ND	14.4	9.8
storage room 1	22/05/88	120	4.2	4.6	34.3	271
storage room 2	24/05/88	120	ND	3.3	9.2	12.5
Residential area 1	19/05/88	240	ND	ND	ND	ND
Residential area 2	25/05/88	600	ND	ND	1.3	ND
Botanical garden	25/05/88	240	1.2	ND	3. 1	ND
Buddha temple	01/06/88	300	1.7	ND	ND	ND

*ND: Not detected.

Zuo Yuegang and Pang Shuwei[9] determined dialkylmercury and phenylmercury in air samples by reaction gas chromatography. Wei Shiqian et al.[10] collected mercury^{2+} from ambient atmosphere using a KCl-denuder. The efficiencies for absorbing inorganic and organic mercury^{2+} were 98%, and around 94%, respectively. The mercury trapped in the denuder can be quantitatively extracted by 1 mol/L HCl and analyzed by the method of $SnCl_2$ reduction-CVAFS. Further investigations towards knowing the effects of O_3, SO_2, HCl etc. were necessary. In order to get enough mercury for analysis, rather long sampling time was needed.

Up to now reliable data on mercury species in air were still very limited and further analytical developments were needed.

Storage and handling of water samples

Cleaning procedures for laboratory ware

Many reports were given in China about the storage of standard solutions and water samples containing mercury. The different factors that influence the storage of samples were researched extensively, such as materials of containers, ware cleaning procedures and choice of preservatives. Some useful guidelines for storage were given.

The common materials for sample storage were Teflon (PTFE), glass, polyethylene. polypropylene or polychloroethylene[11]. Some scientists did many contrast experiments about sample containers. They suggested that glass was the best material. Their experiments showed that Pyrex and silica glass were better than polyethylene and polychloroethylene[12]. Lu Xiankun[13] suggested that storage of sea water samples in polyethylene would lead to serious mercury pollution of the samples. If the samples had to be stored for less than 3 months, Pyrex glass and Teflon would be the best materials. If the storage time was more than 3 months, Teflon may be the only one. But Liu Qizhong[14] suggested that rigid glass and polyethylene containers were adequate, respectively, for the storage of standard solutions in laboratory and for field operations.

Beside the choice of containers, the cleaning procedures of ware were also important. HNO_3 was usually used for ware cleaning. Concentrations of 3%, 10% and 50% were recommended[14]. Yu Muqing[11] suggested to soak the ware in hot HNO_3 at 90°C for 1 hour. Lu Xiankun[13] used the way of soaking all the ware in 1% HNO_3 and 0.01% $K_2Cr_2O_7$ until sampling. Zhang Guangyuan[15] soaked all the ware in 5% HNO_3 and 0.1% $K_2Cr_2O_7$ for more than 24 hours. Liu Qizhong[14] thought that strong acid would hamper the operation of workers, so he proposed a 5% KNO_3 solution to clean polyethylene containers. The cleaning efficiency was 90–98%.

Storage of water samples

Many reports were published about the losses of mercury in water samples during storage that had been reviewed by Yu Muqing[11]. Summarizing the ideas of these reports we may conclude that the common reasons for losses were: (1) Inorganic mercury was reduced to elemental mercury and volatilized; (2) Mercury was adsorbed on container walls; (3) Mercury was converted from simple ions into stable complex forms, or from soluble forms into suspended forms (adsorbed by suspended materials). From these we can conclude that only the losses due to volatilization were real losses that can not be recovered, the other losses were actually conversion of chemical forms in the solution and can be recovered by right methods of sampling, storage and oxidization.

There were three kinds of mercury preservatives, namely strong acid solutions, that reduce the adsorption of mercury, oxidants that may keep mercury in high oxidizing form in the solution and reduce the volatilization of mercury, and acids and oxidants, that can reduce both the adsorption and volatilization of mercury.

At present, 5% HNO_3 + 0.05% $K_2Cr_2O_7$ was the common preservative for trace mercury. Zhang Guangyuan[15] reported that it cannot only preserve mercury very well but also transfer the adsorbed mercury into solution again. He[16] suggested to use 1–2% HNO_3 + 0.05% $K_2Cr_2O_7$ because HNO_3 solution was easy to volatilize and gave much of harmful nitrogen gas. The experiments by Tang Debao[18] showed that it was better to use 5% HNO_3 + 0.2% $K_2Cr_2O_7$. Liu Qizhong[14] suggested that 0.5% KNO_3 was a good and convenient solid preservative and can be used in practice. Xie Yuxiang[17] reported that 5% HNO_3 + 0.05% $K_2Cr_2O_7$, 0.1N KCl + 0.1N HCl and 0.2N H_2SO_4 + 0.1% $(NH_4)MoO_4$ can all be used as preservatives for trace mercury in the sea water, industry waste water and tap, distilled and drinking waters.

The results about losses of mercury during storage of water samples were given in Table II.

The above methods were all used for the storage of total mercury in water samples. There were not many reports in China about the storage of methylmercury. Tang Yijian[19] showed that solid $CuSO_4$ was a perfect preservative for methylmercury in river water sample, which was steady after the storage of 15 days. The common method of storage was to pre-concentrate methylmercury on sulph-hydryl cotton at the sampling site[11]. Then, the sulph-hydryl cotton glass tube was properly preserved and brought back to the lab to wash, separate and determine methylmercury. It was considered to be a very advantageous sampling and preserving method.

Oxidizing methods of water samples

Decomposition of all mercury species into Hg^{2+} was necessary if total mercury was to be measured. There were many kinds of oxidizing agents, among which, $KMnO_4$and $K_2S_2O_8$ were better. Zhang Guangyuan[16] showed that $KMnO_4$ gave poor result in converting CH_3HgCl and PhHgAc, however, the mixture of $KMnO_4$ and $K_2S_2O_8$ can convert them completely at room temperature or heating. The oxidizing methods recommended[15] were (1) cold oxidizing method; (2) heating to boiling point and keeping the temperature method; (3) heating and boiling method. The result about water samples showed that mercury cannot be converted into Hg^{2+} completely only with 5% HNO_3+ 0.05% $K_2Cr_2O_7$ at the room temperature. If H_2SO_4 + $KMnO_4$ + $K_2S_2O_8$ was used as oxidizing reagent, high precision and good accuracy can be obtained. Xiong Huiling[20] found that NH_2OHHCl can reduce $KMnO_4$ and more accurate results can be obtained if NH_2OHHCl was not added. Qiu Guangkui[21] used $KBrO_3$-KBr as bromic reagent to decompose organic-mercury. This method was simple and fast.

TABLE II The Storage of Water Samples Containing Mercury and the Losses of Mercury

Sample	*Mercury concentration* (μg/l)	*Material of container*	*Method of storage*	*Time of storage (d)*	*Losses (%)*	*Ref.*
Sea water	0.5–8*	Pyrex	No preservative or 0.2 mol/lH_2SO_4	30	0	[13]
			1% HNO_3 + 0.01% $K_2Cr_2O_7$	100	0	
		PTFE	No preservative or 0.2 mol/lH_2SO_4	300	0	
			1% HNO_3 + 0.01% $K_2Cr_2O_7$	300	0	
River water	1	Polyethylene	5% HNO_3 + 0.05% $K_2Cr_2O_7$	20	4.82	[14]
			0.2% HNO_3	30	7.31	
			1.0% HNO_3	30	2.21	
			0.1% $K_2S_2O_8$	30	39.45	
			0.5% $K_2S_2O_8$	30	13.66	
			0.75% $K_2S_2O_8$	30	6.63	
			5% HNO_3	30	16.30	
			0.1% $K_2S_2O_8$ + 3% NaCl	30	21.47	
			No preservative	15	72.59	
			3% NaCl	15	62.12	
deionized water	500	Glass	Neutral deionized water. pH7	300	30	[17]
			0.5% Cu agent. pH10	300	0	
			100 μgI^-/ml, pH7	300	6	
			100 μgI_2/ml + 200 μgI^-/ml, pH7	300	0	
			0.1N KCl + 0.1N HCl	300	0	
			100 μg S^{2-}/ml (0.5 NaOH)	300	81	
			5% HNO_3	300	2	
			0.05% $K_2Cr_2O_7$, pH7	300	20	
			5% HNO_3 + 0.05% $K_2Cr_2O_7$		0	
			1N H_2SO_4 + 0.01% $KMnO_4$		0	
			1N H_2SO_4 + 0.05% $K_2Cr_2O_7$		0	
			1N H_2SO_4 + 0.1% $(NH_4)_2MoO_4$		0	

Sample	*Mercury concentration (μg/l)*	*Material of container*	*Method of storage*	*Time of storage (d)*	*Losses (%)*	*Ref.*
Standard solutions	50	Glass	5% HNO_3 + 0.05% $K_2Cr_2O_7$	103	1.37	[14]
			5% HNO_3	103	4.08	
			1N H_2SO_4	103	28.64	
			No preservative	103	66.52	
		Polyethylene	5% HNO_3 + 0.02% $K_2Cr_2O_7$	160	3.58	[18]
			5% HNO_3	160	9.68	
			5% HNO_3 + 1% $K_2S_2O_8$	160	7.32	
			5% HNO_3 + 0.2% KNO_3	160	1.58	
			1% KNO_3	160	11.36	
			Quadratic distilled water	160	71.36	
		Glass	5% HNO_3 + 0.02% $K_2Cr_2O_7$	160	4.35	
			5%HNO_3	160	11.36	
			5% HNO_3 + 1% $K_2S_2O_8$	160	5.74	
			5% HNO_3 + 0.2% HNO_3	160	0.37	
			1% HNO_3	160	2.37	
			Quadratic distilled water	160	61.76	

*Unit is ng/l.

Pre-treatment of solid samples

Wet and dry oxidizing methods were reported for the determination of mercury in sediments. The wet methods recommended[22] included heating and boiling with an electrothermal plate using the following reagent mixtures: H_2SO_4–$K_2Cr_2O_7$, H_2SO_4–HNO_3–$KMnO_4$, H_2SO_4–HNO_3–V_2O_5 and H_2SO_4–HNO_3–$NaNO_3$. Wang Guochao[22] found in the oxidizing tests with H_2SO_4–$KMnO_4$ that if the added quantity of oxidizing agent was changed slightly mercury in sediment can be oxidized completely even if heating with boiling water or electrothermal plate were omitted. Shen Shuping[23] investigated how the above mentioned four different oxidizing reagents affected the measurement of total mercury in sediments and showed that the oxidizing efficiency of organic substances was highest with the recycling oxidizing method. Liu Zhilong[24] used different oxidizing agents at open, high pressure or condensing recycling conditions, and compared ten kinds of oxidizing mixtures suggesting that the use of aqua regia for 3 hours at 150°C was the best when CVAAS was used to measure mercury in the sediment samples.

The H_2SO_4–HNO_3–V_2O_5 oxidizing method was used with fish and shellfish samples[25]. But at present a HCl solution containing Cu^{2+} or NaCl was used in the majority of reports[26,27] Yang Xianhe[28] used HNO_3–H_2O_2 in a Teflon hermetically-sealed jar to oxidize samples when he monitored mercury in biological samples. The operation of this method was simple and the recovery was high. It was commonly used for biological samples.

At present a wet oxidizing method and volatilization at high temperature followed by collection of elemental mercury were often used to treat coal samples. Zheng Ping[29] studied seven types of oxidizing methods and chose Mo catalyzing followed by H_2SO_4–$HClO_4$ oxidation in determining trace mercury in coal samples. Feng Ping[30] used combustion to treat coal samples. He used dissolvable starch as combustion-supporting agent to burn with coal samples in the oxygen flask and 1% $KMnO_4$–1.8M H_2SO_4solution as absorbing solution.

The recovery rates of oxidizing methods for different solid samples were shown in Table III.

Determination of total mercury and speciation of mercury in water and solid samples

Determination of total mercury

The most common method for determining mercury in water and solid samples included CVAAS, CVAFS and dithizone spectrometry[31].

TABLE III The Recovery Rate of Oxidizing Methods for different Solid Samples Containing Mercury

Samples	*Quantity of mercury added (μg)*	*Method of oxidization*	*Time of oxidization (min)*	*Recovery Rate (%)*	*Ref.*
Sediment	2.50	$H_2SO_4 - HNO_3 - V_2O_5$	20	98.0	[24]
		$H_2SO_4 - HNO_3 - NaNO_3$	30	98.2	
		HNO_3 high pressure oxidizing	180	94.7	
		Aqua regia high pressure oxidizing	180	101.6	
Sediment	0.08	$H_2SO_4 - KMnO_4$	several minutes	95.5- 104.5	[22]
Biologic al samples	0.015	$HNO_3 - H_2O_2$	120	96.4	[28]
coal samples	0.46	$H_2SO_4 - HClO_4 - Na_2MoO_4{\cdot}2H_2O$	40	92	[29]
	0.48	$H_2SO_4 - HClO_4 - K_2Cr_2O_7$	80	96	
	0.52	$H_2SO_4 - HClO_4 - V_2O_5$	40	104	
	0.45	$H_2SO_4 - HClO_4$	120	90	
coal samples	0.05	Burning in the oxygen flask method		104	[30]

TABLE IV Certified Reference Materials and Certified Values of Mercury

Category	*Primary*	*Reference*	*Material*			
	Name	*GBW*	*Unit*	*Certified values*	*Standard deviation*	*Supplier*
Nuclear material analysis and radio-measurement CRM'S	Uranium tailing residue	GBW04123	%	0.027	0.003	1
		GBW04125		0.00079	0.00010	
Geological minerals analysis CRM's	Super-bed rock	GBW07101		0.046	0.004	2
	rock	GBW07103	μg/kg	(4.3)		3
		GBW07104		12	4	
		GBW07105		(6.4)		4
		GBW07106		(8.4)		
		GBW07107		9.7	3.1	
		GBW07108		16	2	
		GBW07109		5	4	
		GBW07110		14	4	
		GBW07111		35	1	
		GBW07112		(5)		
		GBW07113		5	3	
		GBW07114		(4)		
	river system sediment	GBW07301	μg/g	0.018	0.004	
		GBW07302		0.04	0.01	
		GBW07303		(0.05)		
		GBW07304		0.044	0.009	
		GBW07305		0.10	0.02	
		GBW07306		0.045	0.008	
		GBW07307		0.053	0.016	
		GBW07308		0.042	0.005	
		GBW07309		0.083	0.014	
		GBW07310		0.28	0.04	

Category	*Primary*	*Reference*	*Material*			
	Name	*GBW*	*Unit*	*Certified values*	*Standard deviation*	*Supplier*
		GBW07311		0.072	0.014	
Geological minerals analysis CRM's	river system sediments	GBW07312	μg/g	0.056	0.008	
	Marine sediment near coast	GBW07314		0.048	[0.012]	5
	Soil	GBW07401	μg/kg	32	6	3
		GBW07402		15	4	
		GBW07403		60	6	4
		GBW07404		590	76	
		GBW07405		294	41	
		GBW07406		72	11	
		GBW07407		61	8	
		GBW07408		16.6	3.9	
		GBW07409		15	6	6
		GBW07410		66	12	7
		GBW07411		150	22	
	Cinnabar electro-probe	GBW07503	%	86.00	[0.27]	8
	human hair powder	GBW07601	μg/g	0.36	0.08	3
	poplar leaves	GBW07604		0.026	0.003	
	tea	GBW07605		(0.013)		
Environmental chemistry analysis CRM's	River sediment	GBW08301	μg/g	0.22	0.02	9 and 10
	Tibent soil	GBW08302		(0.018)		9
	Pollutant farmland soil	GBW08303		2.15	0.06	11
	coal fly ash	GBW08401		(0.039)		9 and 12
	peach leaves	GBW08501		0.046	0.006	
	tea	GBW08505		(0.004)		
	rice	GBW08508		0.038	0.003	
	non-fat milk powder	GBW08509		(0.0005)		13
	pock	GBW08552		(0.023)		14

Category	*Primary*	*Reference*	*Material*			
	Name	*GBW*	*Unit*	*Certified values*	*Standard deviation*	*Supplier*
	mussel	GBW08571		0.067	0.004	9 and 5
	prawn	GBW08572		0.201	0.002	15
	water	GBW08603	ug/g	0.0100	[4%]	13
		GBW08609	μg/ml	1.00	[0.05]	16
		GBW08617		1000	[1]	13
clinical chemistry and pharmaceutical analysis CRM's	human hair	GBW09101	μg/g	2.16	[0.21]	14
	honey cosmetics	GBW09303		1.32	0.06	16
Geological minerals analysis CRM's	river system sediment	GBW(E) 070003		0.06	0.02	17
		GBW(E) 070004		2.18	0.36	
		GBW(E) 070005		22	1	
		GBW(E) 070006		0.27	0.07	
		GBW(E) 070007		2.5	0.4	
		GBW(E) 070008		0.15	0.03	
	soil	GBW(E) 070009	μg/g	2.2	0.4	17
		GBW(E) 070010		19.5	2.1	
		GBW(E) 070011		0.19	0.06	
Environmental chemistry analysis CRM's	tea leaves	GBW(E) 080001		(0.017)		9

Category	Primary	Reference	Material			
	Name	GBW	Unit	Certified values	Standard deviation	Supplier
	water	GBW(E) 080006	μg/ml	100.0	[0.4]	1
	mercury standard solution in water	GBW(E) 080041	μg/l	1.00	[0.06]	5
	mercury standard solution in sea	GBW(E) 080042		1.00	[0.06]	
	water	GBW(E) 080087	μg/ml	10.00	[0.50]	16
	water	GBW(E) 080124		1000	[0.3%]	13
	bovine liver	GBW(E) 080193	μg/g	0. 18		18 and 4

*Values in parentheses are not certified, but are given for information only.
*Values in brackets are uncertainty.

1. Beijing Institute of Chemical Metallury, Ministry of Nuclear Industry;
2. Xian Institute of Geology, Ministry of Geology and Minerals;
3. Institute of Physical and Chemical Exploration, Ministry of Geology and Minerals (Langfang City);
4. Technical Institute of Rock and Minerals Measurement, Ministry of Geology and Minerals (Beijing);
5. Second Institute of Oceanography, National Bureau of Oceanography;
6. Hei Longjiang Pro. Center for Environmental Monitoring Protection Sciences ;
7. Hei Longjiang Pro. Institute of Environmental Protection Sciences Ha Erbin;
8. Hunan Pro. Applied Institute of Minerals Measurement (Changsha);
9. Research Center of Eco-Environmental Sciences, Chinese Academy of Sciences;
10. Hunan Pro. Institute of Environmental Protection;
11. Beijing Center for Environmental Protection and Measurement;
12. Center for Environmental Protection and Measurement Beijing Institute of Food and Oil Inspection;
13. National Research Center for Certified Reference Materials;
14. Shanghai Institute of Nuclear Research, Chinese Academy of Sciences;
15. Institute of Food Examination Science Ministry of Domestic Trade;
16. Shanghai Institute of Testing Technology:
17. Tianjing Institute of Geology, Ministry of Metallurgical Industry;
18. Basic Institute of Clinical Medicine, the Headquarters of the Hospital of the Chinese People's Liberation Army.

$SnCl_2$ was often used to reduce Hg^{2+} in CVAAS and CVAFS. Jing Xuegen[32] used KBH_2 to reduce mercury directly and omitted the oxidization procedure when determining mercury in milk. Li Feiyong[33] produced Ag cathode wires for pre-concentrating mercury quantitatively with an electrical method at constant potential and further quantitative releasing by heating. This method can be used to determine super trace mercury (less than 1 ng/L) in natural waters. Wang Erkang[34] tested the polarographic property of mercury on a rotating glass carbon electrode in IP-MI pulse polarography for the determination of trace mercury in pure water. Some laboratories used neutron activation method to determine mercury in human hair[35,36] Spectrophotometry was extensively used for the determination of Hg(II). The chromophoric reagent used included potassium ferrocyanide[37,38], 4,4-bis (diethylamino) diphenyl methyl thioketone[39], benzothiazolyldiazoaminoazobenzene[40], 1-(2-Benzothiazolyl)-3(4-phenylazophenyl)-triazene[41] and p-sulfamoyl-benzenediazoaminoazobenzene[42].

Speciation of mercury compounds

There are many reports in China about the determination of organomercury. In summary, there were two kinds of methods. One is gas chromatograph, the other is CVAAS or CVAFS.

Sulphhydryl cotton and cysteine were used in methods for determining methylmercury. Because the contents of MeHg in the different matrices and environments were very low, the cysteine method cannot fit with the requirement because its enrichment factor was too small. The sulphhydryl cotton adsorbing methods included one or two steps. The two steps method consisted in adsorbing methylmercury on sulphhydryl gauze before than sulphhydryl cotton. Its operation was tedious and the recovery was worse than the one step method. Packed columns were often used to determine methylmercury in GC. However, Tong Boling[46] recommended the use of a big bore capillary column (Φ0.53mm × 20m PEG-20M). Usually, the GC detector was ECD. Dai Shugui[47] used GC interfaced with CVAAS for the speciation of organomercury compounds .He separated and determined CH_3HgCl, C_2H_5HgCl and $(C_2H_5)_2Hg$. Jiang Guibing[48] analyzed CH_3HgCl in fish with a GC capillary column interfaced with CVAAS. He also determined successfully C_2H_5HgCl, $(C_2H_5)_2Hg$ and PhHg, Huang Zhuoer[49] reported to determine methylmercury by GC-AFS after aqueous phase ethylation.

When organomercury was determined with CVAAS or CVAFS, $SnCl_2$ was used to reduce inorganic mercury in acid conditions and to reduce organomercury in basic conditions[25,50] Li Shunxing[51] suggested to separate inorganomercury, alkylmercury and phenylmercury with modified green tea. The inorganomercury and organomercury were adsorbed on the modified green tea at

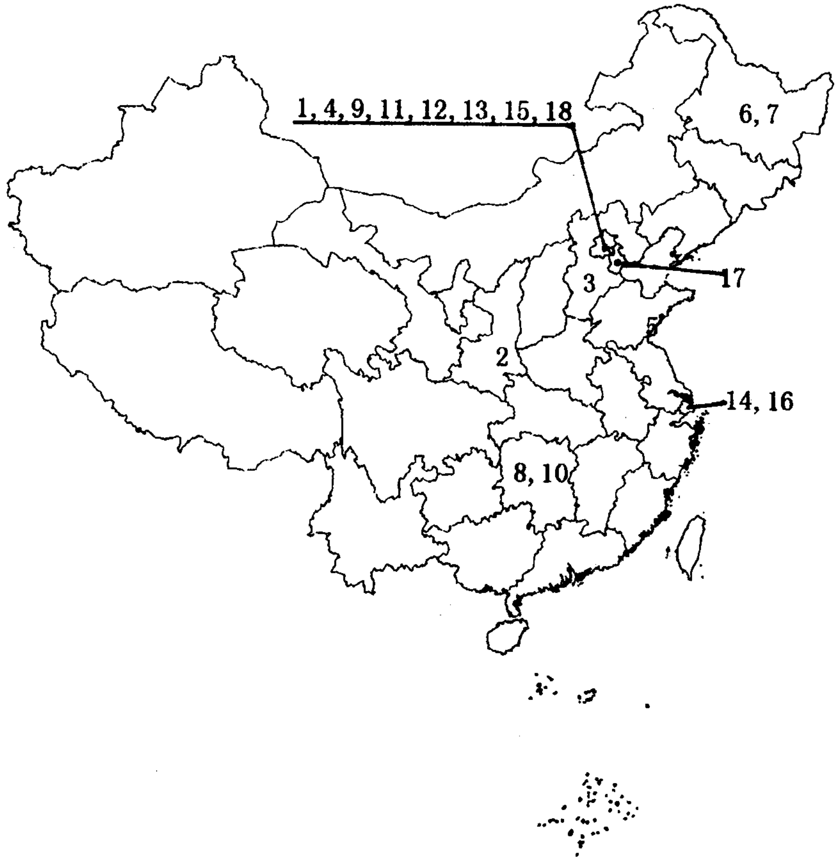

FIGURE 1 The map of China with indication of the places of suppliers in Table IV

pH 5 and 1, respectively. and then inorganomercury, alkyl mercury and phenylmercury were desorbed with 1.5, 3.0 and 6.0 mol·l^{-1} hydrochloric acid, respectively, and determined by CVAAS. A kind of crosslinked chitosan was also applied to the speciation of mercury. Inorganomercury, alkylmercury and phenylmercury were selectively preconcentrated by the crosslinked chitosan and eluted off with 0.4 mol/L NaOH. For the water samples, the detection limits of inorganomercury, ph-Hg and alkyl-Hg were 7.8 ng/L, 9.8 ng/L and 12 ng/L respectively[52].

Some scientists used HPLC to analyze species of mercury. Ying Xuefeng[53] reported that organomercury and inorganic mercury may form complex compounds with di-ethyl-dithocarbamate (DTC).Then, mercury can be determined with reverse HPLC after extraction by chloroform. In this way, methylmercury, ethylmercury, benzoic mercury and inorganic mercury were determined.

Certified reference materials of mercury

Certified Reference Materials (CRM) are essential for the verification of an analytical method. There are over seventy CRM for mercury in various matrices covering geology, environment, clinical medicine, etc. in China. The details are given in Table IV and the places of suppliers are indicated in Figure 1.

References

[1] China Environmental Protection Agency, *Measurement Method for Air and Waste Gases* (China Environmental Science Press 1990).
[2] Pang Shuwei and Qiu Guangkui, *Environmental Sciences in China (in Chinese)*, **2**, 70-74 (1982).
[3] Pang Shuwei. Qiu Guangkui and Xu Liangcai, *Analytical Chemistry (in Chinese)*, **12**, 564–568 (1984).
[4] Yu Guotai and Pang Shuwei. *Ke Xue Tong Bao (in Chinese)*, **18**, 1122–1125 (1982).
[5] Yu Guotai, *Environmental Chemistry (in Chinese)*, **8**, 58–63 (1989).
[6] Jing Zhiyan, Li Yanhong, Feng Xiaobin and Chen Rongli, *Environmental Science collection (in Chinese)*, **13**, 48–66 (1992).
[7] Yuan Lan and Zhong Chonglin, *Environmental Chemistry (in Chinese)*, **12**, 231-235 (1993).
[8] Jiang Guibin, Ni Zheming, Wang Shunrong and Han Hengbin, *J. Anal. Atom. Spectr.*, **4**, 315-318 (1989).
[9] Zuo Yuegang and Pang Shuwei, *Analytical Chemistry (in Chinese)*, **13**, 890–895 (1985).
[10] Wei Shiqiang, Oliver Lindquist and Jonas Sommar, *J. Environ, Sci.*, **9**, 232–240 (1997).
[11] Yu Muqing, *Environmental Science collection (in Chinese)*, **1**, 23–28 (1980).
[12] Ma Quan, *Environmental Science collection (in Chinese)*, **1**, 63–67 (1980).
[13] Lu Xiankun, *Analytical Chemistry (in Chinese)*, **14**, 98–101 (1986).
[14] Liu Qizhong, *Environmental Sciences (in Chinese)*, (3), 52–54 (1979).
[15] Zhang Guangyuan and Jiang Yuying, *Environmental Science collection (in Chinese)*, **3**, 13–18 (1982).
[16] Zhang Guangyuan, Xu Mangying and Fan Meirong, *Environmental Sciences (in Chinese)*, **8**, 10–15 (1987).
[17] Xie Yuxiang, *Environmental Chemistry (in Chinese)*, **4**, 51–55 (1985).
[18] Tang Debao, *Physical and Chemical Analysis, Part B: Chemical Analysis (in Chinese)*, **19**, 51 (1987).
[19] Tang Yijian and Feng Fujian, *Environmental Science collection (in Chinese)*, **1**, 15–20 (1980).
[20] Xiong Huiling and Zhu Zhongban, *Environment Protect (in Chinese)*, **9**, 23–24 (1994).
[21] Qiu Guangkui, Sun Jingfang and Pang Shuwei, *Environmental Science collection (in Chinese)*. **2**, 31-37 (1981).
[22] Wang Guochao, Wang Luhai, Zhou Chunhua and Liu Xingfeng, *Environmental monitoring in China (in Chinese)*, **10**, 10–11 (1994).
[23] Shen Shuping and Wang Xiaomei, *Environmental Pollution Prevention and Cure (in Chinese)*, **7**, 35–38(1985).
[24] Liu Zhilong and Yuan Xiaolong, *Shang Hai Environmental Sciences in China (in Chinese)*, **1**, 31–33 (1987).
[25] Wei Yuying, *Environmental Science collection (in Chinese)*, **3**, 16–18 (1982).
[26] Yang Huifen, Zhu Lin and Wang Huaizhou, *Environmental Sciences in China (in Chinese)*, **2**, 58–61 (1982).
[27] Zang Yanda, *Marine Environmental Sciences (in Chinese)*, **3**, 40–43(1984).
[28] Yang Xianhe, *Environmental Sciences in China (in Chinese)*, **7**, 72–74 (1987).

[29] Zeng Ping and Yao Yanshen, *Environmental Chemistry (in Chinese)*, **10**, 67–63 (1991).

[30] Feng Ping and Lai Weiping, *Chongqing Environmental Sciences (in Chinese)*, **14**, 48–50 (1992).

[31] China Environmental Protection Agency, *Water and waster water monitoring method* (China Environmental Science Press 1989).

[32] Jin Xuegen, *Environmental Pollution Prevention and Cure (in Chinese)*, **75**, 41–44 (1985).

[33] Li Feiyong, *Environment Chemistry (in Chinese)*, **9**, 65–68 (1990).

[34] Wang Erkang, Li Aiguo and Zhang Shousong, *Environmental Sciences (in Chinese)*, (1), 24–27 (1979).

[35] Feng Weiyue, Qian Qinfang, Chai Zhifang, Zhang Peiqun and Lu Xiangli, *Journal of Nuclear and Radiochemistry (in Chinese)*, **18**, 187–192 (1996).

[36] W.Y. Feng, C.F. Chai, and Q.F. Qian, *J, Radioanal. Nucl. Chem., Letters*, **212**, 61–68 (1996).

[37] Fang Guozhen and Tang Zongpei, *Analytical Chemistry (in Chinese)*, **15**, 46–49 (1987).

[38] Liu Changzeng and Wang Shuren, *Analytical Chemistry (in Chinese)*, **18**, 348–351 (1990).

[39] Xue Guang, *Journal of analytical science (in Chinese)*, **13**, 237–239 (1997).

[40] Zhao Shulin, Xia Xinquan, Wu Libo and Yu Gang, *Chinese Journal of Analytical Chemistry (in Chinese)*, **25**, 1206–1209 (1997).

[41] Lü Jianquan, Yang Minghua, Gong Churu, Lü Guiying, Wang Jinming, Chen Aixing and Yao Yunfen, *Journal of analytical science (in Chinese)*, **13**, 237–239 (1997).

[42] He Jiahong, *Physical Testing and Chemical Analysis, Part B; Chemical Analysis (in Chinese)*. **33**, 299–301 (1997).

[43] Feng Fujian and Sheng Suizhen, *Environmental Science collection (in Chinese)*, **2**, 34–39 (1981).

[44] Xu Zhixue and Cai chenzhang. *Environmental Sciences (in Chinese)*, (4), 78–79 (1979).

[45] Shi Wenzhong and Zhao Yushan, *J. Instrument. Anal. (in Chinese)*, **6**, 48–50 (1987).

[46] Tong Boling and Li Xinji, *Rock and Mineral Analysis (in Chinese)*, **12**, 131–134 (1993).

[47] Dai Shugui, Huang Guolan and Fu Xueqi, *ACTA Scientiae Circomstantiae (in Chinese)*, **1**, 363–369 (1981).

[48] Jiang Guibin, Ni Zheming, Wang Shunrong, and Han Heng bin, *Fresenius Z Anal Chem.*, **334**, 27–30 (1989).

[49] Huang Zhuoer, *J. Instrument. Anal. (in Chinese)*, **17**, 22–25 (1998).

[50] Liu Qizhong and Huang Chunying, *Environmental Science collection (in Chinese)*, **1**, 59–60 (1980).

[51] Li Shunxing, Huang Ganquan and Qian Shahua, *Environmental Chemistry (in Chinese)*, **16**, 374–378 (1997).

[52] Wang Meilin, Huang Ganquan, Qian Shahua, Wang Yuting and Jiang Jiansheng, *Chinese Journal of Analytical Chemistry (in Chinese)*, **26**, 12–16 (1998).

[53] Yin Xuefeng, Xu Qing and Xu Xiuzhun, *Chinese Journal of Analytical Chemistry (in Chinese)*. **23**, 1168–1171 (1995).

[54] Shun ruilin and Sheng Zhuohua. *Spectroscopy and Spectral Analysis (in Chinese)*, **11**, 52–53 (1991).

[55] Pang Shuwei, Qiu Guangcai and Sun Jingfang, *ACTA Scientiae Circomstantiae (in Chinese)*, **1**, 234–241 (1981).

[56] Li Shaonan and Chen Xiaomang, *Spectroscopy and Spectral Analysis (in Chinese)*, **13**, 121–127 (1993).

[57] Wu Shiding, *Chinese Journal of Analytical Chemistry (in Chinese)*, **8**, 193–194 (1980).