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Measurement of Total Mercury in Sedments by Graphite-Furnace Atomic Absorption Spectrophotometry Using 2,3-Dimercaptopropane-1-sulfonate as a Complexing Agent

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Abstract

An amount (50 mg) of dried sediment sample was digested with a mixture of aqua regia (700 μL) and hydrofluoric acid (50 μL) at 80°C for 10 min in a 7-mL teflon microvessel. After digestion, the pH of the acidic sediment mixture was adjusted to 6.5 – 7.0 by NaOH. The sediment residue was removed by passing the mixture through a 0.45 μm filter membrane. To the filtrate, sodium acetate buffer (pH = 6.0) and 2,3-dimercaptopropane-1-sulfonate (DMPS) were added to form a mercury-DMPS complex. The complex was preconcentrated on two home-made C_{18} cartridges in series, and each cartridge was eluted with methanol and adjusted to 0.50 mL. A portion (50 μL) was introduced into a graphite tube and then measured by GFAAS. The peak heights in absorbance were used for a quantitative analysis. The method detection limit (MDL, 3σ) was 6.8 ng/g; the calibration graph was linear up to 308 ng/g. Good accuracies were obtained when testing four sediment certified reference materials (GBW 07305, CRM 016-050, GBW 07311, and BCR CRM-580). Four real river sediment samples collected

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from central Taiwan were analyzed, and the recoveries were in the range of 97.0 – 102.0% with a RSD (n = 3) < 4.7 %. The proposed method can be applied to the measurement of total mercury in sediment samples.

Key words:
sediment, total mercury, DMPS, graphite-furnace atomic absorption spectrophotometry

1 Introduction

The contents of mercury (Hg) in the earth's crust [1] and in coal [1-3] are about 80 ng/g and 100 – 1000 ng/g, respectively. By way of rain, Hg and its compounds in the earth's crust, in soil, or in gaseous vapor and fly ash [3] discharged from coal-burning factories or chlor-alkali industrial effluents [4-6] may be dissolved in water, rivers, or seas. Thus, Hg may be deposited in stream, estuarine, or marine sediments.

Fish and marine organisms may eat muds of sediments and small amounts of Hg may accumulate in their tissues. Through diet, Hg may enter a human body by the consumption of fish and fish products [6,7], in which Hg^{2+} causes kidney toxicity while the CH_3Hg^+ causes neurological damage [1].

The levels of total Hg in natural non-polluted sediments [8] are usually in the range of 20 – 100 ng/g, in which the portion of CH_3Hg^+ might be 0.1 to 1.5% [9]. Hence, non-polluted levels of total Hg in sediments are recommended not to exceed 100, 250, or 1000 ng/g by Canada [10], Germany [11], and the United Kingdom [11], respectively. The maximum contaminant level of total Hg in sediment has not yet been regulated by the Taiwan government.

Several methods commonly used for the measurement of total Hg in sediments are cold-vapor atomic absorption spectrometry (CVAAS) [12]; gold-amalgamation / CVAAS [13,14], or / cold-vapor atomic fluorescence spectrometry (CVAFS) [15,16]; head space-solid phase microextraction / ethylation / gas chromatography / inductively coupled plasma-mass spectrometry (HS-SPME-GC-ICP-MS) [17]; hydride-generation / quartz

furnace atomic absorption spectrophotometry (HG / QFAAS) [18]; and permanent modifier coated on graphite tube / direct analysis of solid sample by graphite-furnace atomic absorption spectrophotometry (SS-GFAAS) [19]. 2,3-Dimercaptopropane-1-sulfonate (DMPS) has large formation constants [20,21] with mercury ($10^{42.2}$ for Hg^{2+} and $10^{21.2}$ for CH_3Hg^+) in a sodium acetate buffer (pH 4 – 6), and has been used as an antidote for rats after poisoning with mercury [22-24]. This paper describes how small amounts (0.34 – 15.4 ng) of total Hg in dried sediments (50 mg) could be accurately determined by GFAAS after digesting with aqua regia / HF, complexing with DMPS, preconcentrating on two home-made C_{18} cartridges in series, and finally concentrating in methanol (0.50 mL each).

2 Experimental

2.1 Apparatus

A Hitachi Z-8000 graphite-furnace atomic-absorption spectrophotometer, equipped with a Zeeman background corrector, was used for the atomic-absorption measurement of Hg at 253.7 nm with a slit width of 1.3 nm. A hollow-cathode Hg lamp (S & J Juniper Co., England) was operated at 6 mA. Uncoated graphite tube cuvettes (No. 180-7400, Hitachi Co., Japan) were purchased. A MARS-5 microwave accelerated reaction system (CEM Co., USA), equipped with a temperature-controlled sensor, was used for the microwave digestion of Hg in sediment samples. During microwave digestion, each 7-mL teflon microvessel was placed in a 90-mL teflon PFA vessel that contained about 9.3 mL of pure water for samples (or 10.0 mL of pure water for a temperature-controlled sensor).

2.2 Reagents and solutions

All chemicals used were of analytical reagent grade or better. Nitric acid (double distilled), hydrochloric acid (trace metal grade), and hydrofluoric acid (48%, w/w) were purchased from Fisher Chemical Co., USA. Methanol and a stock standard solution

(1000 mg/L of Hg^{2+} in 0.5 M HNO_3) were purchased from Merck, Germany. Another stock standard solution of 1000 mg/L of CH_3Hg^+ in methanol was prepared from CH_3HgCl (98%, GR, TCI Co., Japan). Working standard solutions of mercury were prepared by diluting the stock solution with methanol. A DMPS stock solution (300 mg/L) was prepared from 2,3-dimercaptopropane-1-sulfonate (95%, Sigma and Aldrich Co., USA) with pure water weekly. Sodium acetate (super pure, Merck) and acetic acid (99.99%, Sigma and Aldrich) were used to prepare an acetate buffer in an aqueous solution monthly.

2.3 Sediment samples and certified reference materials (CRM)

Four river sediment samples (No. 1 – No. 4) were collected from central Taiwan. Among them, No. 1 and No. 2 were from Chi-Lu bridge and Ching-Yu bridge (Nantou County), respectively; No. 3 was from the entrance gate #2 of Lin-Nei, Chow-Shuei River (Yun-Lin County); and No. 4 was from the entrance of Ching-Shuei River (Ten-Wei, Chang-Hua County). Four sediment CRMs were purchased. Among them, two stream sediments GBW 07305 containing (100 ± 20) ng/g of Hg and GBW 07311 containing (72 ± 14) ng/g of Hg were from Shanghai Institute of Nuclear Research, China. Another stream sediment CRM 016-050 containing (110 ± 40) ng/g of Hg was from Resource Technology Corporation, Laramie, WY, USA. An estuarine sediment BCR CRM-580 containing (132 ± 3) μg/g of Hg was from European Communities-Institute for Reference Materials and Measurements, Belgium.

2.4 Pretreatment of sediment samples

Sediment samples (about 10 g) were frozen immediately after collection and freeze-dried in the laboratory for 24 h. Then, they were ground into a powder with the mortar and pestle to pass through a 710 μm (25 mesh) sieve stainless-steel screen. Each of the powdered samples was stored in a plastic bottle and refrigerated at 4°C until analysis. The four CRM sediments were also stored in the refrigerator (4°C) and used as provided

without further treatment. In order to make sure that a dry basis was employed, all samples (about 2 g) were placed in a vacuum desiccator at room temperature over magnesium perchlorate (Merck, GR) for at least 24 h before weighing.

2.5 Analytical procedure for total mercury in sediment

An amount (50 mg) of dried sediment sample was accurately weighed to ± 0.1 mg and placed in a 7-mL teflon microvessel. For spiked recovery tests or the standard addition method, appropriate amounts (0 – 10.0 ng) of mercury (1.00 mg/L of CH_3Hg^+, or Hg^{2+}, prepared in methanol) were added to the samples. After being left standing overnight to allow the methanol to evaporate, a microwave digestion procedure using aqua regia (conc. HCl : conc. HNO_3 = 3 : 1, v/v) and HF was performed.

After cooling to room temperature, the 7-mL teflon microvessels were removed and further cooled in a refrigerator (4ºC) for about 20 min before being opened. Each digested sample was transferred to a teflon beaker (100 mL) and its pH was adjusted to 6.5 – 7.0 by NaOH in order to let $Fe(OH)_3$ form precipitates as much as possible. [Otherwise, the precipitates of $Fe(OH)_3$ would clog the C_{18} cartridges, reduce the flow rate during the preconcentration process, and interfere with the measurement of total Hg in the atomization step]. The mixture was filtered with a 0.45 μm membrane (Millipore, HATF 04700) to remove the sediment residue. To the filtrate, appropriate amounts of sodium acetate buffer and DMPS were added. The mixture was allowed to react at room temperature for about 1 h [25] to form a complex of mercury-DMPS. The complex was preconcentrated on two home-made C_{18} cartridges (160 mg each, Waters Co.) in series, and each cartridge was eluted with methanol and adjusted to 0.50 mL. A portion (50 μL)

of the methanol solution was introduced into a graphite cuvette by a microsyringe (100 μL, Hamilton Co.) and atomized according to a suitable temperature program. The net peak heights in absorbance were used for a quantitative analysis. The amount of total mercury in the sediment measured is the sum of these two C_{18} cartridges.

3. Results and Discussion

Since the Hg content in sediment GBW 07305 was large enough (about 4.8 ng) for a 50 mg dried sample, the following parameters were compared directly by using this CRM sediment.

3.1 Temperature program used for GFAAS

The effect of the ashing temperatures (150 - 200°C for 40 s) and the atomization temperatures (1100 - 1600°C for 3 s) on the absorbance was tested with 0.46 ng of Hg in 50 μL of a methanol solution prepared from cartridge 1 of sediment GBW 07305. This was done because the Hg content in cartridge 1 was dominant (about 95% of the total amount). During ashing, the absorbance increased from 150 to 160°C; remained the same from 160 to 170°C; and then decreased above 170°C (which indicates that the analyte became lost) as shown in Figure 1. During atomization, the absorbance increased as the temperature increased from 1100 to 1300°C for 3 s and decreased from 1400 to 1600°C. Hence, suitable ashing (170°C) and atomization (1300°C) temperatures were used, as tabulated in Table 1.

3.2 Conditions used for microwave digestion

The effect of the amounts (500 - 900 μL) of aqua regia and HF (0 - 90 μL) for digesting a sediment sample (GBW 07305) on the absorbance (the sum of cartridges 1

and 2) was tested with 0.48 ng Hg in 50 μL of the methanol solution. Figure 2 indicates that when 50 μL of HF was used, a relatively large absorbance value was observed at 700 μL. When the amount of aqua regia was smaller than 700 μL, the mercury in the sediment might not be leached out completely from the SiO_2 matrix. When the amount of aqua regia was larger than 700 μL, some of the mercury vapor might be lost through leaking due to the increased pressure inside the teflon microvessel. Similarly, when 700 μL of aqua regia was used, the absorbance increased as the amount of HF was increased from 0 to 50 μL; and then decreased as the amount of HF was increased from 50 to 90 μL as shown in Figure 3. Hence, 700 μL aqua regia and 50 μL of HF were selected for use in this study.

The effects of the digestion temperatures (75 to 90°C holding for 10 min) and the digestion times (5 - 20 min at 80°C) using aqua regia / HF on the absorbance were tested with 0.48 ng Hg in 50 μL of the methanol solution. The results indicate that the absorbance increased as the digestion temperature increased from 75 to 80°C, and then decreased at 85 and 90°C; further, the absorbance increased when the digestion time increased from 5 to 10 min at 80°C, and then decreased when the digestion time was longer than 10 min. Hence, digestion at 80°C for 10 min was used.

3.3 Amounts of DMPS and acetate buffer used

The effect of the amount (0.12 – 0.84 μmol) of DMPS on the absorbance was tested with 0.48 ng of Hg in 50 μL of the methanol solution. Figure 4 indicates that the absorbance increased as the amount of DMPS increased from 0.12 to 0.60 μmol. This might be because the DMPS complexed with Hg^{2+} more completely. The absorbance decreased when 0.72 and 0.84 μmol of DMPS were used. This might have been due to excess sodium salts in DMPS, which might not be removed completely during the ashing step, and would interfere with the atomization of Hg. Hence, 0.60 μmol of DMPS was used in this work.

The effect of the pH (5.0 - 7.0) of sodium acetate buffer (1.0 mmol) on the absorbance was tested with 0.48 ng of Hg in 50 μL of the methanol solution. Figure 5

indicates that the absorbance increased as the pH increased from 5.0 to 6.0. This might be because the complex of DMPS-Hg is more stable at pH 6.0. The absorbance decreased at pH 6.5 and 7.0. This might have been due to some precipitates of mercuric hydroxide (or HgO) formed at higher pH. Hence, an acetate buffer pH of 6.0 was used. Similarly, the amounts of acetate buffer (0.5 – 3.0 mmol of pH 6.0) were varied. The results indicate that when 0.60 μmol of DMPS was used, the absorbance increased as the amount of acetate buffer was increased from 0.5 to 1.0 mmol, and then the absorbance decreased as the amount of acetate buffer was increased from 1.0 to 3.0 mmol. This might have been due to the excess salts of the buffer, which were not completely removed during the ashing step, and would interfere with the atomization of Hg. Hence, 1.0 mmol of acetate buffer was selected for use.

3.4 Calibration graphs

In order to know whether the sediment matrix would interfere with the measurement of total Hg after microwave digestion, the following two sets of calibration graphs were compared. In the first set, a typical calibration graph for total Hg from the standard addition method was $y = 2.70 \times 10^{-3}\, x + 1.37 \times 10^{-2}$ when 0 – 10.0 ng of CH_3Hg^+ was added to GBW 07305 sediment (or, $y = 2.71 \times 10^{-3}\, x + 1.32 \times 10^{-2}$ when 0 – 10.0 ng of Hg^{2+} was added). The correlation coefficients were 0.9995 and 0.9996, respectively. Similar results were obtained for CRM 016-050 sediment, as listed in Table 2. The second set was prepared by adding corresponding amounts (0 – 15.0 ng) of mercury (CH_3Hg^+ or Hg^{2+} in methanol) directly to a methanol solution (0.50 mL) containing the same amount of DMPS (0.60 μmol) and a proportional amount (10 μmol) of sodium acetate buffer. A typical calibration graph from the second set was $y = 2.71 \times 10^{-3}\, x + 1.10 \times 10^{-3}$ when CH_3Hg^+ was added (or, $y = 2.72 \times 10^{-3}\, x + 1.30 \times 10^{-3}$ when Hg^{2+} was added). The correlation coefficients were 0.9998 and 0.9996, respectively. By comparing the slopes of eighteen calibration graphs obtained from these two sets for total Hg, the relative error was within 2.3%. These results indicate that the various sediment matrices do not significantly interfere with the measurement of Hg after microwave

digestion and the pretreatment procedure. Thus, the calibration graphs prepared from the second set can be used for quantification of total Hg in sediment samples.

3.5 Accuracy test

The accuracies of the proposed method were checked by testing with four sediment CRMs. The concentrations of total Hg measured from the mean of six determinations were (96.0 ± 2.4) ng/g, (107.2 ± 2.8) ng/g, (61.8 ± 3.0) ng/g, and (132.4 ± 1.8) μg/g for GBW 07305, CRM 016-050, GBW 07311, and BCR-580, respectively. The measured results are all within the corresponding certified values of (100 ± 20) ng/g, (110 ± 40) ng/g, (72 ±14) ng/g, and (132 ± 3) μg/g, as listed in Table 3, with the RSD (n = 6) within 4.9%.

3.6 The contents of total Hg in real samples and recovery tests

Four real river sediment samples (No. 1 – No. 4) were analyzed according to the proposed method. The amounts of total Hg measured from the mean of three determinations were 1.68 ± 0.03, 1.98 ± 0.02, 2.94 ± 0.17, and 3.36 ± 0.18 ng, respectively, in 50.0 mg with the RSD (n = 3) within 5.8%. These correspond to concentrations of 33.6 ± 0.6, 39.6 ± 0.4, 58.8 ± 3.4, and 67.2 ± 3.6 ng/g. According to the Canadian regulation [10] for the maximum contaminant level (100 ng/g) for total Hg in sediment, these four real river sediments are classified as non-polluted levels. Table 4 shows that the spiked recoveries of total Hg for four real sediment samples (No. 1 – No. 4) and three CRM sediments were in the range of 96.8 – 102.0% with the RSD (n = 3) within 4.7%.

3.7 Method detection limit (MDL)

Following the proposed method, the MDL for total Hg was determined as the amount corresponding to three times the standard deviation of twelve replicates using 50

μL of a methanol solution containing 0.30 ng of Hg prepared from cartridge 1 of CRM GBW 07311. The MDL (3 σ) value of total Hg in sediment from the mean of six determinations was found to be (0.34 ± 0.04) ng for a 50.0 mg sediment sample, or (6.8 ± 0.8) ng/g. The MDL value of total mercury obtained in this work was comparable to those (1.0 ng/g for a 250 mg sediment sample by FI-ICP-MS [11]; 1.5 ng/g for a 1 g sediment sample [15], or 5 ng/g [16] by Au-amalgamation / CVAFS; 2 ng/g for a 100 mg sediment sample by Au-amalgamation / CVAAS [14]; 200 ng/g for a 1 mg sediment sample by SS-GFAAS [19]), lower than that (50 ng/g for a 50 mg sediment sample by CVAAS [12]), but higher than those (0.6 ng/g for a 500 mg sediment sample by HG / QFAAS [18]; 0.27 pg/g for a 100 mg sediment sample by HS-SPME / GC / ICP-MS [17]) reported elsewhere. Since the strictest maximum contaminant level at present is 100 ng/g for total Hg in sediment [10], this MDL value (6.8 ng/g) might still be useful in practice for a 50 mg dried sediment sample. The calibration graph was linear up to 308 ng/g.

4. Conclusion

Good accuracies for total mercury were obtained by testing with four sediment CRM (GBW 07305, CRM 016-050, GBW 07311, and BCR-580) according to the proposed method. The MDL value for total Hg was found to be 6.8 ng/g and the calibration graph was linear up to 308 ng/g. The levels of total Hg in four real river sediments (No. 1 – No. 4) collected in central Taiwan were in the range of 33.6 – 67.2 ng/g, with a RSD (n = 3) within 4.7%. According to the Canadian regulation for total Hg in sediments, these four real river sediment samples are classified as non-polluted levels. It is concluded that the content (0.34 – 15.4 ng) of total Hg in a dried sediment sample (50 mg) can be accurately determined by the proposed method.

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Table 1 Suitable temperature program for mercury in sediment samples by GFAAS

Step	Temperature (^{o}C)	Time (s)	Flow rate of Ar (mL/min)
Drying	60 - 120	30	200
Ashing	170 - 170	40	200
Atomization	1300 - 1300	3	0
Cleaning	1800 - 1800	5	200

Table 2 Comparison of calibration graphs prepared from the first and the second sets

Set #	Sample matrix	Typical linear equation	Correlation coefficient
First [a]	GBW 07305 [c]	$y = 2.70 \times 10^{-3} x + 1.37 \times 10^{-2}$	0.9995
	GBW 07305 [d]	$y = 2.71 \times 10^{-3} x + 1.32 \times 10^{-2}$	0.9996
	CRM 016-050 [c]	$y = 2.73 \times 10^{-3} x + 1.50 \times 10^{-2}$	0.9996
	CRM 016-050 [d]	$y = 2.71 \times 10^{-3} x + 1.47 \times 10^{-2}$	0.9997
Second [b]	methanol [e]	$y = 2.71 \times 10^{-3} x + 1.10 \times 10^{-2}$	0.9998
	methanol [f]	$y = 2.72 \times 10^{-3} x + 1.30 \times 10^{-2}$	0.9996

[a] Standard addition method was employed by spiking mercury on a 50.0 mg sample of dried sediment.
[b] Mercury was added directly to 0.50 mL methanol containing 0.60 µmol of DMPS and 10 µmol of NaOAc buffer.
[c] 0 – 10.0 ng of CH_3Hg^+ was spiked.
[d] 0 – 10.0 ng of Hg^{2+} was spiked.
[e] 0 – 15.0 ng of CH_3Hg^+ was added.
[f] 0 – 15.0 ng of Hg^{2+} was added.

Table 3 Accuracy tests for total mercury in sediment

Sediment CRM	Total Hg measured		Certified value for total Hg (ng/g)
	Amount [a] (ng)	Conc. [a] (ng/g)	
GBW 07305	4.80 ± 0.12	96.0 ± 2.4	100 ± 20
CRM 016-050	5.36 ± 0.14	107.2 ± 2.8	110 ± 40
GBW 07311	3.09 ± 0.15	61.8 ± 3.0	72 ± 14
BCR-580	6.62 ± 0.09 [b]	132.4 ± 1.8 [c,d] (μg/g)	132 ± 3 [d] (μg/g)

[a] Mean of six determinations and standard deviation.

[b] Aqua regia and HF were added to 50.0 mg of the sample and the mixture was microwave digested at 80°C for 10 min. The pH of the digested mixture was adjusted to 6.5 – 7.0 and then filtered with a 0.45 μm membrane. The filtrate was diluted to 1000 mL with pure water. An aliquot (1.00 mL) was transferred to a small test tube (5.0 mL), to which sodium acetate buffer (1.0 mmol) and DMPS (0.60 μmol) were added. The mixture was allowed to react for about 1 h to form the Hg-DMPS complex. The complex was preconcentrated on three home-made C_{18} cartridges in series, and each cartridge was eluted with methanol and adjusted to 0.50 mL. The total amount of Hg measured was the sum of these three C_{18} cartridges. However, the amount of Hg on the third C_{18} cartridge was zero.

[c] After considering a dilution factor of 1000.

[d] The unit of concentration for total Hg in BCR-580 is μg/g.

Table 4 Recovery tests for total Hg in sediment samples

Sample [a]	Amount of Hg (ng)		Recovery
	Added	Found	(%)
No. 1	2.00	1.97 ± 0.05 [b]	98.5 ± 2.5 [b]
	5.00	4.85 ± 0.09 [b]	97.0 ± 1.8 [b]
No. 2	2.00	2.02 ± 0.05 [b]	101.0 ± 2.5 [b]
	5.00	5.09 ± 0.07 [b]	101.8 ± 1.4 [b]
No. 3	3.00	3.04 ± 0.14 [b]	101.3 ± 4.7 [b]
	6.00	5.97 ± 0.05 [b]	99.5 ± 0.8 [b]
No. 4	3.00	3.06 ± 0.12 [b]	102.0 ± 4.0 [b]
	6.00	5.83 ± 0.15 [b]	97.2 ± 2.5 [b]
GBW 07305	2.50	2.49 ± 0.09 [c]	99.6 ± 3.6 [c]
	5.00	4.95 ± 0.13 [c]	99.0 ± 2.6 [c]
	7.50	7.47 ± 0.09 [c]	99.6 ± 1.2 [c]
	10.00	10.12 ± 0.11 [c]	101.2 ± 1.1 [c]
CRM 016-050	2.50	2.42 ± 0.10 [c]	96.8 ± 4.0 [c]
	5.00	4.96 ± 0.09 [c]	99.2 ± 1.8 [c]
	7.50	7.52 ± 0.12 [c]	100.3 ± 1.6 [c]
	10.00	10.09 ± 0.07 [c]	100.9 ± 0.7 [c]
GBW 07311	4.00	3.87 ± 0.14 [c]	96.8 ± 3.5 [c]
	8.00	7.86 ± 0.22 [c]	98.3 ± 2.8 [c]

[a] The amounts of total Hg measured in samples No. 1 to No. 4, GBW 07305, CRM 016-050, and GBW 07311 were 1.68 ± 0.03, 1.98 ± 0.02, 2.94 ± 0.17, 3.36 ± 0.18, 4.80 ± 0.12, 5.36 ±0.14, and 3.09 ± 0.15 ng, respectively, for a 50.0 mg dried sediment sample in three or six replicates.

[b] Mean of three determinations with standard deviation by spiking Hg^{2+}.

[c] Mean of six determinations with standard deviation. Among them, three of Hg^{2+} and another three of CH_3Hg^+ were spiked, respectively.

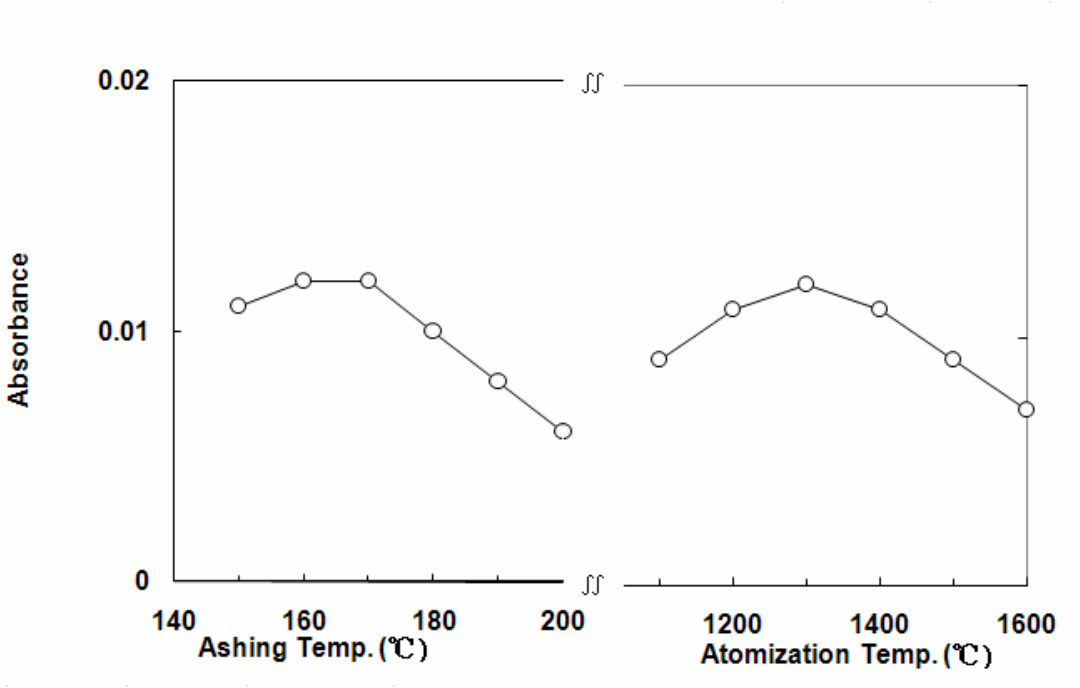

Fig. 1 Effect of the ashing and atomization temperatures on the absorbance of Hg for 0.46 ng Hg in 50 μL of concentrated methanol solution.

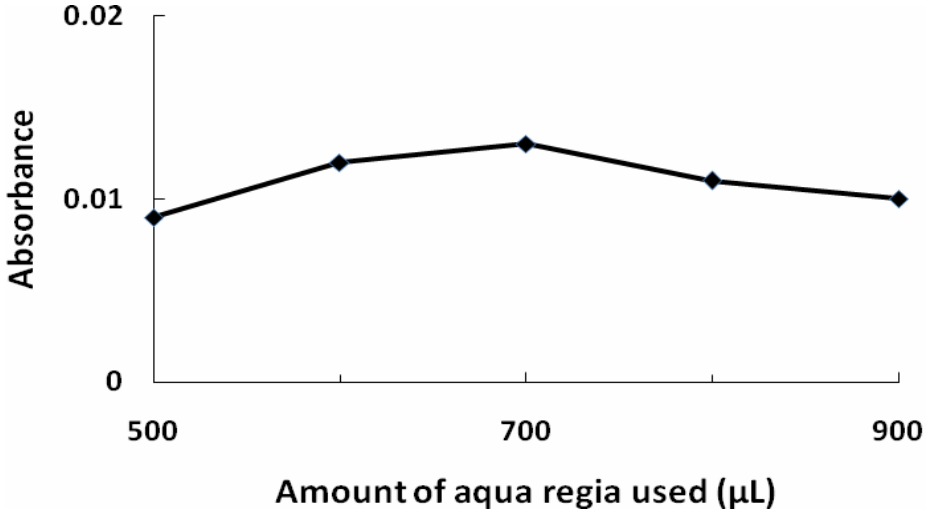

Fig. 2 Effect of the amount of aqua regia on the absorbance of Hg for 0.48 ng Hg in 50 µL of concentrated methanol solution.

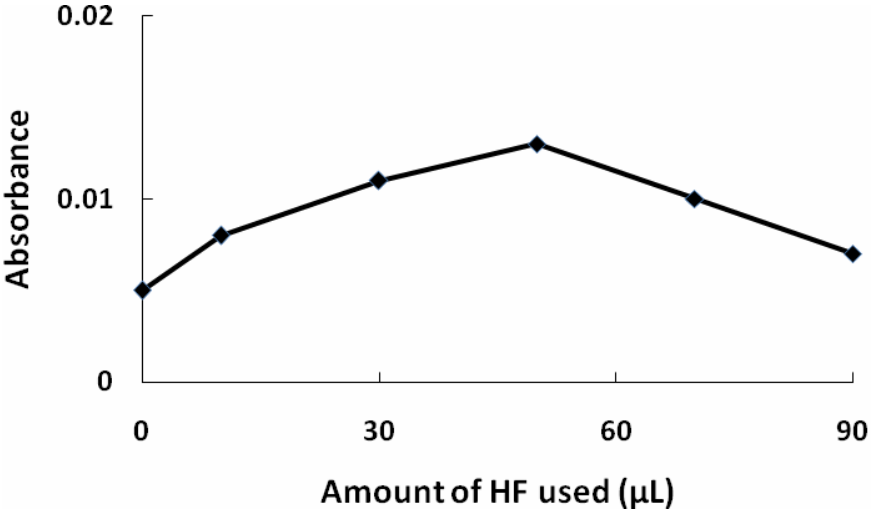

Fig. 3 Effect of the amount of HF on the absorbance of Hg for 0.48 ng Hg in 50 μL of concentrated methanol solution.

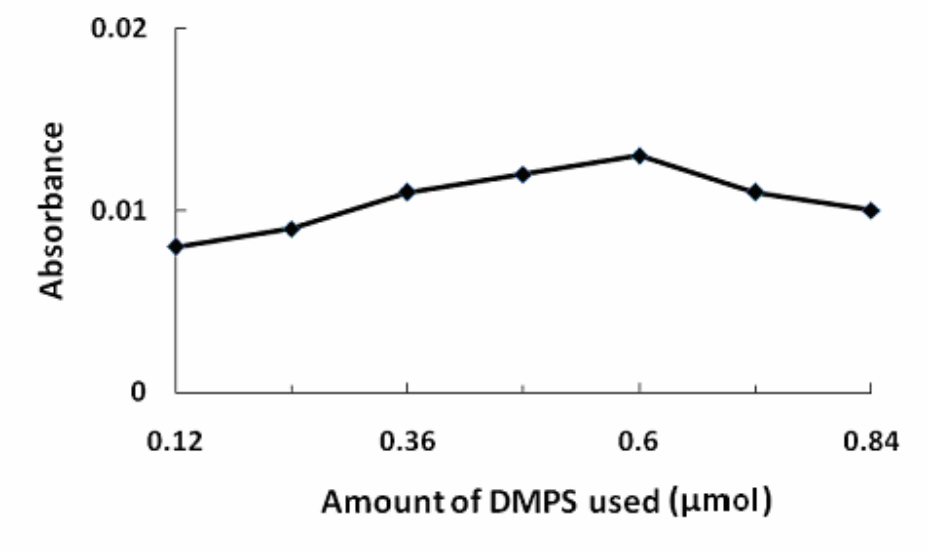

Fig. 4 Effect of the amount of DMPS on the absorbance of Hg for 0.48 ng Hg in 50 µL of concentrated methanol solution.

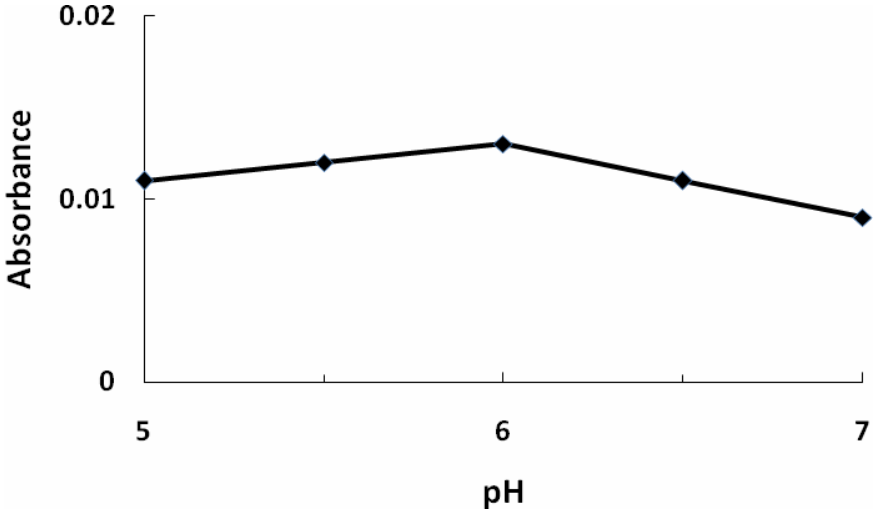

Fig. 5 Effect of pH of sodium acetate buffer on the absorbance of Hg for 0.48 ng in 50 µL of concentrated methanol solution.

以DMPS作爲複合劑及使用石墨式原子吸光法測定底泥中總汞的含量

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摘要

本研究秤取50 mg乾燥的底泥樣品，放入7-mL鐵氟龍瓶中，加入王水(700 μL)和氫氟酸(50 μL)，經微波消化(80℃，10 min)將底泥中的總汞萃取出。以氫氧化鈉溶液調整消化混合物之pH值至6.5 - 7.0，經過濾移除底泥殘渣後，加入醋酸鈉緩衝溶液(pH 6.0)和DMPS，使形成汞-DMPS之複合物，經兩支自製串聯之C_{18} cartridge預濃縮後，每支cartridge用甲醇將複合物沖洗出，並定量至0.50 mL。取出50 μL注入石墨式原子吸光儀，測定總汞的含量。本方法之偵測極限值(MDL，3σ)爲6.8 ng/g，線性可達308 ng/g。使用本方法測試四種底泥參考樣品(GBW 07305，CRM 016-050，GBW 07311，和BCR CRM-580)，所得的值都能落在確認值之範圍內，表示準確度良好。測試四種台灣中部地區的河川底泥樣品，濃度介於33.6至67.2 ng/g之間，添加回收率介於97.0至102.0%之間，RSD(n=3)在4.7%以內。本方法應可應用在測定底泥樣品中總汞的濃度和含量。

關鍵字：底泥、總汞、DMPS、石墨式原子吸光法