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Rapid determination of total mercury in treated waste water by cold vapor atomic absorption spectrometry in alkaline medium with sodium hypochlorite solution

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Abstract

Addition of a sodium hypochlorite solution (9.2% (w/v)) was effective to reduce a sulfide interference in determination of organic mercury, including methylmercury and phenylmercury, as well as a previously reported determination of inorganic mercury by cold vapor atomic absorption spectrometry (CVAAS) in an alkaline medium. Total mercury ranging from 0.17 to 33 $\mu g L^{-1}$ in 15 mL of sample solutions containing up to 200 $mg L^{-1}$ of sulfide can be determined without any serious interference by sulfide when 1 mL of the sodium hypochlorite solution was added after dilution of the sample solution to 25 mL. The proposed method was simple and rapid because no digestion processes were required for the determination of total mercury; the time required for the determination was only about 5 min. The proposed method was applicable to the analysis of treated waste water.

Keywords: Total Hg; Cold vapor atomic absorption spectrometry; Alkaline medium; Sodium hypochlorite solution; Sulfide interference

1. Introduction

Mercury, including inorganic mercury and organic mercury such as methylmercury and phenylmercury, is one of the most toxic metals [1]. A proper treatment of waste water containing mercury and a strict process control involving the monitoring of water quality in treated waste water are essential to prevent a discharge of not only inorganic but also organic mercury into the environment. The sulfide precipitation technique is often applied to the treatment of waste water containing some heavy metals including mercury [2]. To determine the total amounts of inorganic and organic mercury in treated waste water after treatment using this technique, a method in which sulfide does not interfere in the determination is needed because the sulfide sometimes remains in the treated waste water. Simplicity and rapidity are also important factors for the determination method used in process control; additionally, it is preferable not to use any complicated equipment.

Cold vapor atomic absorption spectrometry (CVAAS) is widely used for the determination of mercury in various samples [1,3]. For the determination of total mercury in water samples, a wet digestion process using oxidizing reagents is generally combined with CVAAS in order to decompose organic mercury to inorganic mercury [4]. However, the digestion process is a tedious and time-consuming operation. The flow injection technique has been conveniently utilized for the digestion process in the determination of total mercury to overcome these weak points [5–16]; chemical digestion [5–10], ultraviolet digestion [11–13], and microwave digestion [14–16] have been applied to the flow injection—mercury analysis system. In contrast, CVAAS in an alkaline medium [17–19] is a simple and rapid determination method for total mercury. Not only inorganic but also organic mercury, including methylmercury, ethylmercury, and phenylmercury, can be readily determined without any digestion processes and special equipment. In this method, however, the presence of sulfide caused serious interference [18,19]; therefore, this method is no applied as often to the process control for the treatment of waste water, especially using the sulfide precipitation technique. In a previous report, we investigated the elimination of sulfide interference

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in CVAAS in an alkaline medium and found that the addition of sodium hypochlorite solution was effective to reduce interference in the determination of inorganic mercury [20]. The addition of a sodium hypochlorite solution would be useful for the determination of organic mercury by CVAAS in an alkaline medium. In this paper, we report the effectiveness of the addition of a sodium hypochlorite solution to reduce the sulfide interference in the organic mercury determination. The results of the investigation of the optimum conditions for the determination of total mercury and the application of the proposed method to analysis of treated waste water are also described.

2. Experimental

2.1. Apparatus

The reduction of mercury was carried out using a Pyrex test tube (diameter 30 mm, length 200 mm, volume ca. 87 mL) equipped with a ball glass filter for the aeration of the solution. A Hiranuma HG-1 mercury analyzer (cold vapor atomic absorption spectrometer; closed circulation system) was used for the measurement of mercury; the relative atomic absorbance at 253.7 nm was indicated in this instrument.

2.2. Reagents

A commercially available standard stock solution of inorganic mercury (50 mg L^{-1}, Kanto Chemicals) was used. A standard stock solution of methylmercury or phenylmercury (50 mg L^{-1} Hg) was prepared by dissolving methylmercury chloride (Aldrich) or phenylmercury nitrate (Tokyo Chemical Industry) in distilled-deionized water. These solutions were diluted to the desired concentration in each experiments. A commercially available sodium hypochlorite solution (practical grade, Nacalai Tesque) was used; the concentration of sodium hypochlorite determined by iodometric titration [21] was 9.2% (w/v). A solution containing 1000 mg L^{-1} of copper(II) was prepared by dissolving copper(II) sulfate hexahydrate (guaranteed reagent grade, Wako Pure Chemicals) with approximately 0.2 mol L^{-1} sulfuric acid (for poisonous metal analysis, Kanto Chemicals). A tin(II) chloride solution (10% (w/v)) was prepared by dissolving tin(II) chloride dihydrate (for poisonous metal analysis; Wako Pure Chemicals) with approximately 0.5 mol L^{-1} sulfuric acid. The other reagents used in this experiment were of guaranteed reagent grade.

2.3. Recommended procedure for determination of total mercury

A waste water sample (15 mL) containing 0.17–33 μg L^{-1} of mercury and up to 200 mg L^{-1} of sulfide is diluted to approximately 25 mL with distilled-deionized water. To the solution, 5 mL of a 5 mol L^{-1} sodium hydroxide solution, 1 mL of the sodium hypochlorite solution, and 0.4 mL of the copper(II) solution are added, in that order. The tin(II) chloride solution (5 mL) is then added, and the atomic absorbance of mercury is immediately measured. A blank, using distilled-deionized water as a sample solution, is also measured; the mercury content obtained is subtracted from the content for each sample solution.

3. Method development

The addition of a sodium hypochlorite solution was effective to reduce the interference of sulfide in the determination of not only inorganic mercury [20] but also organic mercury. When 5 μg L^{-1} Hg of methylmercury in 25 mL of a sample solution including sulfide was measured without the sodium hypochlorite solution, the atomic absorbance of mercury decreased as the sulfide concentration in the solution increased (Fig. 1). The color of the solution changed from colorless to brown after the addition of copper(II); colloidal copper(II) sulfide would be formed. By adding 1 mL of sodium hypochlorite solution before the addition of copper(II), however, up to 120 mg L^{-1} of sulfide could not interfere in the determination of methylmercury as well as inorganic mercury (Fig. 1). In this case, no color change in the solution was observed even when copper(II) was added. When barium ion was added to the solution, a white precipitate was formed. These results suggest that the elimination of sulfide interference is due to the oxidation of sulfide to sulfate by hypochlorite [22]. The same results were obtained in the investigation using phenylmercury. In the proposed method involving the dilution of 15 mL of the sample solution to 25 mL, 200 mg L^{-1} of sulfide in the sample solution can be permitted.

The added amounts of the reagents were optimized using sample solutions containing methylmercury. The atomic

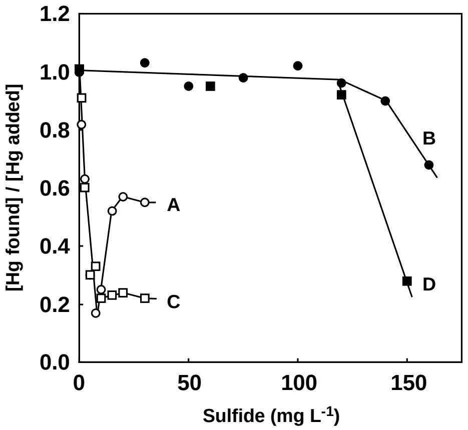

Fig. 1. Effect of concentration of sulfide on determination of 5 μg L^{-1} Hg of inorganic mercury (A and B) and methylmercury (C and D) in 25 mL of sample solution with 1 mL of 9.2% (w/v) sodium hypochlorite solution (B and D), or without the solution (A and C).

absorbance of mercury increased with increasing the added amount of a 5 mol L^{-1} sodium hydroxide solution and reached almost constant values when more than 4 mL was added. An addition of a 10% (w/v) tin(II) chloride solution ranging from 4 to at least 7 mL gave almost constant absorbance in the determination. In the CVAAS in an alkaline medium, copper(II) was used as a catalyst for the reduction of organic mercury [18,20]. More than 0.2 mL of a 1000 mg L^{-1} copper(II) solution was required to obtain almost constant atomic absorbance. From these results, 5 mL of the sodium hydroxide solution, 0.4 mL of the copper(II) solution, and 5 mL of the tin(II) chloride solution were used in this method. Both inorganic mercury and phenylmercury could be satisfactorily determined under these conditions as well.

The relation between the atomic absorbance of mercury and the concentration of inorganic and organic mercury was investigated. Straight lines, passing through the point of origin, were obtained over the concentration range of 0.17–33 μg L^{-1} Hg of inorganic mercury, methylmercury, and phenylmercury in 15 mL of the sample solution. When the atomic absorbance for 10.0 μg L^{-1} Hg of inorganic mercury in 15 mL of the sample solution was defined as 1.00, the slopes were 0.0899 L μg^{-1} for inorganic mercury, 0.0900 for methylmercury, and 0.0939 for phenylmercury. These results suggest that the total amounts of inorganic mercury, methylmercury, and phenylmercury can be determined by calibration using the standard solution of inorganic mercury; the method proposed here would also enable the determination of other types of organic mercury such as ethylmercury [18,19]. The detection limit, defined as three times the standard deviation obtained from eight replicate determinations of a blank, was 0.058 μg L^{-1} Hg in 15 mL of the sample solution.

The influence of 13 diverse ions other than sulfide, which are sometimes contained in treated waste water, was investigated using 25 mL of sample solutions containing 5 μg L^{-1} Hg of each mercury species. As shown in Table 1, all of the mercury species could be recovered within 10% error in the presence of large amounts of calcium, aluminum, phosphate, and nitrate. It is well known that the presence of thiosulfate in a sample solution significantly interferes with the determination of mercury as well [18,19]. In our investigation without the sodium hypochlorite solution, the recovery of mercury from 25 mL of the solution containing 200 mg L^{-1} of thiosulfate was 47% for inorganic mercury, 39% for methylmercury, and 33% for phenylmercury. However, the interference could be considerably reduced by the addition of the sodium hypochlorite solution (Table 1). The other ions tested did not cause any serious interference in the determination. Compared with the concentration of the diverse ions in Table 1, a concentration that is about 1.7 times higher can coexist in the sample solution (15 mL) in the proposed method, which involves a dilution process.

Table 1
Effect of diverse ions on the determination of inorganic or organic mercury

Ion	Ion concentration (mg L^{-1})[a]	Recovery (%)		
		Hg^{2+}	$MeHg^{+}$	$PhHg^{+}$
Ca^{2+}	250	96	91	90
Al^{3+}	500	94	105	95
Pb^{2+}	10	105	98	100
Mn^{2+}	50	108	98	100
Zn^{2+}	10	102	92	100
Ni^{2+}	10	102	104	103
Fe^{3+}	50	97	98	96
Cd^{2+}	10	92	103	109
Co^{2+}	5	93	95	97
$PO_4{}^{3-}$	500	93	96	101
$NO_3{}^{-}$	500	100	92	103
$S_2O_3{}^{2-}$	200	97	91	101

[a] The concentration of diverse ions in 25 mL of the sample solution was shown.

Based on the results mentioned above, the determination of total mercury in some treated waste water samples was tried. The treated waste water used was sampled on different days at the Water Quality Management Center in Toyama University, where the sulfide precipitation technique is often used for the treatment of waste water containing heavy metals. The results obtained by the

Table 2
Results for determination of total mercury in treated waste water samples and measurement of mercury from the samples spiked with each mercury species

Sample[a]	Added (ng Hg)	Added as	Found[b]		Recovery (%)
			(μg L^{-1} Hg)	(ng Hg)	
HM-1			2.30	34.6 ± 3.0	
	12.5	Hg^{2+}		46.4 ± 2.2	94.4
	50.0	Hg^{2+}		81.6 ± 1.7	94.0
	12.5	$MeHg^{+}$		46.2 ± 2.1	92.7
	12.5	$PhHg^{+}$		46.2 ± 2.2	93.3
HM-2			(0.13)[c]	(2.0 ± 0.3)[c]	
	12.5	Hg^{2+}		14.4 ± 0.4	99.9
	50.0	Hg^{2+}		52.2 ± 1.1	101
	12.5	$MeHg^{+}$		14.0 ± 0.7	96.1
	12.5	$PhHg^{+}$		14.2 ± 0.7	97.7
HM-3			(0.12)[c]	(1.7 ± 0.3)[c]	
	12.5	Hg^{2+}		14.6 ± 0.2	103
	50.0	Hg^{2+}		49.9 ± 4.0	96.4
	12.5	$MeHg^{+}$		13.7 ± 0.5	95.5
	12.5	$PhHg^{+}$		13.7 ± 0.3	96.0
SD-1			1.44	21.6 ± 1.3	
	12.5	Hg^{2+}		34.3 ± 1.0	102
	50.0	Hg^{2+}		73.4 ± 0.9	104
	12.5	$MeHg^{+}$		33.6 ± 1.0	96.1
	12.5	$PhHg^{+}$		33.7 ± 1.0	96.6

[a] Treated waste water for heavy metal (HM, sampled on different days) and effluent from sludge dehydration process (SD) were used for samples.

[b] The concentration and amount (mean ± standard deviation, $n = 3$) in 15 mL of the sample solution were shown.

[c] The result was estimated by the extrapolation of the calibration curve.

calibration curve method are shown in Table 2; the time required for the determination of total mercury was about 5 min. Additionally, 92.7–104% of recoveries were also obtained from a sample solution spiked with each mercury species.

4. Conclusion

The addition of a sodium hypochlorite solution was effective to reduce the sulfide interference in the determination of organic mercury as well as inorganic mercury by CVAAS in an alkaline medium. In the method using 1 mL of a 9.2% (w/v) sodium hypochlorite solution, 0.17–33 $\mu g\,L^{-1}$ of total mercury in 15 mL of sample solutions including up to 200 $mg\,L^{-1}$ of sulfide can be determined in just about 5 min without any serious interference. The proposed method will serve as the determination method of total mercury for process control in the treatment of waste water. In addition, this method would also be useful for the analyses of some water samples including large amounts of sulfide such as hot springs water.

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