ORGANIC MERCURY DETERMINATION IN DRINKING WATERS BY COLD VAPOUR ATOMIC ABSORPTION

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Using tin(II) chloride as a reductant in a basic medium, a method of general utility is proposed for the estimation of organic mercury in drinking waters by the cold vapour atomic absorption technique. The estimation of mercury is quantitatively studied as a function of eluent (air) flow rate, sample volume, reduction-vessel volume and mercury content of various drinking water samples. A low-cost absorption cell fabricated from locally available materials is used for recording the absorption of mercury vapour. For a 50.0 ml aliquot of water sample in a total volume of 100.0 ml in the reduction vessel a lower detection limit of 10 ng/1 with ± 0.50 ng/1 as the standard deviation at 2S confidence level is achieved. The method does not involve any blank adjustments.

Key words: Organic mercury; Cold vapour analysis of mercury; Organic mercury in natural waters.

INTRODUCTION

In recent years, concern over mercury pollution has grown more intense in the wake of increased industrial and agricultural activities in many parts of the world. Industrial waste waters are known to contain both inorganic and organic mercury. In muds, the inorganic form is converted to methyl mercury (CH_3Hg^+ or $(CH_3)_2Hg$), in the presence of anaerobic bacteria [1]. Organic mercury is accumulated in the body and attacks the nervous system. The organic part of the molecule to which mercury is attached makes it easily soluble in fats. Alkyl mercury compounds are thus more toxic than the corresponding inorganic forms of the metal and are the cause of current deep interest in the estimation of organomercurials [2]. The genesis of health hazards of mercury and its compounds found in human environment is well known and well documented [3,4].

Several sensitive methods are known for the estimation of low concentrations of mercury. Photo-oxidation has been used for the decomposition and subsequent estimation of organic mercury compounds [5,6]. Atomic fluorescence technique has also been used for the estimation of total mercury [7]. Fractional determination of mercury compounds has been effected through thin-layer chromatography using dithiozone-chloroform extraction method [8]. Organic and total mercury content of sea water has been determined through complexation with sodium diethyl dithiocarbamate concentrated on XAD-2 resin [9,10]. A chelationresin method coupled with reduction/aeration was used by Yamagami to the same effect [11]. However,

the most popular and sensitive method is based upon absorption of the mercury line at 253.7 nm by mercury vapour expelled from the basic acidic medium stannous chloride reduction [12]. An attempt has been made in the present investigation to introduce a simple and direct method for organic mercury estimation involving the use of low-cost, locally available components. This work basically stems from the previous work on inorganic mercury estimation in drinking waters [13]. The proposed method involves the reduction of organic mercury in a basic medium. The absorption sensitivity is studied as a function of eluent (air) expulsion rate, sample volume, reduction-vessel volume and the mercury content of various samples. The stannous chloride-cadmium chloride system is used as a reductant in 30 % sodium hydroxide. The method is direct and requires only a 50.0 ml aliquot of the water sample for analysis. The lower detection limit achieved is 10 ng/l Hg with a precision of about ± 0.5 ng at this level.

EXPERIMENTAL

The absorption signals of mercury vapour were recorded at 253.7 nm line at a band pass of 0.4 nm on a Hitachi atomic absorption spectrophotometer (Model 170-10). The construction aspects of the absorption cell used are described in earlier work [13]. The air used as the eluent was obtained form an oil-free air compressor, the optimum flow rate being 20.0 l/h. The outline of the experimental procedure is given in a self-explanatory figure (Fig. 1). The absorption peaks were recorded on a Servogor, x-y recorder.

Filtration flasks, ranging in capacity from 100 to 500 ml were used as reduction vessels. The air volumetric flow rate was maintained for the entire range of pressure between 10 and 50 l/h. The drying tube was packed with glass wool impregnated with magnesium perchlorate and was repacked after a spell of about 20 runs.

A mercury (II) stock solution (100 ng/ml) was prepared by the method given in earlier work [13]. Working standards upto a minimum of 10 ng Hg/l were prepared by the subsequent dilution of the standard. The tin(II) chloride-cadmium chloride reduction solution was prepared by dissolving 25 g $SnCl_2$ in 50.0 ml bidistilled warm water. The reduction mixture was prepared by mixing 20.0 ml of the above solution with 50.0 ml of 30 % NaOH solution. Then, 50.0 ml aliquot of the water sample to be analyzed was added to this mixture in a filtration flask. It was shaken gently for 10–15 sec. The flask was then stoppered tightly and air was allowed to bubble through the vessel by opening the stop cock S–1 (Fig. 1). The absorption of resonance radiation caused by the expelled mercury vapour was recorded; the rest of the procedural details are the same as given earlier [13].

RESULTS AND DISCUSSION

The schematic of the experimental setup used for the estimation of organic mercury in drinking waters by the cold vapour atomic absorption method is shown in Fig. 1. The estimated mercury concentrations in various waters are given in Table 1. It will be observed that the mercury concentrations range between 15.9 to 60.7 ng/l in these waters. Relatively higher concentrations are observed in the case of underground waters with drawn from 40–60 feet deep well sources. On the other hand, lower mercury concentration is found in surface water sample S–5 belonging to the filtration plant, Rawal Dam. In general, the overall mercury concentration (organic + inorganic) in these local public utility waters is far below the upper permissible level of 1 μg/l allowed internationally for safe use. Thus, the local waters pose no physiological problem for the consumers.

The absorption is observed to depend functionally on such parameters as air flow rate, solution volume and reduction vessel volume, as shown in Fig. 2–4. In Fig. 2 is shown the quantitative dependence of absorption on air expulsion flow rate. An optimum absorption is achieved at about 20 l/h air flow rate. At all other flow rates, however, the absorption falls drastically. Likewise, the volume of the reduction vessel plays a critical role towards absorption. Fig. 3 shows that smaller reduction vessels give better

absorption. This is in line with the view that smaller volumes require smaller elution times resulting in a quick build-up of the absorption signal. Thus, for a given mercury content in a sample, there exists an inverse relationship between absorption and volume of the reduction vessel. A reduction vessel of 100–200 ml capacity is found to be the most suitable for the elution purpose. It is also observed that absorption increases directly with the increase in sample volume (Fig. 4). However, this puts a limit on the volume of the reduction vessel being used. Consequently, a

Table 1. Estimated concentration of organic mercury in local waters.

Sample No.	Location/Nature of sample	Average organic mercury (ng/l ± 2S)
S–1	Dhok Ratta; well water, used for drinking and general purposes.	44.7 ± 0.5
S–2	Bank Road; municipa supply, public utility water.	25.0 ± 0.4
S–3	Ghanda; tube well supply, general utility water	60.7 ± 0.4
S–4	Mareer; Rawal Dam water; drinking water.	30.5 ± 0.5
S–5	Rawal Dam; filtration plant, drinking and general purpose water.	15.9 ± 0.6
S–6	Simili Dam; Campus site, drinking water.	18.0 ± 0.4
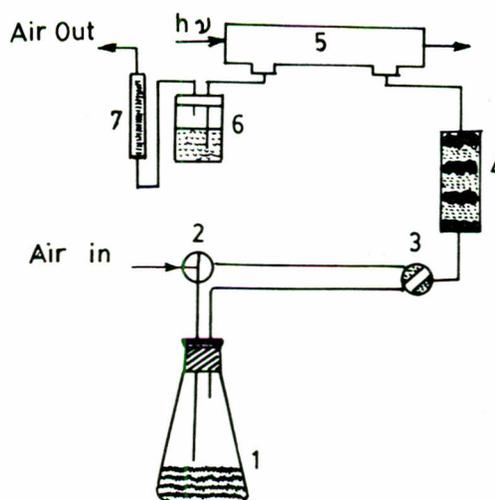
Fig. 1. Scheme of the experimental setup. 1. Reduction flask;. 2,3, Two-way stopcocks ; 4. Drying tube; 5. Absorption Cell; 6. Hg absorber; 7. Rotameter.
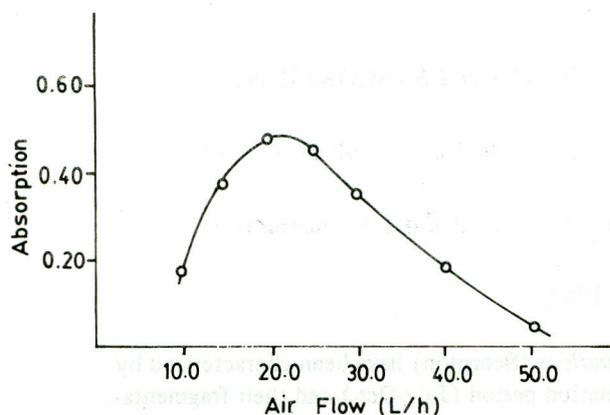
Fig. 2. Variation in absorption as a function of air expulsion flow rate for 30 ng/l Hg water.
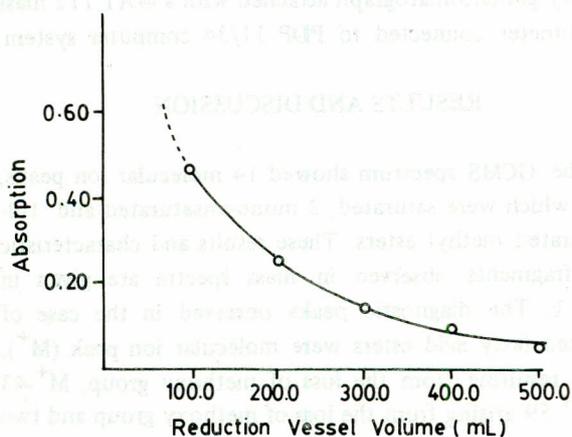
Fig. 3. Variation of absorption as a function of volume of reduction vessel for 30 ng/l Hg sample.
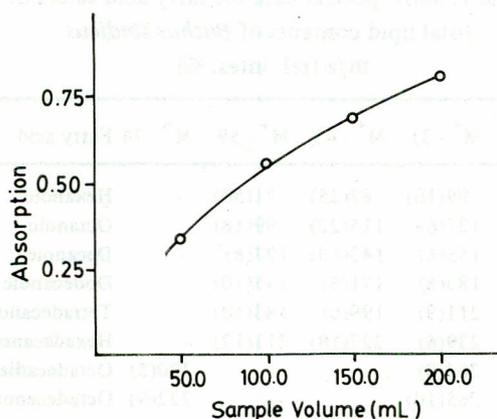
Fig. 4. Absorption vs. sample volume for 10 ng/l Hg water sample.

compromise in term as of these variables led to a workable range between 100–150 ml sample volume for obtaining satisfactory absorption signals.

In conclusion, the proposed basic medium reduction method affords a simple way for the estimation of organic mercury in drinking waters from various origins. The method does not involve any blank adjustments since their contribution is not significant at the detection level of mercury in various samples. In addition, the method is based on a direct analytical procedure without involving a pretreatment step and affords detection of mercury even down to few ng/l level. The average standard deviation for the method is about ± 0.50 ng/l at 95 % confidence level. The method is checked quantitatively with standards of known mercury concentrations ranging from 5 to 60 ng/l and a fairly acceptable linearity in absorption is observed. The method has the potential of application to waters of varied nature for the estimation of organic mercury.

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