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INORGANIC MERCURY DETERMINATION IN LOCAL PUBLIC UTILITY WATERS BY FLAMELESS ATOMIC ABSORPTION TECHNIQUE

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Based on the acid-medium reduction of mercury, a flameless atomic absorption method of general utility is proposed for the determination of inorganic mercury in public utility waters. Practical evaluation is made of the parameters governing the expelled mercury absorbance in an optical cell fabricated from inexpensive materials. These include dimensions of the reduction vessel, eluent flow rate and the volume of the solution as related to the optimum sensitivity conditions. Surface and underground water samples, originatig from various local water supply systems, ranging in depth from 30-60 feet and feeding, on the average, a population of 10,000 or more, were analyzed for mercury content. A lower detection limit of 100 ng/1 mercury for the proposed method is established with an average precision of ± 2.5% corresponding to 2S confidence level for replicate measurements. The methods has the potential of application to mercury assay in food stuffs and beverages.

INTRODUCTION

During recent years studies on trace metal contamination of the environment have gained a rapid impetus with the introduction of more and more sensitive detection instruments. This is specifically true of mercury pollution in the surface and underground waters since man is directly exposed to the health hazard arising from mercury ingestion from these waters. Besides water, industrial and agricultural activities contribute towards mercury pollution of food, as is true of air. Mercury pollution chiefly results from a mercury compound, methyl mercury, which is well known to be destructive to the human nervous system[1]. It is also well established that mercury gets accumulated in a soluble form in the tissues of aquatic animals including fish[2].

The concern regarding mercury pollution has currently started to arise in developing countries in view of their fastly expanding industrial interests. Although, more often, the primary objective of keeping water resources clean with respect to mercury pollution is not being presently achieved, yet attention is now being devoted to estimate the mercury levels in public utility waters. The usual analytical methodology available for the estimation of low concentrations of mercury includes colorimetric[3], neutron activation[4], emission spectrometric[5], and gas chromatographic techniques. However, the most sensitive detection technique is based on the ultraviolet absorption of mercury vapour first described in 1963[6]. Various experimental modifications for observing the mercury vapour absorbance in the atomic absorption flame have since appeared and analytical methods based on this phenomenon have been proposed by various workers[7-9].

Attempt has been made in the present investigation to propose a method of general utility for the estimation of inorganic mercury in surface and underground water samples utilizing stannous chloride reduction of mercury in acidic medium. Critical evaluation is made of the parameters governing the absorption of mercury vapour expelled from the reduction solution into an optical absorption cell fabricated from inexpensive material. The parameters studies include the dimensions of the cell the flow rate of the eluent (air) and the volume of solution in the reduction vessel. Under the optimum conditions thus achieved, the trace mercury concentrations are then measured through flameless atomic absorption spectrophotometric (AAS) system. The proposed method has a lower detection limit of 100 ng/1 mercury with a precision of ± 2.5% for duplicate runs.

EXPERIMENTAL

Hitachi Atomic Absorption Spectrophotometer, Model 170-10, was used for the flameless estimation of mercury vapour employing a hollow cathode mercury lamp operating at 253.7 nm at a bandpass of 0.4. The absorption cell giving optimum performance has been dimensionally shown in Fig.1. A pyrex cylinderical tube of the indicated dia-

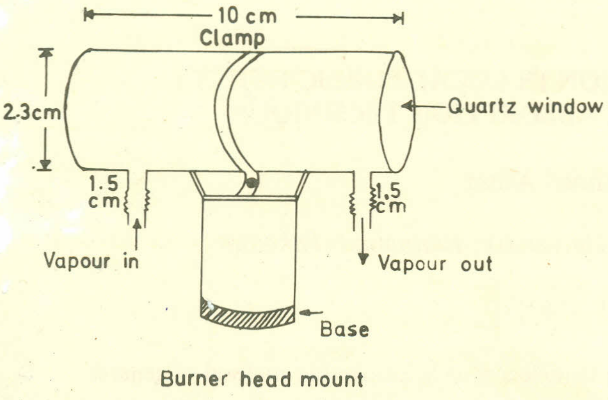

Fig. 1. Schematic of the absorption cell.

meter and length was used with quartz windows fixed with Araldite. Air was used from a compressor at an optimal flow rate of 30 1/h as the eluent. The outline of the experimental procedure is self-contained in Fig. 3. The absorption peaks were recorded on a Servogor X-Y recorder.

Apparatus, Chemicals and Standard Solutions. Cylindercal gas washing bottles, ranging in capacity from 50 to 250 cm^3, were used as reduction vessels. The flow rate of air was measured by a rotameter for the entire range of air pressure between 10 and 70 1/h. The drying tube (shown as inset in Fig. 2) was packed with glass wool impregnated with magnesium perchlorate that was renewed after 20-30 runs.

A stock solution of Mercury (II) was prepared by dissolving 1.3540 g mercury (II) chloride in 50 cm^3 of concentrated nitric acid and diluting to 1 litre with doubly distilled water in a measuring flask. This gave a 1000 μg/cm^3 mercury solution. Working standards at concentrations of 10 μg/cm^3 and 0.1 μg/cm^3 were subsequently prepared by appropriately diluting the stock solution. The tin (II) chloride solution used for the reduction purpose was made by dissolving 10 g $SnCl_2$ in 1 N H_2SO_4 to make 100 ml solution. This solution was prepared fresh for daily use. Sulphuric acid used for the reduction purpose was 20%. All the chemicals used were of ultra high purity, research chemicals.

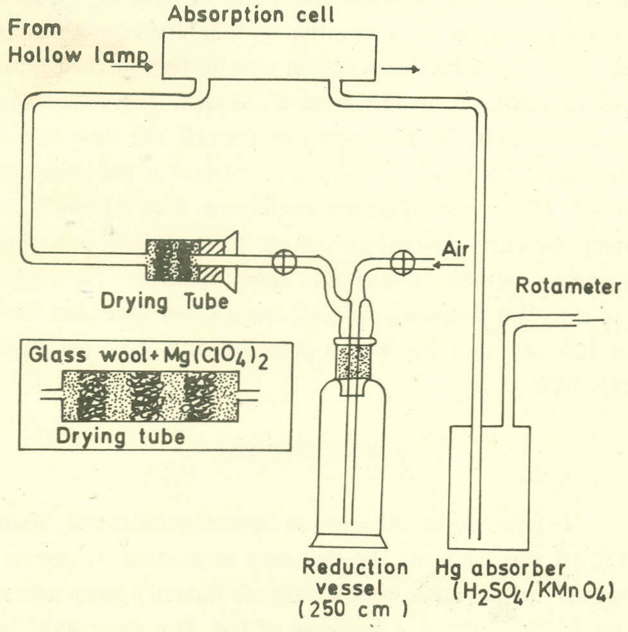

Fig. 2. Schematic of the mercury determination apparatus.

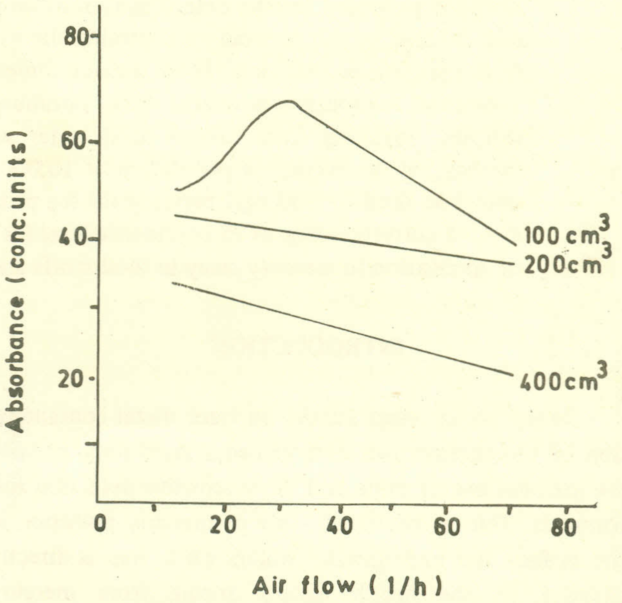

Fig. 3. Absorbance vs air flow for various volumes of solutions.

Sampling. Plastic cans of 2.5 litre capacity well washed and cleaned with chromic acid/distilled water, dried and finally rinsed with excess distilled water, were checked for any probable background mercury contamination. These cans were then used for the sampling purpose. After sampling, the mercury measurements were completed within 72 hours.

Procedure. The procedure given here applies to the case of mercury reduction being carried out in a 250 cm^3 gas washing bottle, an equivalent proportion of the added materials may well apply to small capacity bottles. After having added to the bottle 20 cm^3 of 20% H_2SO_4 and 10 cm^3 of 10% tin (II) chloride solution, air is bubbled through the bottle to remove the possible mercury content of the reagents. Then, a 70 cm^3 portion of the water sample to be analyzed is added. The bottle is immediately closed, and the solution is shaken for 10-15 seconds. Air is then passed through the solution. The air leaving the solution is allowed to percolate through the absorption cell mounted coaxially in place of the atomic abosrption burner. The abosrbance is recorded for duplicate runs as absorption peaks onto the recorder. Similarly, absorption of the standard series prepared, are recorded for appropriately diluted portion of the 0.1 $\mu g/cm^3$ solution (1 cm^3 of this solution corresponds to 100 ng Hg) giving 100, 250, 500, 750 and 1000 ng Hg in solution. Any mercury impurity accumulated between various runs can be removed from the vessels by frequently flushing them with a 1% tin (II) chloride solution, followed by rinsing with 1:1 HNO_3 and finally with simple distilled water.

DISCUSSION

The present investigation reveals that mercury absorption is a function of closely interrelated parameters pertaining to the dimensions of the reduction vessel, air flow rate and the volume of solution under study. For cylinderical vessles of 150 to 500 cm^3 capacity, at various individual volume of solutions, pertaining to a fixed amount of mercury, it is found that detection sensitivity is considerably improved with small volume reduction vessels, as shown in Fig.3. The absolute precision obtained is ± 2.5% corresponding to an optimum air flow rate of 30 1/h for 100 cm^3 sample volume. Although absorbance increases considerably by a further decrease of solution volume (say, to 50 cm^3) the precision deteriorates considerably. At larger solution volumes, however, the absorbance is found to decrease drastically, rendering the peaks to broaden and thus resulting in poor quantification.

The measured concentrations of mercury, at the optimum conditions, for various water samples are given in Table 1. The statutory upper limits laid down for mercury in drinking and public utility waters is 0.001 mg/1[10]. The measured values range from 1.50×10^{-4} to 7.8×10^{-4} mg/1. Thus, the mercury content of these waters is well below the allowed upper concentration limit, and as such, does not pose a health hazard for the consumers.

In brief, the present investigation indicates that local public utility waters are clean with respect to any probable mercury pollution emanating either from industry or agriculture. The aquatic life, too, in the area is safe. The present method is now being checked for a possible extension to the estimation of organo-mercurials in these waters.

Table 1. Measured concentrations of mercury in various waters.

Sample number	Water supply system	Hg Concentration mg/1 ($\times 10^{-4}$)
1.	Helay Water Works (TW)	2.34
2.	Greater Rawalpindi Water Supply (T)	3.10
3.	Satellite Town Water Supply (T)	1.50
4.	Ashgar Mall Scheme (TW)	1.87
5.	Rawal Dam (S)	3.10
6.	Filtration Plant, Rawal Dam (ST)	3.90
7.	New Katarian Scheme (TW)	2.34
8.	Commercial Centre Scheme (TW)	3.12
9.	Millat Colony (TW)	6.25
10.	Pir Wadhai Water Scheme (TW)	2.34
11.	Committee Chowk Water Supply (TW)	3.13
12.	Liqauat Bagh Supply (TW)	3.13
13.	New Mohanpura Supply (TW)	4.69
14.	Ratta Amral Supply (W)	3.13
15.	Purana Qila Water Scheme (TW)	7.80

S = Surface Water; T = Tank Supply; TW = Tube Well; W = Well; ST = Surface Treated Water.

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REFERENCES

1. Hazards of Mercury, Report, Department of Health Education and Wellfare, USA, Environmental Research, **4**, 1 (1971).
2. P.H. Abelson, Science, **1969**, 237 (1970).
3. E.B. Sandell, *Colorimetric Determination of Traces of Metals*, (Interscience, N.Y., 1965), third edition.
4. H.V Weiss and T.E. Crozier, Anal. Chim. Acta., **58**, 231 (1972).
5. R.S. Braman, Anal Chem., **43**, 1462 (1971).
6. N.S. Poluektov and R.A. Vitkun, Zs. Anal. Chim., **18**, 33 (1963).
7. W. Hatch and W.L. Ott, Anal. Chem., **40**, 2085 (1968).
8. G.W. Kalb, At. Abs. Newslett., **9**, 84 (1970).
9. J.T. Kopp *et al.* J. Am. Water Works Assoc., **64**, 20 (1972).
10. *International Standards for Drinking Water* (WHO, Geneva, 1971), third edition.