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Cold Vapour Generation and Atomic Fluorescence Spectrometry for the Determination of Mercury

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A new cold vapour generation and atomic fluorescence spectrometry method for the determination of mercury was developed by the simple addition of NaOH or other base to generate the mercury vapour at high pH. The samples were digested using HNO_3 and H_2O_2 in a closed microwave vessel and the pH of the sample solution is increased to 13 by the addition of NaOH. After standing for 1.5 h in a closed vessel, the Hg^0 was directly transfered into the atomic fluorescence spectrometry by a flow of argon. The conditions for the generation of volatile mercury species, the tolerance to the interference of coexisting ions were carefully examined. Under optimal conditions, the detection limits (3s) were evaluated to be 8.0 ng L^{-1} for mercury. This method was successfully applied to the determination of mercury in biological samples. The relative standard deviations are 3.3-3.6 %. The recoveries are 88-97 %.

Key Words: Mercury, Alkaline pH, Atomic fluorescence spectrometry, Cold vapour generation, Biological samples.

INTRODUCTION

Considering the toxicity of mercury, its determination at trace levels in biological samples is very important[1,2]. The relatively low boiling point and high volatility of mercury brings forth the possibility of measuring mercury without additional thermal energy supplied by a flame or electrothermal heating. As a consequence, the cold vapour atomic spectrometry technique has become the preferred technique for trace mercury analysis[3-6]. The chemical transformation of an analyte species to a volatile form is known as chemical vapour generation (CVG). The main advantages of CVG are the separation of the analyte from the matrix and high sample introduction efficiency, resulting in enhanced sensitivity, selectivity and detection limits. This is a widely utilized methodology in atomic spectrometry for the determination of metal ions. Currently, $NaBH_4$ is the most popular reagent for CVG[7,8]. Several alternative means of CVG, not using $NaBH_4$, have also been proposed[9-11]. In this work, it is found that mercury ions in aqueous solution can be reduced to elemental mercury

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by simply increasing the pH of the solution through addition of NaOH or other base, without the need for any additional reducing agent. Taking into account of this finding, an analytical method for the determination of mercury by CV-AFS is presented and this method has been successfully applied to the determination of mercury in biological samples with good results.

EXPERIMENTAL

A model AFS-230 double-channel non-dispersive atomic fluorescence spectrometry coupled to an on-line continuous vapour generation system (Beijing Haiguang Instrument Co., Beijing, China) was used throughout this work. The mercury high performance hollow cathode lamp (HPHCL) was used as the excitation sources for the determination of mercury. A scheme illustrating of the chemical vapour generation system coupled to the atomic fluorescence spectrometry is show in Fig. 1. The experimental conditions for CV-AFS are summarized in Table-1.

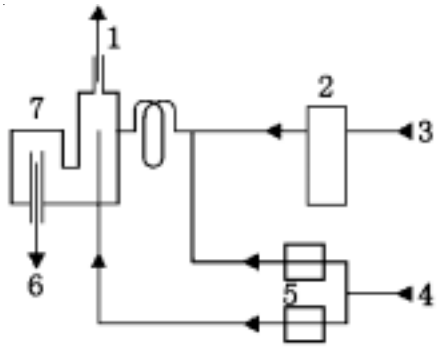

Fig. 1. Scheme of chemical vapour generation system (1) to the AFS; (2) peristaltic pump (50 rpm); (3) sample (flow rate of 4.0 mL min^{-1}); (4) carrier gas flow rate (0.45 L min); (5) flow controller; (6) drain (Nalgene tubing); (7) phase separator

TABLE-1
OPERATING PARAMETERS OF THE AFS INSTRUMENT

Parameter	Mercury
High voltage of PMT (V)	300
Peak current of lamp (mA)	30
Atomizer height (mm)	8.0
Flow rate of carrier gas (Ar, L min^{-1})	0.45
Flow rate of shield gas (Ar, L min^{-1})	1.0
Flow rates of sample (mL min^{-1})	4.0
Measurement mode	Standard curve

A Milestone MLS 1200 microwave digestion system (MW) with Teflon digestion vessels and high pressure supports (Milestone, Monroe, Connecticut, USA) was used.

All chemicals were of analytical grade, unless otherwise specified. High purity water (resistivity of 18.2 MΩ cm) was de-ionized in a Milli-Q system (Bedford, MA, USA). The following reagents were used: 65 % (v/v) HNO_3 (Merck, Darmstadt, Germany No. 1.00441. 1000), sodium hydroxide (Merck, No. 1.06498. 1000), 30 % (v/v) hydrogen peroxide (Merck No. 1.07210. 1000), 1000 μg mL^{-1} mercury standard solution (Merck No. 1.19795. 0500).

Analytical procedures: A 0.2-0.5 g samples of were weighed into the microwave vessel, followed by the addition of 8.0 mL concentrated HNO_3 and 5.0 mL of 30 % (v/v) H_2O_2. After standing for 20 min, the samples were digested in the microwave system in accordance with EPA method SW 846-3051 (closed vessel). The digestion solution was heated to near dryness (about 0.5 mL) to eliminate the interference of HNO_3 and H_2O_2. The resultant clear solutions were transferred to 25 mL volumetric flasks. Sufficient NaOH was added to each digested sample solution to achieve pH 13 (reached when the NaOH concentration was typically 0.1 mol L^{-1}). The volume was made up with high purity water and the flask was capped. After standing for 1.5 h in the closed flask under normal laboratory conditions, the sample (or standard calibration solutions which had been similarly mixed with the base) was introduced into the on-line generation system and the emission from Hg was measured. The quantitation was performed against simple aqueous calibration solutions containing 0.1-50 μg L^{-1} Hg^{2+}. A reagent blank solution was run parallel to the determination and its result was taken into consideration.

RESULTS AND DISCUSSION

Effect of pH: Aqueous solutions containing 10 μg L^{-1} of Hg^{2+} were adjusted to different pH by addition of NaOH or HNO_3. The results show that signal increases with the increasing of pH and most intensively in the range of pH 11-13. The mechanism of reduction arising by the addition of NaOH is not known and therefore currently have no explanation for this observation.

Effect of time: The signal intensity arising from a 10 μg L^{-1} solution of Hg^{2+} containing 0.1 mol L^{-1} NaOH (pH = 13) as a function of the reaction time. It is clear that an incubation period of 1.5 h is required to obtain a maximum signal. This time was adopted for the standard and for the sample solutions. The vessel was kept capped during the incubation time.

Effect of visible light: The signal intensity arising from a solution containing 10 μg L^{-1} Hg^{2+} in 0.1 mol L^{-1} NaOH, prepared and measured in the dark (flask covered with aluminum foil in the dark) was identical to that arising from a solution prepared under normal laboratory illumination conditions, demonstrating that the reduction of mercury is not influenced by light.

Effect of temperature: The results show that the signal intensity arising from a solution containing 10 μg L^{-1} Hg^{2+} in 0.1 mol L^{-1} NaOH as a function of the temperature of the reaction vessel. The signal intensity increases up to 50 ºC, decreasing for higher temperature. Certainly, mercury is lost from the flask during heating.

The loss is especially noticeable for temperatures higher than 50 ºC. Increased temperature likely favours liberation of the vapour from the solution due to decreased solubility[12]. Better precision was obtained at room temperature, which was adopted for all further experiments.

Effect of lamp current: Investigations on the influence of lamp current indicated that the signal intensities of Hg significantly increased along with increase of the lamp current. This result is similar to that of conventional AFS analysis. Nevertheless, higher lamp current resulted in higher noise which may reduce the lifetime of the lamps. So, as a compromise, a current of 30 mA for the Hg lamp was employed in the present work.

Effect of the carrier gas flow rate: Different carrier gas flow rates in the range 0.1-2.0 L min^{-1} were tested, again for a solution containing 10 μg L^{-1} Hg^{2+} in 0.1 mol L^{-1} NaOH. Measurements commenced after 1.5 h the addition of the NaOH. The results show that response increases rapidly for flow rates up to 0.4 L min^{-1} and thereafter less intensively. A flow rate of 0.45 L min^{-1} was adopted for further study as this was optimal for efficient operation of the phase separator and the transfer of Hg^0 from the solution. Without a carrier gas, the signal intensity is the same as for the blank, indicating that insufficient Hg^0 is transferred from the solution to the AFS to produce a signal under this condition.

Effect of shield gas: An argon shield gas was employed in this system to isolate the volatile species from the outside air. When the flow rate was less than 0.9 L min^{-1}, the fluorescence signal intensity of mercury decreased. There was a plateau appearing between 1.0 to 1.8 L min^{-1}. Considering the higher cost of argon, a 1.0 L min^{-1} argon shield gas was used.

Effect of sample flow rates: The effect of sample flow rates on the fluorescence signal intensity was also tested. By increasing the flow rates, the intensity of the signal for mercury was improved. There was a plateau appearing between the flow rates of 3.5 to 5.0 L min^{-1}. In this work, a 4.0 L min^{-1} sample flow rate was used.

Interference: The selectivity of the proposed method was investigated by the determination 1.0 μg L^{-1} of Hg(II) in the presence of various ions within a relative error of ± 5 %. The results show that 10000-fold of alkaline and alkaline-earth ions, chloride, nitrate, hydrogen carbonate, carbonate and sulfate, 500-fold Zn(II), Fe(II), Ni(II), Pd(II), V(III), Mn(II), Cu(II), Cd(II), Al(III), Mo(VI), Co(II), Cr(III), Ag(I), Pb(II), did not interfere. This method is of high selectivity.

Calibration curve and sensitivity: The calibration curve shows that linearity is obeyed in the concentration range of 0.1-50 μg L^{-1} for Hg(II). The linear regression equation obtained was: If = 1819 C (μg L^{-1}) + 18.5, (r = 0.9994). The detect limit, based on 3 times the relative standard deviation of the blank 8.0 ng L^{-1}.

Generation of Hg^0: In order to verify the formation of Hg^0 by the addition of NaOH, as opposed to other Hg species that would be decomposed in the AFS, measurements were also made based on cold vapour atomic absorption spectrometry using a quartz cell at room temperature and the same vapour generation equipment. A calibration curve was obtained, demonstrating that Hg^0 is in fact formed.

Sample analysis: The proposed method has been applied to the determination of mercury in biological samples. The accuracy of the developed method was tested with recovery experiments by spiking standard solutions into the digest solution. The analytical results and recoveries are shown in Table-2.

TABLE-2
DETERMINATION RESULTS OF CERTIFIED STANDARD BIOLOGICAL SAMPLES

Samples	Standard value (μg/g)	By this method (μg/g)	RSD % (n=7)	Recovery % (n=5)
Tobacco leaf (GBW07452)	Ag (-), As (0.326), B (54.4), Bi (0.428), Ca (2560), Cd (0.323), Ce (1.02), Co (5.21), Cr (3.18), Cu (11.2), Fe (52.3), Hg (0.226), Mg (428), Mn (22.6), Mo (1.63), Ni (4.18), Pb (1.47), V (3.28), Zn (16.3)	0.205	3.3	88-96
Human hair (GBW08126)	Ag (-), As (0.121), B (38.4), Bi (0.825), Ce (0.643), Cd (0.528), Co (6.25), Cr (0.816), Cu (11.2), Fe (123), Hg (0.142), Mg (136), Mn (68.2), Ni (5.61), Pb (1.06), Sn (1.24), Se (0.0412), V (3.86), Zn (18.7)	0.158	3.6	90-97

Conclusion

Aqueous inorganic mercury can be reduced to Hg^0 by the single addition of NaOH (in the absence of any further reducing agent such as $NaBH_4$ or $SnCl_2$). The mechanism of reduction is not yet known, but requires a high pH, most probably indicating production of the Hg^0 from $Hg(OH)_2$. This new finding was applied to the determination of total Hg in digested biological samples by simply treating them with NaOH. Only Hg^{2+} can be converted to Hg^0, any organo-mercury species present must be decomposed.

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