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Design of cold vapor system and assembled on Atomic Absorption Spectrometer for Mercury determination in several waste water samples

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Abstract : A simple and well designed cold vapor system for mercury determination is being reported. The range of the method is 0.2-10 µg L^{-1} of mercury. The range may be extended above or below the normal range by increasing or decreasing sample size. Accuracy of system was tested with standard reference material (SRM). The detection limit for Hg was 51 ng L^{-1}. Mercury concentration in water samples from Bandar Imam Lake was measured. Good agreement was found between results for the analysis of SRM and real samples.

Keywords: Cold vapor, Mercury Determination, water samples

1. Introduction

Mercury contamination of the environment and its toxic effects has been known for centuries. Because mercury in some forms is very volatile it can easily be transported in the atmosphere and it is therefore classified as a global pollutant. The solubility for elemental mercury in water is only 0.025 mg l^{-1} but as it can be transformed into other forms that are more soluble, mercury can be found almost everywhere in the environment; for example in water, sediment, soil and fish. Mercury in its different forms is poisonous and can be inhaled, ingested and even absorbed through unbroken skin; it is bio-accumulated and bio-magnified and some organometallic mercury species, such as monomethyl- and dimethyl mercury, are known to be extremely toxic[1,2].

A wide range of analytical methods have been used for the determination of mercury in real samples. These includes spectrophotometry[3], graphite – furnace atomic absoroption spectrometry (GFAAS) [4], inductively coupled plasma atomic emission spectrometry (ICP-AES) [5], high performance liquid chromatography inductively coupled plasma mass spectrometry (HPLC-ICP-MS) [6], Cloud point extraction[7], anodic stripping voltammetry[8], X-ray fluorescence spectrometry[9], inductively coupled plasma mass spectrometry (ICP-MS) [10], electrothermal atomic absorption spectrometry[11], atomic fluorescence spectrometry[12] and cold vapor atomic absorption spectrometry[13].

Cold vapor-atomic absorption spectrometry, CV-AAS, is traditionally the most widely used technique for mercury determination. Mercury in a liquid sample is reduced, normally with $SnCl_2$ or $NaBH_4$, to Hg0. With an inert gas the mercury vapor is purged out of the solution and transported to an AAS where the absorption at 253.7 or 185 nm is measured. A typical absorption cell for mercury determination with CV-AAS is made of quartz, is 25 cm long and has an inner diameter of about 0.5 cm. This method provides sensitivities approximately four orders of magnitude better than flame AA. The limit for mercury in drinking water has a 2 µg/L or 2 ppb. The cold vapor technique is the only approved method for determining mercury at this level.

In the present work we made and assembled a quartz cell for mercury determination with AAS, in 10 cm long and has an inner of about 1.0 cm. Also used suitable pumps, tubes, valves, and connections. After set up do the optimum conditions and analysis water samples from Bandar Imam Lake (city in south of IRAN) with purposed methods.

2. Experimental

2.1. Apparatus

A Perkin Elmer A Analyst double beam atomic absorption spectrophotometer (AAS) with hollow cathode lamp operating at 3mA was used for the determination of mercury which was made at 253.7 nm. Measurements were performed in the integration mode.

2.2. Reagents

All the reagents were supplied from Merck Company. A stock solution of 1000 µg mL^{-1} Hg^{2+} ion was prepared by dissolving 0.0680 gr of $HgCl_2$ (Merck) in distilled water and diluted to the mark in a 50 mL volumetric flask. Nitric Acid (HNO_3), concentrated (sp.gr. 1.41), assayed mercury level is not to exceed 1 µg/L. Sulfuric Acid (H_2SO_4), concentrated (sp. gr. 1.84), assayed mercury level is not to exceed 1 µg/L. Stannous chloride solution - Add 25 g of SnCl2. $2H_2O$ to 250 mL of 0.5 N H_2SO_4.

This mixture is a suspension and should be stirred continuously during use.

2.3. Procedures

Transfer 100 mL of the water sample [or an aliquot diluted with reagent water to 100 mL] into a sample container. Note: For reduced volume analysis, adjust sample and reagent volumes to maintain the required sample to reagent ratios. Add 5 mL of H_2SO_4 and 2.5 mL of HNO_3 to the container. Remove the sample containers from the water bath and cool to room temperature. (During the cool down period proceed with instrument warm up and calibration.)

3. Results and discussion

A calibration curve was constructed by 100 ml of sample standard solutions. Table 3 shows the analytical characteristics of the method. Under the optimum experimental conditions, the calibration curve for mercury was linear from 0.2-10 µg L^{-1}. The limit of detection was sufficiently low.

Before beginning daily calibration the instrument should be reconfigured to the optimized conditions. Turn on the instrument and circulating pump. Adjust pump rate to 1 L/min. or as required. Allow system to stabilize. Treating each standard solution container individually, add 5 mL of $SnCl_2$ solution and immediately attach the container to the aeration apparatus. The absorbance, as exhibited either on the instrument or recording device, will increase and reach maximum within 30 sec. As soon as the maximum response is obtained, approximately one minute, open the bypass value (or optionally remove aspirator from the sample container if it is vented under the hood) and continue aeration until the absorbance returns to its minimum value. Close the by-pass value, remove the aspirator from the standard solution container and continue aeration. Repeat until data from all standards have been collected.

4. Construction and Assembled

In the present work we construction and assembled of CV-AAS as follows. Any atomic absorption unit having an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed. The use of background correction is recommended, but is not mandatory. Single element hollow cathode lamp or electrodeless discharge lamp and associated power supply.

A quartz cell has an inner of about 1.0 cm 10-cm long, having quartz windows may be used. Suitable cells may be constructed from Plexiglas tubing, 1 in. O. D. by 4 ½ in. long. The ends are ground perpendicular to the longitudinal axis and quartz windows (1 in. diameter by 1/16 in. thickness) are cemented in place. Gas inlet and outlet ports (also of Plexiglas but ¼ in. O. D.) are attached approximately ½ in. from each end. The cell is strapped to a burner for support and aligned in the light beam to give the maximum transmittance.

Inert mercury-free tubing is used for passage of mercury vapor from the sample bottle to the absorption cell. In some systems, mercury vapor is recycled. Straight glass tubing terminating in a coarse porous glass aspirator is used for purging mercury released from the water sample in the BOD bottle.

Any pump (pressure or vacuum system) capable of passing air 1 L/min. is used. Regulated compressed air can be used in an open one-pass system. The apparatus for flameless mercury determination are shown in Figure 1.

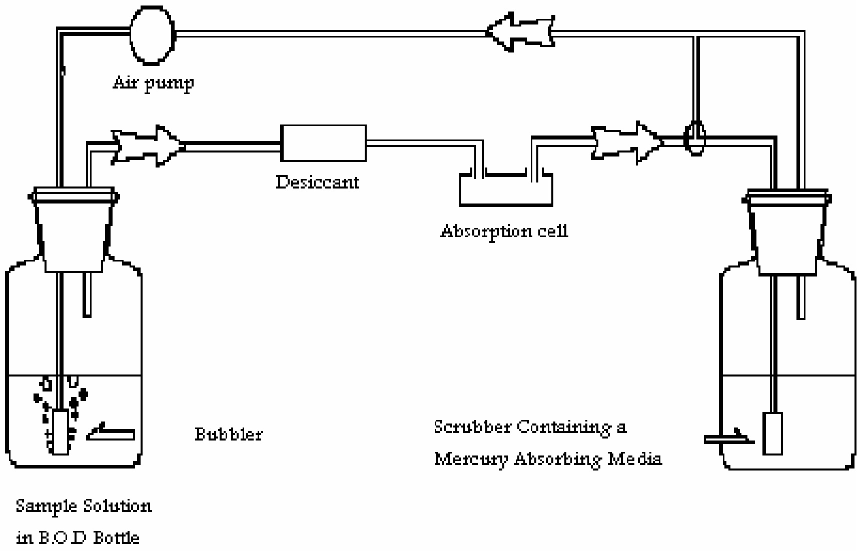

Figure 1. Apparatus for Flameless Mercury Determination

Because of the toxic nature of mercury vapor, inhalation must be avoided. Therefore, a bypass has been included in the system to either vent the mercury vapor into an exhaust hood or pass the vapor through some absorbing media, such as:

a) equal volumes of 0.1 N $KMnO_4$ and 10% H_2SO_4

b) 0.25% iodine in a 3% KI solution.

5. Sample Collection, Preservation, and Storage

Because of the extreme sensitivity of the analytical procedure and the presence of mercury in a laboratory environment, care must be taken to avoid extraneous contamination. Sampling devices, sample containers and plastic items should be determined to be free of mercury; the sample should not be exposed to any condition in the laboratory that may result in contamination from airborne mercury vapor. For the determination of total mercury (inorganic + organic) in aqueous samples, samples are not filtered, but acidified with (1+1) nitric acid to pH <2 (normally, 3 mL of (1+1) acid per liter of sample is sufficient for most ambient and drinking water samples).

6. Application to real samples

A method was applied to the determination of trace amounts of mercury ion in water samples from Bandar Imam Lake. They were filtered through Whatman 42 filter to remove the suspended particulate matter and were stored in polyethylene bottles at 4°C in the dark. The results which compared by standard reference material (SRM) and shown in Table 2 and 3.

Table 1. Analytical characteristics of the proposed method

Concentration range (µg L^{-1})	0.2-10
Slope	0.0354
Intercept	0.0231
Correlation coefficient (r)	0.9991
% RSD (n=3)[a]	2.80
LOD (ng L^{-1})[b]	51

[a] Mercury concentration was 1 µg L^{-1} for which the R.S.D. was obtained.

[b] Limit of detection. Calculated as three times the S.D.(3σ) of the blank signal.

Table 2: Interlaboratory precision and accuracy data for flameless atomic absorption.

Number of experiment	True Values[a] (µg L^{-1})	Mean Values (µg L^{-1})	SD	%RSD
1	0.21	0.349	0.276	89
2	0.27	0.414	0.279	67
3	0.51	0.674	0.541	80
4	0.60	0.709	0.390	55
5	3.4	3.41	1.49	44
6	4.1	3.81	1.12	29
7	8.8	8.77	3.69	42

[a] From standard reference material (SRM)

Table 3: Determination of Hg^{2+} in Bandar Imam lake water samples.

Number of Sample	Hg^{2+}concentration (µg L^{-1})		Recovery% (n = 5)
	Taken	Found	
1	-	5.50	-
	1.0	6.40	90
	1.5	6.80	86
	2.0	7.30	90
2	-	2.00	-
	3.0	4.95	98
	3.5	5.35	96
	4.0	5.90	98
3	-	7.40	-
	0.5	7.90	100
	1.0	8.25	85
	1.5	8.85	97

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