

Determination of Hg(II) as A Pollutant in Karachi Coastal Waters by Cold Vapor Atomic Absorption Spectroscopy

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Summary: Nowadays, environmental monitoring has great importance and mercury is well known for its toxicity. Mercury (which is at trace level) is analyzed by cold vapor atomic absorption spectroscopy with amendments that are appropriate to the present laboratory need. The results are consistent with previous analysis, through other methods. Two areas namely Ibrahim Hyderi and Fisheries were found to have mercury levels around 0.193 µg/L and 0.110µg/L, respectively. Whereas other areas have mercury levels similar to other places reported earlier.

Introduction

Mercury is one of the common harmful and toxic metals. The occurrences of mercury poisoning are well documented [1] and wide spread incidents have been reported during the last three decades which occurred due to the eating of contaminated fish or the seed grains treated with mercury compounds. Estimation of trace mercury in the environment has drawn great interest during the recent past and extensive studies have been carried out [2,3]. Out of the several methods used for such analysis, classical methods failed to determine mercury at trace level, while instrumental methods gave reliable results because of their high sensitivity. The methods that have proven reliability are some usual analytical methods [4,5], spectrophotometric methods [6], atomic absorption, emission spectroscopic techniques [7,8] and plasma spectroscopy. However analytical determination of mercury, at ppb and sub-ppb levels are based on the cold vapor technique reported by Hatch & Ott [9]. Cold vapor atomic absorption method is strictly confined to the determination of mercury in elemental state. Mercury has an appreciable vapor pressure even at room temperature and this facilitates its determination through cold vapor technique, as the vapors need not to be produced through any special treatment [10]. This method is widely reported for the analysis of mercury in environmental samples [11].

Result and Discussion

Absorbance of different HgCl₂ standard solutions were plotted against respective

concentration to develop the working curve. It was found that absorbance values are higher in basic medium than those of acidic medium. This indicates that firstly the partition of reduced mercury into vapor phase is more favorable in alkaline medium. The results primarily confirm that mercuric compounds are reducible only under alkaline condition, as reported earlier [12] and secondly the evidence for the presence of methyl mercury in samples is also substantiated. Such behavior of absorbance in acidic & basic media could also be attributed to the instability of NaBH₄ in acidic medium as it liberates H₂ gas [13], which has been suggested to suppress the partition of mercury vapors and decreases the population of mercury vapors in absorption cell. However, as this difference is less pronounced in standard samples, it is very likely that higher results, yielded by test samples in basic media, are due to its capability to reduce organic mercury against acidic media which is unable to do so, as reduction of organic mercury has been reported to be less favorable in acidic media [13].

The highest concentration of mercury (as given in table 1) was detected near the small fishing port 'Ibrahim Hyderi' where the water (used as coolant) from electric power plant is introduced to the open sea. While 2km away from that spot, concentration of mercury was approximately four times lower (table 1). These results indicate that the power plant is a likely source for mercury pollution. Samples collected from Karachi Fisheries, also

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contained considerable amounts of mercury. The mercury level near the fishing port is higher than in the samples collected 2 km away from the port (table 1). The two major sources for mercury pollution in this region that could be identified are industries (i.e. chemical manufacturing, petroleum and electric power plant etc.) and effluent into the seas. Further to that human sewage and other wastes from ships and port also goes into sea. Especially oil from exhaust pipes of ship engines form a layer at the surface water. Other samples collected from various spots of Karachi's coastal area (sea view, Boat basin, Hawks bay etc.) are found to have low mercury content (table 1) as these are distinctly pollution free areas. Comparatively, the results from present analysis are consistent with analysis from past. In 1987 mercury level at Pakistani coast of Arabian Sea was $0.012 \mu\text{g/L}$ [14]. Except the mercury level found in Korangi creek and fisheries, these results are fairly higher than the present average of mercury levels [15] of oceans (i.e. Baltic ocean, Netherlands coast, German Bight, UK coast central north sea etc.). The waste water from the industries and other sources which are supposed to add mercury, must be treated for its removal [16].

The results observed in this analysis are summarized below:

Table 1

Sample location	Hg(II) concentration ($\mu\text{g/L}$)
Korangi Creek. (2 km away from Electric plant).	0.031 ± 0.003
Korangi Creek (Electric plant). Fisheries.	0.193 ± 0.001
Fisheries (2 km away).	0.110 ± 0.016
Sands-pit/ Hawks-bay.	0.075 ± 0.004
Clifton/ Sea-view/ Boat-basin.	0.0099 ± 0.0001
	0.001 ± 0.0002

Experimental

Apparatus

All absorbances were measured at atomic absorption spectrophotometer (Perkin Elmer model 3100); the nebulizer and burner of the instrument were replaced by SCVAA attachment, and magnetic stirrer was placed under the attachment. Air pump was attached through the tube to the inlet of the SCVAA attachment. (see figure 1).

The SCVAA attachment consists of cylindrical absorption cell of 60-mm length with an internal diameter of 9mm. Two quartz windows were joined at the two ends of cell by means of a transparent adhesive whose commercial name is

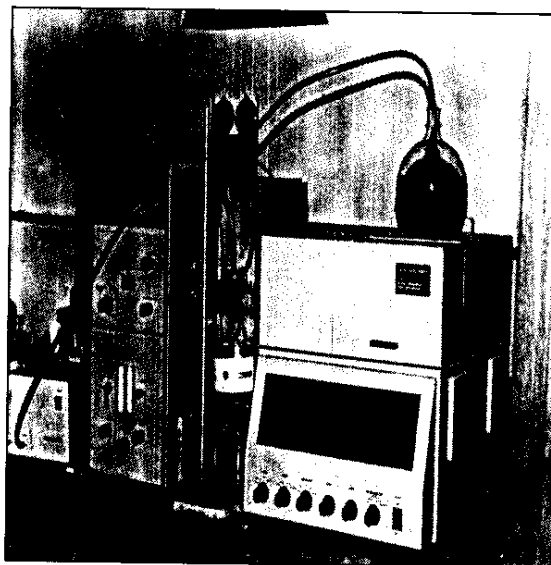


Fig. 1 SCVAA attachment installed at AAS.

'Elfy'. A reaction vessel of 10 ml volumetric flask is attached to the center of absorption cell through quickfit 10/13, shown in figure 1. There is an inlet and outlet for air that sweeps out the atomized mercury from the cell to the waste reservoir. These inlet and outlet paths are controlled through Teflon valves. The waste reservoir is provided with a solution of potassium per manganate, which oxidizes mercury from atomic form to Hg(II), a less toxic form of mercury.

Reagents

Reagents of extra purity were used throughout the analysis. Stock mercury(II) solution of 1000ppm was prepared by dissolving 0.5018 gm of mercuric chloride in 5% HNO₃. Working standards were prepared by appropriate dilution of the stock solution in 0.01% K₂Cr₂O₇ solution, which was previously prepared in 5% HNO₃. 1%(w/v) NaBH₄ solution (used as reductant) was prepared in 0.05M KOH.

Sample pretreatment

Samples were collected between the months of July and September. They were filtered immediately after collection to separate the living or dead particulates and un-dissolved organic and inorganic substances. Acidification of the samples was done by adding 2M HCl to prevent samples from the precipitation of metals and biological activities.

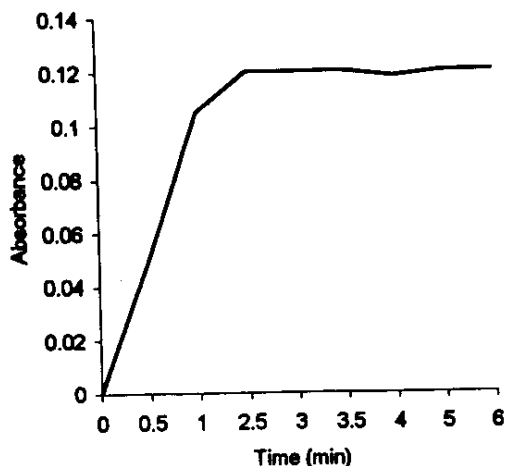


Fig. 2: Study of saturation time of cell

Procedure

45 ml of acidified sample solution was pipetted out into a 50mL volumetric flask and neutralized by NaOH using pH meter and the volume was made up to 50mL. 1 ml of sample or standard solution was taken in a 10mL reagent flask, which already contained a magnetic bead. 5mL of the diluent solution (4M H₂SO₄ or 0.25 M NaOH) was used in separate runs, to study the effect of acidic and basic medium on results. Following the addition of 0.5mL of reductant (NaBH₄) solution, the stop watch was started and the reagent flask attached was commissioned and absorbance was observed after 2.5 minutes (because at this time, the cell was expected to be saturated with mercury vapors), as it is evident from the graph shown in figure 2. After each run, Teflon valves are opened and the air pump was

turned on, in order to sweep all the vaporized mercury to the waste reservoir. The air was passed until absorbance decreased to zero.

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