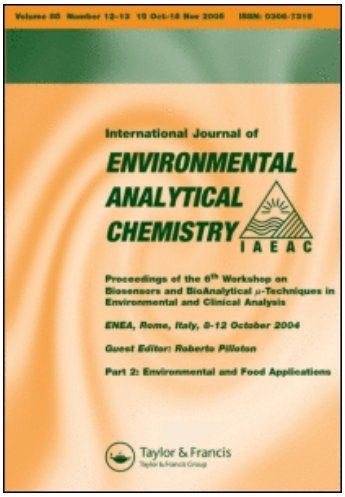

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Rapid Separation on Copper Powder of Total Mercury in Blood and Determination of Mercury by Flameless Atomic Absorption Spectrometry

S. Dogan[a]; W. Haerdi[a]
[a] Department of Inorganic, Analytical and Applied Chemistry, University of Geneva, Geneva 4, Switzerland

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Rapid Separation on Copper Powder of Total Mercury in Blood and Determination of Mercury by Flameless Atomic Absorption Spectrometry

S. DOGAN and W. HAERDI

Department of Inorganic, Analytical and Applied Chemistry. University of Geneva. Sciences II. 30 quai E. Ansermet. CH-1211 Geneva 4. Switzerland.

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The determination of mercury in blood by flameless atomic absorption spectrometry (FAAS) has been described. Prior to its analysis, the sample was decomposed by combustion and separated on a copper powder micro-column. A special type of cell has been used which gives a better sensitivity compared with the types of cells described in the literature and the method of FAAS analysis has been improved. The sensitivity of 0.1 ng for 1% absorbance was observed and the standard deviation for six determinations at this level was found to be ±0.05 ng, for 95% probability.

KEY WORDS: Total mercury analysis, separation on copper powder, blood analysis, flameless atomic absorption of mercury.

INTRODUCTION

The analysis of mercury in blood samples requires a sensitive technique especially because only low levels of this are found in persons who are not exposed to contamination by mercury sources. Several methods, mostly involving the use of flameless atomic absorption spectrometry (FAAS) have been proposed for the determination of mercury. The techniques used prior to its analysis are: Wet ashing followed by extraction with dithizone,[1,2] cold vapour technique in undigested biological and blood samples and determination of inorganic and organic mercury,[3,4] preconcentration of mercury on copper powder after digestion of blood

samples in teflon decomposition vessel,[5] decomposition by combustion of biological matters and blood for deposition of mercury on gold filter.[6,7]

Methods such as neutron activation analysis for the determination of mercury in blood[8] and biological samples,[9] and gas chromatography for analysis of a specific form of organic mercury compounds[10] have been reported.

However, some of the methods are too long. Furthermore the use of several reagents and numerous operations involved in the procedure would either contaminate the sample or result in a loss of mercury which might be non-negligible in some cases.

In this work, a rapid and sensitive technique for the determination of total mercury in human blood has been described. This method is based on the combustion of blood in a quartz tube and deposition of mercury on a micro-column of copper powder. This method is very rapid with a minimum source of error. In our technique, after the separation step, the micro-column is directly incorporated in the measuring system used for FAAS analysis. We have modified the previously described working cell[5] in such a way that the new cell has the form of a convergent beam of light. This eliminates the dead-volume in the cell and the sensitivity is increased to about seven to ten times that of a cylindrical cell of 20 mm diameter and of the same length. We have also investigated some important parameters such as temperature, flow rate affecting the FAAS analysis so as to simplify and improve the method previously described.[11]

EXPERIMENTAL

Apparatus and reagents

—Copper powder (Siegfried). The copper powder micro-column was prepared as shown in Figure 1 and purified by heating it to 400°C in an atmosphere of nitrogen. The micro-column can be directly used for preconcentration of mercury of aqueous sample by the technique published previously.[5,11] The heating of the copper powder causes the formation of lumps and these have to be broken with a wire before the separation by combustion technique. This has to be done in order to make it more permeable to gas coming from the combustion of the sample. Once this is done, the micro-column can be used several times without repeating this procedure (one can prevent the formation of lumps if the purification of copper powder by heating is carried out before filling the micro-column).

—Combustion tube in quartz (see Figure 1)

—FAAS measuring system (see Figure 2)

—Atomic absorption spectrometer Pye Unicam SP 1900.

Combustion procedure

10–200 μl blood sample taken in a quartz crucible is burnt by heating slowly at first and then strongly with a Bunsen burner in a stream of oxygen (flow rate ~45 ml/min), see Figure 1. The mercury is carried over by

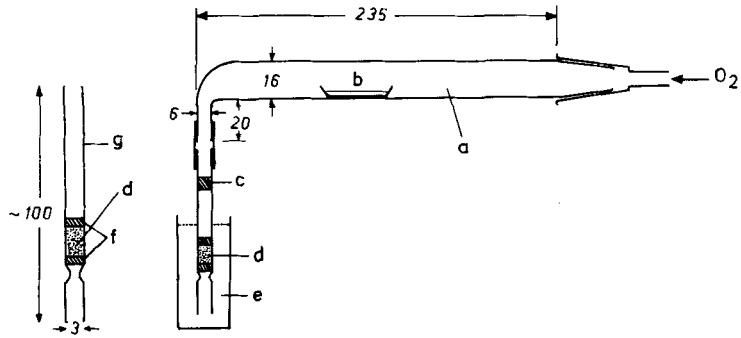

FIGURE 1 Combustion and separation apparatus. (a) combustion tube in quartz, (b) crucible in quartz, (c) quartz wool, (d) copper powder micro-column (150–200 mg), (e) ice bath, (f) quartz wool to retain copper powder, (g) tube in pyrex ($\emptyset_{ext}$: 6 mm). Dimensions in mm.

the gas resulting from combustion and separated on a copper micro-column (d). The micro-column is connected to the combustion tube by means of a short p.v.c. tube and is cooled in an ice bath to ensure a quantitative separation of mercury. The quartz wool (c) used acts as a filter for any particulate matter which may be carried along by the gas and this should be removed before FAAS analysis.

The blank was prepared similarly without the sample.

The micro-column is rinsed with methanol (p.a. Merck) to remove organic compounds which have condensed on the copper powder and finally it is directly used for FAAS analysis.

FAAS analysis

The effect of the flow rate and temperature on the results of FAAS analysis was first studied. For this purpose, mercury was separated from mercuric nitrate solution (p.a. Merck) by carrying out a redox reaction on copper powder as described previously.[11] The micro-column was then rinsed with methanol and the last traces of methanol was removed by passing nitrogen at a high flow rate. Finally the micro-column is incorporated in the measuring system as shown in Figure 2. The analysis of mercury was carried out in two ways:

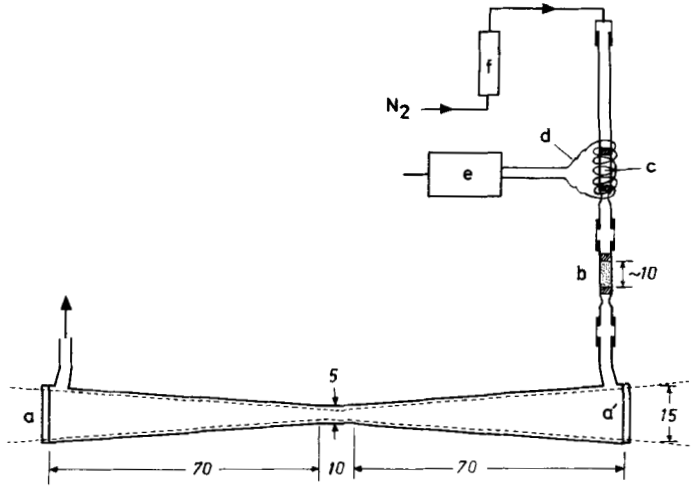

FIGURE 2 FAAS measuring system. (a, a') quartz windows (2 mm), (b) alumina micro-column for retention volatile organic compounds to avoid interferences (~0.1 g, Al_2O_3 standardized for chromatographic adsorption analysis acc. to Brockman), (c) copper powder micro-column, (d) heating coil, (e) e.m.f. cell, (f) flowmeter.

The dotted lines represent the convergent beam of light. Dimensions in mm.

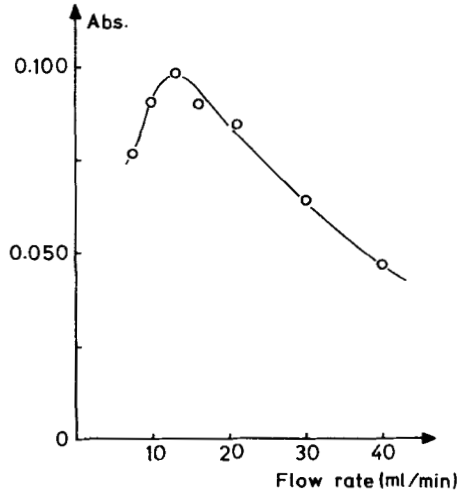

FIGURE 3 Effect of flow rate on the absorbance (first technique). Hg total: 4.0 ng.

1) The nitrogen flow rate was set to a given value and a current of 5.0 Amps (4.8 V) was passed the heating coil (Figure 2, d), by applying appropriate potential by means of potentiometer (e), (the temperature of copper powder is about 360°C). The mercury was carried in the cell with nitrogen and measured by recording the absorption as a function of time. The maximum absorbance observed is then proportional to the amount of mercury. After recording the maximum of absorption peak, the nitrogen flow rate was increased to clean the cell quickly.

In this technique the sensitivity and reproducibility is largely dependent on the flow rate of nitrogen particularly when a small cell is used, for example 13 ml of volume in our case. From Figure 3, it can be seen that, for a given amount of mercury, the maximum absorbance is observed for a flow rate of 13 ml/min. Thus a value of 1 was obtained for the ratio of cell volume to flow rate.

The disadvantage of this technique is that the permeability of the copper powder decreases during the heating step which causes a variation in the flow rate and affects the sensitivity and reproducibility of the results.

2) The micro-column was first heated sufficiently to release the mercury from the copper powder and then a stream of nitrogen was passed at various flow rates (8–150 ml/min) and the maximum absorbance was recorded. It can be seen from Figure 4, that the width of the peaks varies with the flow rate, but the height remains constant. This shows that all the mercury is carried over at the same time and this enables one to obtain a better sensitivity and reproducibility of the results. The heating time (temperature) for extracting mercury from copper is important in this technique. The time required is fairly short. For a current 5.0 Amps, the

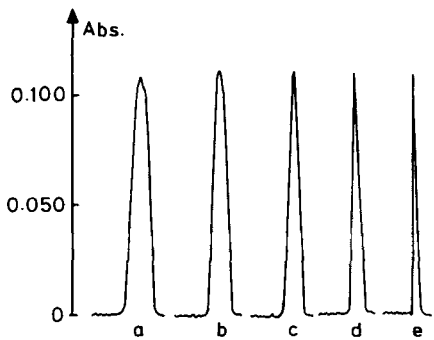

FIGURE 4 Typical absorption peaks for various flow rates (second technique). Hg total: 4.0 ng.

Flow rate (ml/min): (a) 8, (b) 13, (c) 40, (d) 90, (e) 150.

time needed is 60–70 sec. and the copper powder micro-column attains a temperature of about 300°C; Figure 5. It was found that the sensitivity decreases when the heating time is long (since 120 sec., temperature 400°C) probably because of the occurrence of phenomena such as diffusion and dispersion of mercury vapours into the tube containing copper powder.

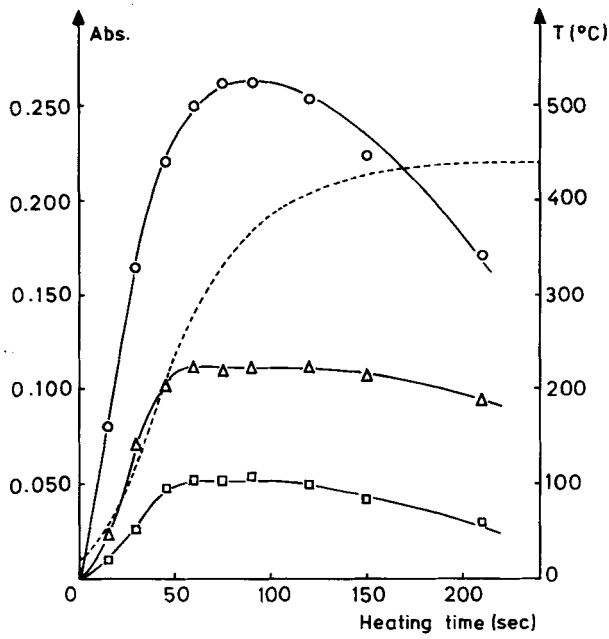

FIGURE 5 Effect of heating time (temperature) on the absorbance (second technique). Hg total: (□) 2.0 ng, (△) 4.0 ng, (○) 10.0 ng. ----: curve of temperature obtained in the copper powder micro-column for 5.0 A and 4.8 V in function of heating time.

Because of the simplicity of the method and reproducibility of the results, this technique was chosen for the analysis of mercury. By keeping heating time of 80 sec (temperature: ~360°C) and flow rate about 120 ml/min constant, a perfectly linear relationship between the absorbance and the amount of mercury, was obtained in the range 0.2–12 ng studied. The method is sensitive up to 0.1 ng for 1% absorbance and the standard deviation at this level for 95% probability and for the result of 6 analyses

is ± 0.05 ng. This limit can be lowered by using the expanded scale of the atomic absorption apparatus and improving the measuring system.

The whole analysis including combustion-separation step takes about 10–15 minutes.

RESULTS AND DISCUSSION

The accuracy and reproducibility of the results was checked by testing NBS standard sample (standard orchard leaves, reference material number 1571). A value of 154 ± 13 ppb was obtained which is in good agreement with that certified by NBS (155 ± 15 ppb), thus showing the validity of our technique.

The reproducibility of the results by this technique was also checked on a blood sample and the dispersion in the results for 10 determinations is given in Table I. The standard deviation for 95% probability was computed.

TABLE I

Reproducibility of the results obtained from 10 determinations of whole blood

Volume of sample (μl)	Hg (ng/ml)
50	12.6
50	11.4
50	12.6
50	10.6
100	10.0
100	9.4
100	11.7
100	13.7
200	10.7
200	11.5

Mean: 11.4 ± 2.9 ng/ml.

The analysis of mercury in blood samples of some of the chemists working in our department and of other people are given in Table II.

The concentration of mercury in blood of normal people is reported to be 5 ppb. In general one considers the tolerable limit to be about 20 ppb and about 200 ppb for the symptoms of poisoning. Thus the results obtained in Table II can be considered as normal.

In the case of mercury intoxication in persons, the analysis of mercury can be carried out rapidly by our technique and this in turn will enable the patient to receive medical treatment on time.

TABLE II

Analysis of mercury in blood samples in normal subjects

Subject	Hg total in whole blood (ng/ml)
1	10±2
2	8±2
3	6±2
4	8±2
5	7±2
6	8±2
7	3±1
8	7±2
9	11±3
10	5±1
11	4±1
12	9±2
13	5±1

Résumé

La détermination du mercure total dans le sang par spectrométrie d'absorption atomique sans flamme est décrite. Pour ce faire, l'échantillon de sang est tout d'abord brulé dans un tube de combustion et le mercure est séparé sur une micro-colonne de cuivre métallique en poudre et ensuite la micro-colonne est couplée à une cellule pour le dosage analytique du mercure. La forme spéciale de la cellule a permis d'obtenir une meilleure sensibilité par rapport à des cellules décrites dans la litérature et le dosage analytique a été amélioré. La limite de sensibilité pour 1% d'absorbance est de 0,1 ng absolu avec une déviation standard de ±0,05 ng pour 95% de probabilité et sur 6 mesures.

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