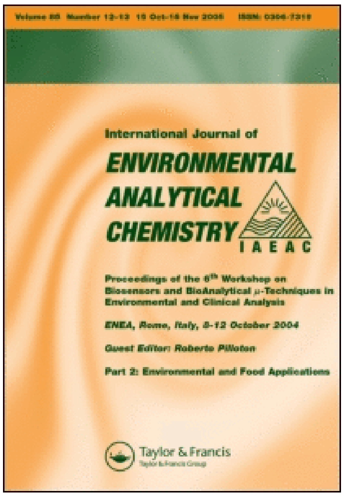

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Collection and Determination of Mercury in Air

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A method has been developed for the determination of low concentrations of mercury in air (nanograms/m^3), i.e. in the range of the believed natural levels of mercury in the atmosphere (20 ng/m^3). Mercury vapour has been collected from up to 200 l of air in glass tubes containing thin films of gold on sieved ceramic powder. In the laboratory the absorbed mercury was then released into a quartz-window cell by heating the tube in an oven at 500°C.

In this paper it is demonstrated that, by using extremely thin films of precipitated gold, quantitative recovery is obtained and memory effects, which result from the use of thicker films, are avoided.

INTRODUCTION

Spectrophotometric techniques have often been applied to the determination of small amounts of mercury,[1–8] and in two of these studies[4,8] atomic absorption spectrophotometers have been used. With conventional flames and burners, the instrument has a relatively low sensitivity for mercury, *viz.* 0.5 ppm in the prepared sample.[9] However, the sensitivity can be greatly improved by using the "cold cell" technique, in which the mercury vapour derived from the sample is introduced into an absorption cell equipped with quartz windows.

In the use of such absorption cells, enrichment methods have been used with the dual purpose of collecting the mercury and eliminating interfering substances. The ability of mercury to amalgamate with certain metals has often been utilized. For example, Brandenberger and Bader amalgamated mercury from solution on to a copper wire,[4] and Ulfvarson used gold foil to collect mercury vapour from the dithizone-mercury complex after it had been decomposed by heat.[6] In a later publication, Lidmus and Ulfvarson describe the use of granular gold to collect mercury obtained from biological material.[7] However, to the best of our knowledge, it has not been previously demonstrated that the recovery of mercury is markedly influenced by the character of the surface of the amalgamating metal.

This paper describes an atomic absorption spectrophotometric method for the determination of mercury, which utilizes a long, narrow absorption cell. To collect mercury from air, we have used filters containing only a very thin film of gold on sieved ceramic powder. These filters, in glass tubing, have been used for up to 200 l of air, but the maximum volume of air which may be handled has not yet been determined. We have found that collecting devices composed of foils or grains of gold show a considerable memory effect which therefore tends to result in determinations of poor reproducibility. Our filter construction shows no memory effect, provided that the layer is sufficiently thin, thus allowing accurate determination of nanogram quantities of mercury.

The method was originally developed for the determination of low concentrations of mercury in air, preferably less than those found naturally, i.e. 20 ng/m^3.[10] However, the present method seems to be equally applicable to any system where mercury occurs as a vapour or where it can be converted conveniently into the vapour form. Present sensitivity is less than one nanogram per cubic metre of air.

EXPERIMENTAL

Instrumentation

The instrument used was a Jarrell-Ash atomic absorption spectrophotometer, model 82–537, with a Servogor 10 mV recorder. The optical bench was lengthened, thus allowing a long gas absorption cell to replace the flame. Light from the mercury hollow cathode source was collimated by an auxiliary lens of 10 cm focal length and another such lens focussed the light on to the entrance slit of the monochromator. A schematic diagram is shown in Figure 1.

The absorption cell consisted of a quartz tube (length 500 mm, i.d. 9 mm) on to which two quartz windows were fused. The cell was fitted with two side capillary tubes, one inlet and one outlet (i.d. 2 mm). To avoid interfering absorption on the walls of the absorption cell and the tubes, these were heated in an oven kept at 360°C. This temperature was originally selected after some experimentation and it has not been altered in subsequent work.

A collecting tube containing the mercury obtained, after air sampling, was fitted to the inlet tube with a ground joint. The mercury was released by heating with a demountable oven at 500°C, which was applied to the tube, and the vapour was transferred by a slow stream of nitrogen from the collecting tube into the quartz cell. The nitrogen, from a cylinder, entered the collecting tube through a hypodermic needle inserted through the rubber membrane.

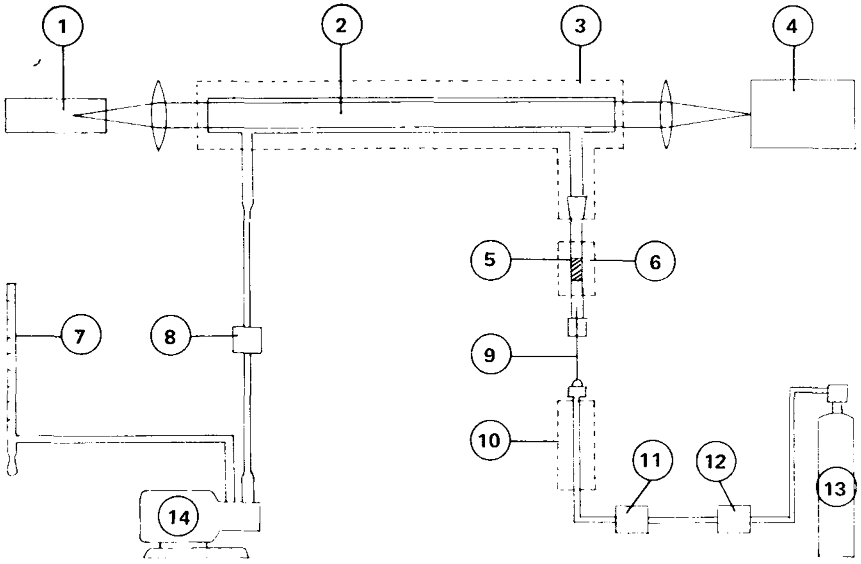

FIGURE 1 Schematic diagram of the apparatus.

1. Hollow cathode
2. Gas absorption cell
3. Heating oven
4. Monochromator
5. Collecting tube
6. Heating oven
7. Flow meter
8. Needle valve
9. Hypodermic needle
10. Heating oven
11. Valve
12. Gold trap
13. Nitrogen cylinder
14. Rotary pump

The nitrogen flow was regulated by a constant flow regulator and after passing through a gold trap[11] to remove mercury, was then preheated in an oven kept at 400°C. The absorption cell could be evacuated by a rotary pump connected to the outlet tube. This arrangement ensured constant low blanks during routine analysis.

The Collecting Tube

A sketch of the collecting tube is shown in Figure 2. The tube (i.d. 7 mm) was made of vycor glass and had a ground joint at one end. The other cooler end was fixed by means of epoxy resin on to a length of brass tubing with external threads. A rubber septum was attached to the brass tube by means of a compression nut. The overall length of the tube was about 150 mm.

The tube was filled to a length of 25 mm with gold-plated ceramic powder which was kept in place with two asbestos plugs. In order to prevent the contents from being sucked into the absorption cell, a constriction was made at one end of the tube.

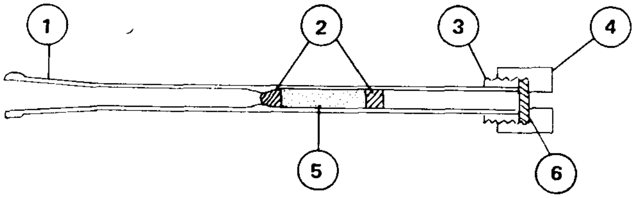

FIGURE 2

1. Ground joint
2. Asbestos plugs
3. Threaded brass tubing
4. Lock nut
5. Gold plated ceramic powder
6. Rubber membrane

A method for coating ceramic powder with gold has been described by Ormerod and Scott.[12] A slightly modified form of this method was used in the present investigation. Ceramic powder (340 mg), Sterchamol, was ground and sieved to pass 60–72 mesh and treated with brown gold chloride. Ten millilitre of a solution of the gold chloride in absolute alcohol, containing 15 mg of gold, was added to the ceramic powder and the mixture was degassed by rapidly applying vacuum from a water pump. After exactly 5 min under reduced pressure, when only part of the gold was reduced, the surplus liquid, together with some colloidal gold, was filtered off and the gilded powder was heated at 150°C for 2 hr. The actual amount of gold on the powder has not been determined, but it is assumed that the absence of a memory effect is due to the gold being thinly and evenly distributed on the ceramic surface.

ANALYTICAL PROCEDURE

On analysis, the monochromator is set so that maximum light transmission is obtained at the mercury resonance line of 253.7 nm. The carrier gas flow is then regulated to 55 ml of nitrogen per minute, a flow rate which has been found to give maximum response with the present instrumentation.

At the sampling location, the previously tested collecting tube is opened by removing both the nut and septum and the ground joint stopper. The latter end of the collecting tube is connected to a constant speed rotary pump through a flow meter. The maximum flow used was 700 ml/min at 25°C. After having been calibrated once, the gas volume passing through the tube is determined by the pumping time. During transport to the laboratory and during storage, the tube is closed tightly by the membrane and the glass stopper.

When a sample is to be analyzed at the laboratory, the collecting tube is attached to the absorption cell of the spectrophotometer and the carrier gas line is connected as described above. The demountable heating oven is then placed around the tube. After 1 min the mercury peak is recorded. Sometimes a preceding peak, originating from u.v.-absorbing organic materials is also found. This peak is, however, always to be found separated from the mercury peak. After sufficient training, one can carry out the whole measuring process at the spectrophotometer in about 2 min.

Standard samples and blanks were conveniently and frequently added to the collecting tube by injection through the rubber septum, using gas-tight syringes. This was most usually done when the collecting tube was attached to the gas cell, but some checks were made outside the laboratory. The standard gas samples were usually taken from 500-ml membrane-sealed glass flasks containing nitrogen and a droplet of mercury. Some empty flasks were also used to allow dilution of the standards. All flasks were kept in a box at a fairly constant temperature of 20 ± 2°C. It has been found that within 1 hr, five or more 0.5-ml aliquots can be withdrawn by syringe from the same flask, giving the same mercury value.

RESULTS AND DISCUSSION

Previous investigations of different kinds of collecting tubes, at this laboratory, have shown that the amount of gold in the amalgamating filters influenced the analytical results for small quantities of mercury. To study this phenomenon in detail, four collection tubes were prepared which contained different amounts of gold as obtained by *total* reduction of the gold chloride added in alcoholic solution, thus following exactly the description of Ormerod and Scott.[12] Each tube contained 340 mg of inert carrier, Sterchamol, 60–72 mesh, and a gold load of 100, 10, 1, and 0.1 mg, respectively.

Typical absorption curves of such a study are given in Figure 3. It can be seen from this figure that with increasing amounts of gold and using the same volume of mercury-nitrogen gas, less mercury is released per unit time. Moreover, these collecting tubes show a time-dependent memory effect. Even tubes loaded with only 0.1 mg of gold showed slight memory effects, detected at injection from flasks. These slight losses were not easily detected, since the same recorded peak height was obtained as that given by the same amount of mercury vapour when injected into the absorption cell of the spectrophotometer (*cf.* Figure 3).

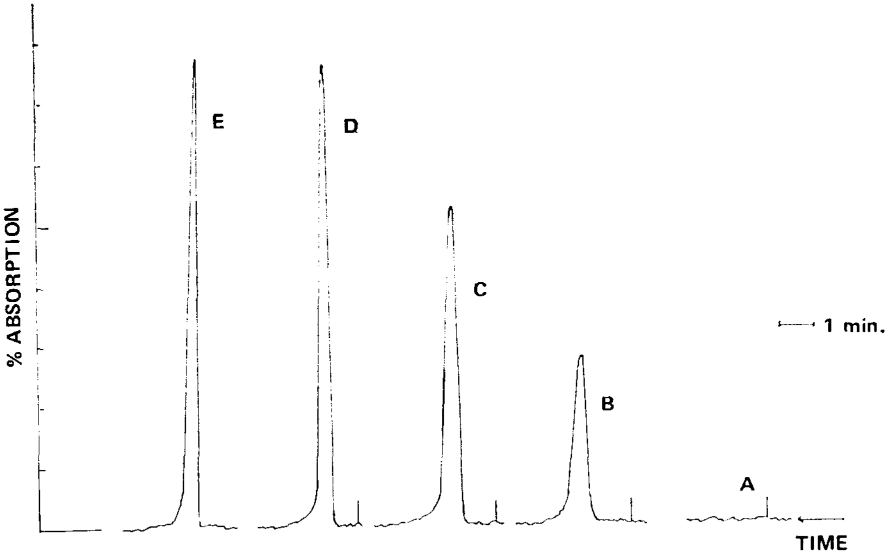

FIGURE 3 Recorder response for 10 ng of mercury released from collecting tubes plated with different amounts of gold. A, B, C, and D represent ceramic powder filters obtained from total reduction of gold chloride solutions containing 100, 10, 1, and 0.1 mg gold, respectively. E: 10 ng of mercury introduced directly into the absorption cell.

When applying small amounts of gold by precipitation according to the modified method described in this paper, the collecting tubes showed no detectable memory effects. This is probably due to the even distribution of the gold on the ceramic powder. A series of analyses was performed on four such collecting tubes. In this series, five known nanogram quantities of mercury in nitrogen were introduced into the tubes with a syringe. These samples were prepared by diluting some samples of nitrogen saturated with mercury. The results of these analyses are given in Table I and it is demonstrated that acceptable reproducibility is obtained.

Aerating mercury-loaded collection tubes with considerable volumes of air is not found to have any detectable effect on the size of the response obtained later on spectrophotometric analysis. However, this finding must not necessarily be taken as an indication that there are no losses when collecting large samples of air containing nanogram quantities of mercury. One of the most likely reasons for losses to occur is that, during the collection, reactive impurities of the air might oxidize the elementary mercury present in the sample. Although considered to be less probable, reduction might also occur in the collection tube when the air pumped through the tube contains some mercury salt aerosol. The possible presence of alkylmercury compounds in some air samples will contribute further to the complex nature of the analysis of mercury in air.

TABLE I

Detection of mercury by the present method of atomic absorption

	Collecting tubes†					
Hg (ng)	1	2	3	4	Total‡	
	0.0896	0.0998	0.0905	0.0941	0.0931	average absorbance
2.7	0.0054	0.0070	0.0047	0.0032	0.0063	S.D.
	6.1	7.0	6.3	2.4	6.8	% rel. S.D.
	0.1623	0.1663	0.1702	0.1559	0.1636	average absorbance
4.5	0.0113	0.0106	0.0114	0.0030	0.0104	S.D.
	6.9	5.7	6.7	1.9	6.4	% rel. S.D.
	0.3055	0.2878	0.3133	0.2860	0.2963	average absorbance
6.9	0.0130	0.0127	0.0128	0.0057	0.0184	S.D.
	4.3	4.4	4.1	2.0	6.3	% rel. S.D.
	0.4327	0.3989	0.4391	0.4015	0.4165	average absorbance
8.8	0.0261	0.0251	0.0174	0.0107	0.0261	S.D.
	6.0	6.3	4.0	2.8	6.2	% rel. S.D.
	0.5517	0.5286	0.5161	0.5260	0.5306	avarage absorbance
9.9	0.0312	0.0341	0.0222	0.0287	0.0305	S.D.
	5.7	6.5	4.3	5.5	5.7	% rel. S.D.

†Each collecting tube has been used for five analyses of each amount of mercury in the range of nanograms as indicated.

‡Total refers to 20 analyses.

The results obtained with the present method of analysis on some air samples will be dealt with elsewhere.

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