Mercury

Application	Determination in blood and urine
Analytical principle	Atomic absorption spectrometry – cold vapour method
Completed in	December 1983

Summary

The method described here for the determination of mercury in blood and urine is representative of current technical knowledge. It is a further development of the cold vapour method used up to now. The use of a gold/platinum gauze brings about an enrichment of the mercury after its displacement from the biological material. The resulting increase in the sensitivity of the method as well as the associated reduction of background interference makes it possible to carry out measurements not only in the range relevant to occupational exposures but also in that required for ecological studies. The determination of mercury in biological materials is carried out directly by atomic absorption spectrometry with the so-called cold vapour method. A commercially available hydride system with amalgamation device (gold/platinum gauze) is used for the analysis after reduction of the sample with sodium borohydride. The method determines the total mercury content of the processed material. The quantitative evaluation is carried out by means of standards dissolved in water or in whole blood. The reliability criteria of the method fulfill the requirements of statistical quality control.

Within-series imprecision:	Standard deviation (rel.)	s_w = 1.9– 6.2 %
	Prognostic range	u = 5.0–17.2 %
	At concentrations ranging from 6.38 to 270 µg mercury per litre urine and where n = 10 and 5 determinations	
	Standard deviation (rel.)	s_w = 1.7–3.2 %
	Prognostic range	u = 3.8–8.9 %
	At concentrations ranging from 3.13 to 98.5 µg mercury per litre blood and where n = 10 and 5 determinations	
Between-day imprecision:	Standard deviation (rel.)	s = 4.9–3.1 %
	Prognostic range	u = 11.1–7.6 %
	At concentrations ranging from 28.7–38.8 µg mercury per litre urine and where n = 10 and 7 days	
	Standard deviation (rel.)	s = 3.5–3.6 %
	Prognostic range	u = 7.9–8.1 %
	At concentrations ranging from 40.5–77.3 µg mercury per litre blood and where n = 10 days	

Inaccuracy:	The inaccuracy of the method for urine and blood was determined using independent analytical methods as well as by the analysis of a NBS Reference sample (lyophilized urine) Recovery rate r = 99 % (urine) Recovery rate r = 98 % (blood)
Detection limit:	0.3 – 0.4 µg Mercury per litre urine 0.3 µg Mercury per litre blood

Mercury

Mercury (Hg) and its chemical compounds play an important role as workplace and polluting chemicals. Determination of the mercury level in various biological matrices, in particular in blood and urine, is recommended as a means of estimating the degree of mercury contamination at the work place and in the environment. The mercury level in biological materials depends on the route of intake, on the chemical form of the element and on the duration and level of mercury incorporation. The mercury concentration in blood and urine is a measure of the dose taken up during the previous weeks [1–3].

In Regulation G9 of the Berufsgenossenschaftlichen Grundsätze für arbeitsmedizinische Vorsorgeuntersuchungen (Professional Association's Guidelines for Occupational Health Examinations) [4], the analysis of mercury in urine or blood is specified as essential for examining persons exposed to mercury. Within the definition of "biological monitoring", the mercury level in blood and urine provides a suitably objective basis for the decision whether health surveillance should be practiced according to TRgA 101 (Regulation 101 of the German Code on Hazardous Working Materials) [5].

A knowledge of "normal" mercury levels is of importance in the evaluation of the mercury concentrations in body fluids. These levels are currently given as less than 5 µg/L (in both urine and blood). The average mercury levels in the general population are less than 1 µg per litre urine or blood [6]. However, it is known that marked interindividual variation can occur. In addition, the mercury concentrations in blood and urine can be affected when mercury-containing medicines are taken. In the Federal Republic of Germany, a large number of such medicines are still available [7].

For the occupational health-toxicological evaluation of the mercury level in the blood and urine of occupationally exposed persons, BAT values (Biological Tolerance Values for Working Materials) are available. The BAT values for exposure to inorganic mercury compounds or metallic mercury are 50 µg per litre blood and 200 µg per litre urine.

The mercury level in whole blood is measured for the evaluation of occupational exposure to organic mercury compounds, in particular the alkyl mercury compounds. In this case the BAT value is 100 µg/L.

On a collective basis, these BAT values correlate with the current (1986) MAK values of 0.01 ml/m^3 (0.1 mg/m^3) for mercury and 0.01 mg/m^3 for organic mercury compounds. Detailed justification reports are available for the BAT values [7, 8].

Author: *K.-H. Schaller*
Examiners: *M. Fleischer, H. Seiler*

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Contents

1 General principles

Mercury is determined directly in whole blood and urine by means of the so-called cold vapour method and atomic absorption spectrometry. The analysis makes use of a commercially available hydride system with an amalgamation device (gold/platinum gauze)

which is applied after reduction of the sample with sodium borohydride to metallic mercury. The volumes of the blood or urine samples are chosen according to the expected mercury levels. The total mercury content of the test sample is determined.

The quantitative evaluation of the data requires calibration standards which are dissolved in either water or blood.

2 Equipment, chemicals and solutions

2.1 Equipment

Atomic absorption spectrometer with background correction at 253.7 nm
Hydride system with amalgamation device, interchangeable cartridge and chart recorder
Mercury hollow cathode lamp, preferably ED lamp with power supply
10, 50,100, 500 and 1000 mL Volumetric flasks
500 mL Conical flasks with stoppers
Plastic centrifuge tubes (approx. 12 mL) with caps
Automatic pipettes, adjustable from 20 to 200 µL and from 200 to 1000 µL
Disposable syringes containing anticoagulant (e.g. K-EDTA Monovetten® from Sarstedt, Nümbrecht, FRG)

2.2 Chemicals

All chemicals must be analytical grade or purer. Some suppliers deliver reagents specially prepared for mercury analysis.
96 % Acetic acid (e.g. Suprapur from Merck)
Sodium borohydride, p.a.
Sodium hydroxide, monohydrate (e.g. Suprapur from Merck)
95 – 97 % Sulfuric acid with guaranteed maximum mercury content of 0.0000005 % (e.g. Merck)
65 % Nitric acid (e.g. Suprapur from Merck)
Potassium permanganate with guaranteed maximum mercury content of 0.000005 % (e.g. Merck)
1-Octanol, pure
Silicon anti-foaming agent (e.g. Antifoam 110 A from Dow Corning)
n-Heptane for spectroscopy
Mercury standard (e.g. Fixanal from Riedel-de Haën) containing 0.1 g mercury (as $HgCl_2$)
Transfusion blood or animal blood (e.g. from GMN, Waldorf)
Ultrapure water (ASTM type 1) or double-distilled water
Nitrogen (99.999 %) or argon (99.95 %)

Compressed air
Samples for quality control (e.g. Lanonorm®-Metalle and Kontrollblut für Metalle from Behringwerke or Ortho® Control Urine II from Ortho Diagnostic Systems)

2.3 Solutions

Nitric acid solution (15 g/L):
Approximately 400 mL ultrapure water is placed in a 500 mL volumetric flask. 8.5 mL 65 % nitric acid is added with a graduated pipette and the flask filled to the mark with ultrapure water.

Sulfuric acid solution (15 g/L):
Approximately 400 mL ultrapure water is placed in a 500 mL volumetric flask. 4.3 mL 96 % sulfuric acid is added with a graduated pipette and the flask is filled to the mark with ultrapure water.

Acid solution (nitric acid/sulfuric acid):
Equal volumes of the nitric and sulfuric acid solutions are mixed in a 500 mL conical flask (acid content, each 15 g/L).

Anti-foaming agent:
The silicon anti-foaming agent is diluted 100 times with ultrapure water

5 % Aqueous potassium permanganate solution

3 % Sodium borohydride in 1 % sodium hydroxide solution:
30 g sodium borohydride is dissolved in 1 L 1 % sodium hydroxide solution. This solution must be freshly prepared at least every second day. Unused sodium borohydride solution must be decomposed in a fume cupboard by dropwise addition of dilute sulfuric acid.

1 M Nitric acid for cleaning tubes and glassware

2.4 Calibration standards

Starting solution:
0.1 g mercury (e.g. Fixanal ampoule) is placed in a volumetric flask and made up to 1 L with ultrapure water (0.1 g/L).

Stock solution:
1 mL starting solution is pipetted into a 100 mL volumetric flask which is then filled to the mark with ultrapure water (1 mg/L).

Calibration standards containing between 0.5 and 100 µg mercury per litre are prepared from the stock solution by further dilution with the acid solution. The standards must be freshly prepared each day. The following pipetting scheme should be followed:

Volume of stock solution µL	Final volume of calibration standard mL	Concentration of calibration standard µg/L
25	50	0.5
20	10	2
100	10	10
400	10	40
1000	10	100

3 Specimen collection and sample preparation

To prevent any exogenous contamination all plastic tubes used for specimen collection and sample preparation must be cleaned with 1 M nitric acid before use and then rinsed three times with ultrapure water and dried at room temperature.

3.1 Urine

Urine specimens are collected in plastic bottles, acidified with acetic acid (1 mL to 100 mL urine) and then stored in the laboratory refrigerator until analysis. The acid should be added as soon as possible after specimen collection. Dilute nitric acid can also be used for this purpose. An essential requirement for exact analytical results is homogeneity of the urine sample. The working group, Analytische Chemie (Analytical Chemistry), has carried out detailed investigations concerning this point and has produced recommendations for the sampling of urine specimens [9, 10].

As a rule, a 1 mL sample of the test specimen is analysed for the determination of mercury in urine. If the mercury level does not lie within the linear range of the method the specimens must be diluted appropriately. For mercury levels in ecological investigations 4 mL aliquots of the urine specimens may be analysed.

The reaction vessel of the hydride system is rinsed with ultrapure water before use. The urine sample is pipetted directly into the reaction vessel and 100 µL potassium permanganate solution together with 10 mL acid solution is added. After adding 50 µL 1-octanol or the anti-foaming agent the reaction vessel is connected to the hydride system. A reagent blank is included in each analytical series.

3.2 Blood

Blood is collected with disposable plastic syringes. If these do not already contain liquid potassium-EDTA as anticoagulant for a given volume of blood (e.g. Sicherheits-Monovette for 5 or 10 mL from Sarstedt) then a known amount of 3.8 % sodium citrate solu-

tion should be drawn up first with which the blood will then be diluted in the ratio 1+9. The mixture is shaken well and transferred to a rinsed plastic centrifuge tube. If the analysis cannot be carried out immediately, the sample may be stored in the laboratory refrigerator at + 4 °C for several days or can be deep frozen.

For the mercury determination 1 mL whole blood is pipetted into the reaction vessel of the hydride system. The reaction vessel must have previously been rinsed well with ultrapure water. It has proved advantageous to rinse the disposable pipette tips with n-hexane before use. 10 mL acid solution and 200 µL 1-octanol are then added and the reaction vessel is connected to the hydride system. For blood mercury levels which lie outside the linear range of the method, appropriately smaller sample volumes (500 or 200 µL) are employed. The sample volume is made up to 1 mL with ultrapure water. A reagent blank is included in each analytical series.

4 Operational parameters for atomic absorption spectrometry

Atomic absorption spectrometer:

Wave length:	253.7 nm
Background correction:	Deuterium lamp
Spectral slit width:	0.7 nm
Lamp current:	According to manufacturer's instructions

Hydride system:
The settings of the hydride system vary from one type of instrument to another. The optimal time settings must be ascertained by each operator on his own instrument. The following time programs have proved reliable for the author and examiner and are intended as a guide.

Program for urine analysis

Analytical step	Step duration s	Procedure
Reaction	15	Addition of sodium borohydride solution
Purge I	40	Release of the free metallic mercury and its transfer into the amalgamation device
Manual heat	15	Heating the gold/platinum gauze filter and vaporization of the mercury
Purge II	40	Transfer of the mercury vapour into the quartz cuvette
Cooling	50	

Program for blood analysis

Analytical step	Step duration s	Procedure
Reaction	20	Addition of sodium borohydride solution
Purge I	40	Release of the free metallic mercury and its transfer into the amalgamation device
Manual heat	15	Heating the gold/platinum gauze filter and vaporization of the mercury
Purge II	40	Transfer of the mercury vapour into the quartz cuvette
Cooling	50	

Further details may be found in the manufacturer's instructions for the hydride system.

5 Analytical determination

The peak height or extinction of the measured signal is recorded. If the extinction for the sample lies outside the linear range of the calibration curve, the volume of the specimen to be analysed is reduced.

6 Calibration

6.1 Urine

Aqueous calibration standards of known mercury content (see Section 2.4) are used for calibration of the method. 1 mL samples of each of the urine specimens are processed and analysed. Any reagent blank values are allowed for by subtraction. The calibration curves are linear up to 100 µg mercury per litre. The procedure used by the examiner was more sensitive and the linear range was accordingly reduced to a maximum of 50 µg/L. An example of a calibration curve is shown in Fig. 1.

6.2 Blood

Calibration curves established with aqueous standards have a different slope from curves plotted for standards made up with whole blood (Fig. 2). Therefore matrix standards are required for calibration. It is sufficient to prepare a calibration curve based on pooled normal human blood since the curves obtained with a variety of blood samples are strictly parallel to the curve obtained with pooled blood (Fig. 2).

For each point on the calibration curve, 1 mL of pooled blood is mixed with 1 mL of an aqueous calibration standard (see Section 2.4), 9 mL acid solution and 200 µL 1-octanol. The mixture is analysed as described above. In parallel, the blood without the addition of the mercury-containing calibration standard is analysed.

The extinction of the unspiked blood is subtracted from the other measured values. The extinction values so obtained are plotted against the mercury concentrations used to give the calibration curve.

7 Calculation of the analytical result

The extinction value or peak height for the sample is corrected for the reagent blank value if necessary. Using the peak height or the extinction value, the corresponding mercury concentration in the biological material is read off the calibration curve. Any dilution of the urine sample or any blood volumes of less than 1 mL must be taken into account.

8 Standardization and quality control

Quality control of the analytical results is carried out as stipulated by Article TRgA 410 [11] and in the relevant preliminary remarks. Commercially available standards (e.g. Lanonorm®-Metalle and Kontrollblut für Metalle from Behringwerke or Ortho® Control Urine II from Ortho Diagnostic Systems) are used for quality control. Another reference material is freeze dried urine with defined mercury level, available from the National Bureau of Standards (NBS), Washington.

9 Reliability of the method

9.1 Precision

The within-series imprecision is determined by carrying out multiple analyses in the three concentration ranges important in practice. The resulting data, including average mercury level, relative standard deviation and prognostic range, are given in Tab. 1. The relative standard deviations obtained for the urine analyses lie between 1.9 and 6.2% and for the blood analyses between 1.7 and 3.2 %. Also given in Tab. 1 are the data for between-day imprecision, obtained with quality control standards during a time period of

14 days. In the case of the urine samples the data were obtained both from a synthetic matrix and from native urine (Lanonorm®-Metalle from Behringwerke and Ortho® Control Urine II from Ortho Diagnostic Systems).

9.2 Accuracy

The accuracy of the determination of mercury in urine was tested by comparison with an analytical method independent in every step of the process. 15 urine samples from persons who were occupationally exposed to mercury were analysed both with the cold vapour method described here and with a polarographic method. The results obtained with the two methods correlated at the 99.99 % level ($r = 0.982$). The slope of the linear correlation curve was 1.06, demonstrating that systematic errors are not to be expected (Fig. 3).

The accuracy of the urine analyses was also demonstrated by analysis of a standard reference urine from the National Bureau of Standards. A value of 49 µg/L was obtained for a given urine concentration of 49.8 ± 4.2 µg/L, and an average value of 93 µg/L was found for an expected value of 105 ± 8 µg/L.

For the blood analysis, a parallel assay of 16 blood samples from persons occupationally exposed to mercury was also possible. A cold vapour method was also used as a reference method but this time with sulfuric acid-permanganate decomposition and with a hydride system which is not commercially available [12]. The correlation coefficient obtained was 0.996 (Fig. 4).

Finally, recovery experiments were carried out. Urine and blood from persons not occupationally exposed to mercury were pooled and defined amounts of mercury were added. At a level of approximately 7 µg per litre urine the recovery rate was 99 % mercury. In blood to which 8 µg mercury per litre had been added the recovery rate averaged 98 %.

Evaluation was carried out with aqueous calibration standards in the case of urine analyses or with standards prepared in whole blood.

9.3 Detection limit

Under the given conditions the detection limit for mercury in urine was calculated as 0.3 to 0.4 µg/L. For blood analysis with 1 mL blood samples the limit was 0.3 µg mercury per litre blood.

9.4 Sources of error

The specificity of the method is apparently greatly improved by the use of the amalgamation device. In a comprehensive test series, various metal salts and organic impurities were mixed with urine samples of known mercury content (see Tab. 2). The

added amounts of impurities considerably exceeded the physiologically and toxicologically possible concentrations. It was demonstrated that the recovery rates of mercury were hardly altered by the substances tested. Only L-cysteine seemed to have an effect on the recovery rate (r = 90 %). The studies with added metals indicated that the addition of copper(II) ions eliminates interference from other metal ions such as nickel, arsenic, cadmium, chromium and lead.

If the chemicals listed are used, the reagent blank values are approximately 0.06 µg/L or 0.6 ng per test and thus need not be taken into account in analyses in biological material. It is recommended, however, that the chemicals used are checked for their mercury content in each new analytical series.

Experience has shown that a number of points must be observed if reliable analytical results are to be obtained. Blood and urine foam considerably on addition of the sodium borohydride solution. A large amount of foam production results in poor precision, reduction of peak height and the possibility of contamination of the whole apparatus. Tests of various anti-foaming agents have demonstrated that 1-octanol and the silicon anti-foaming agent Antifoam 110 A are equally effective. For the analysis of blood samples 1-octanol is superior to the other agents and should, therefore, be used. A disadvantage of this agent is that it could result in considerable interference in other analytical procedures (arsenic, selenium) involving the hydride method. Therefore it is recommended that other elements are not determined in an apparatus used for mercury analyses.

A further critical point is the manual winding of the gold/platinum gauze which has a decided effect on the peak height of the mercury signal. It must be wound so than no air space is present and so that no mercury vapour can enter the light path during the reduction step. This may be tested most effectively with a sample containing 100 ng mercury. If the mercury is not quantitatively adsorbed it must be ensured that the gold/platinum gauze occupies the whole cross-section of the quartz tube. If the filter is wound too tightly the gas flow may be hindered leading to unpredictable pressure changes in the system which result in poor reproducibility, especially in the desorption process. It is also important to ensure that the gold/platinum gauze is properly attached in the quartz tube and that it does not slip out of the heating zone. Poor attachment can lead to loss of mercury. Movement of the gold/platinum gauze requires a new calibration of the analytical method. If marked reductions in sensitivity occur, the gold/platinum gauze must be cleaned. Suitable methods are soaking the gold/platinum gauze overnight in concentrated nitric acid or treating it with hot concentrated nitric acid [13]. In addition, it is important that the gas flow is adjusted precisely. This greatly influences the quantity of the sodium borohydride applied. The whole system must be free of leaks. In blood analysis the precision of the results is affected by the speed at which the acid solution is added. Slow acidification causes the formation of large lumps of protein which lead to poor precision and losses of up to 50 %. In order to avoid this, the blood is first pipetted into the reaction vessel and then 10 mL of the acid solution is added rapidly. This produces a protein precipitate which is very finely divided.

10 Discussion of the method

The various versions of the so-called cold vapour method have proved themselves suitable for mercury determination in biological materials [14–17]. In most cases they are based on the reduction of Hg^{2+} with Sn^{2+} to elementary mercury which is then released from the solution and detected in the light path of an atomic absorption spectrometer. The specificity and, in particular, the sensitivity of the method can be increased if the mercury is enriched in the form of a gold or silver amalgam before the final analysis [18.-20]. In the meantime, a so-called amalgamation device (with a gold/platinum gauze) is commercially available and provides the basis for a routine method [21, 13]. The research group *Welz* and *Melcher* published the first methods for the determination of mercury in urine using an amalgamation device. The method described here for urine mercury analysis is a modification of their procedure. The advantages of this system include, on the one hand, the specificity of the amalgamation method which prevents interference caused by molecule formation in the quartz cuvette or by unspecific absorption due to carbon dioxide formation [20] and, on the other hand, the high sensitivity of the system which allows the measurement of mercury at levels relevant to ecological investigations without previous sample processing. Recently, *Welz* and *Melcher* discussed the amalgamation technique in detail [13].

The present method determines the total mercury content in urine and in whole blood. The reducing agent, sodium borohydride, is able to reduce even the particularly stable alkyl-mercury compounds which can occur physiologically. This is demonstrated convincingly by the fact that urine samples which have been subjected to a total mineralization yield the same analytical results. A time-consuming decomposition of the sample is thus unnecessary. In conclusion, the use of the described reducing agent together with the amalgamation device yields a simple, sensitive and specific determination of mercury in biological material.

Instruments used:
Atomic absorption spectrometer model 410 or 280 with hydride system MHS-20 with amalgamation device from Perkin-Elmer

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Author: *K. H. Schaller*
Examiners: *M. Fleischer, H. Seiler*

Tab. 1. Within-series imprecision and between-day imprecision for the analysis of mercury in urine and whole blood.

Matrix	*n*		$\bar{x}$ µg/L	*s* %	*u* %
Urine	10	Within-series imprecision	6.38	2.2–3.9	5.0–8.8
	5		19.5	6.2	17.2
	5		270	1.9	5.3
	10	Between-day imprecision	28.7	4.9	11.1
	7		38.8	3.1	7.6
Blood	10	Within-series imprecision	3.13	1.7	3.8
	5		47.5	3.2	8.9
	5		98.5	2.0	5.6
	10	Between-day imprecision	40.5	3.5	7.9
	10		77.3	3.6	8.1

Tab. 2. Recovery experiments for the analysis of mercury in urine in the presence of possible interfering substances.

Interfering substances Concentration	Calculated value (µg/L)		Recovery rate (%)	
	Author	Examiner	Author	Examiner
Ni(II), 200 µg/L	100	6.5	99.2	93.0
As(III), 700 µg/L	100	6.5	95.9	98.6
Cr(VI), 100 µg/L	100	6.5	97.1	97.2
Cd(II), 100 µg/L	100	6.5	98.7	96.8
Pb(II), 400 µg/L	100	6.5	97.5	92.4
Cu(II), 200 µg/L	–	6.5	–	93.8
Ni, As, Cd, Cr, Pb, Cu	–	6.5	–	101.7
Ni, As, Cd, Cr, Pb, Cu	–	11.2	–	100.5
Ni, As, Cd, Cr, Pb	100	11.2	92.1	95.3
L-Glutathione, 1 g/L	–	11.2	–	97.1
L-Cysteine, 1 g/L	–	11.2	–	90.5
L-Cystine, 1 g/L	–	11.2	–	98.3
Glucose, 0.5 g/L	100	–	99	–
Uric acid, 1 g/L	100	–	100	–
Ascorbic acid, 0.05 g/L	100	–	100	–
Urea, 50 g/L	100	–	101	–

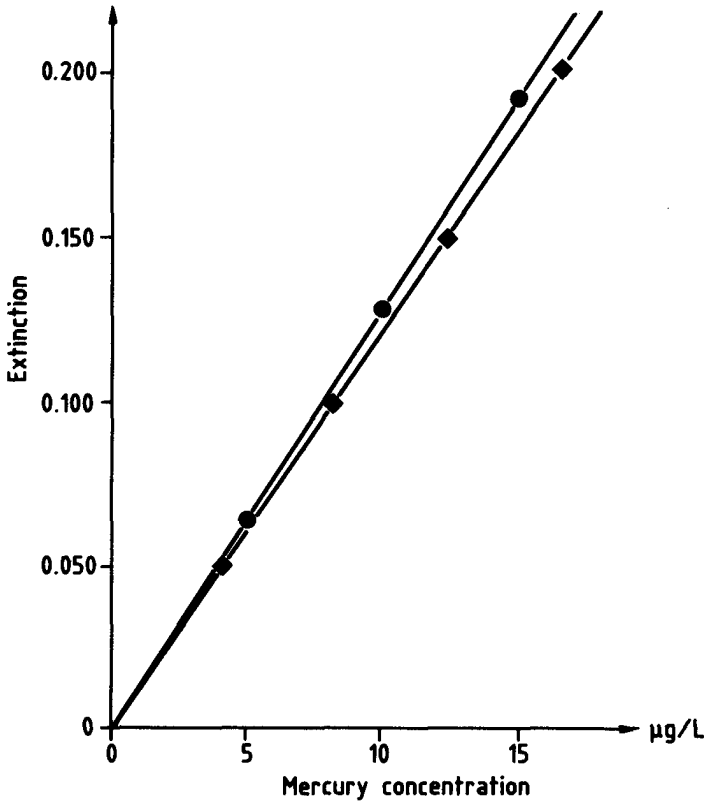

Fig. 1. Calibration curve for the analysis of mercury in urine by the cold vapour method with atomic absorption spectrometry.

- ● Calibration standards in urine
- ♦ Calibration standards in mixed acid solution

The anti-foaming agent used in this case was a 100 times dilution of Antifoam 110 A (Dow Corning).

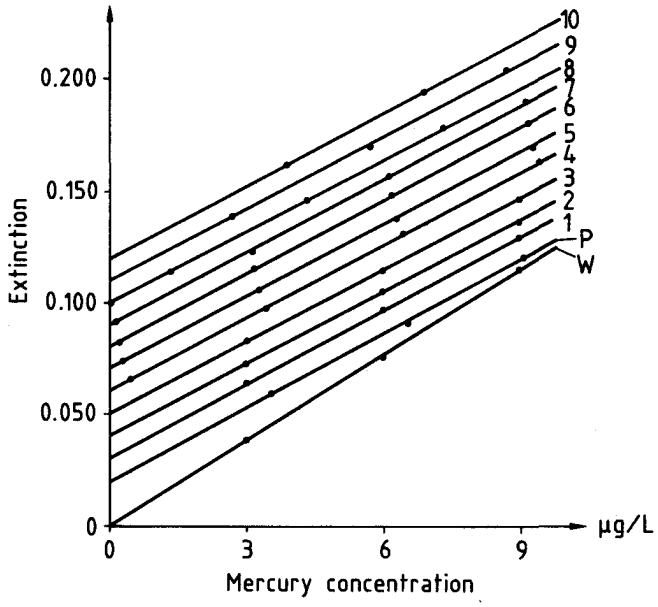

Fig. 2. Calibration curve for the analysis of mercury in blood by the cold vapour method with atomic absorption spectrometry.
W Calibration curve from standards dissolved in mixed acid solution
P Calibration curve from standards dissolved in pooled blood prepared by mixing 20 EDTA-blood samples
1–10 Calibration curves from standards dissolved in 10 individual EDTA-blood specimens

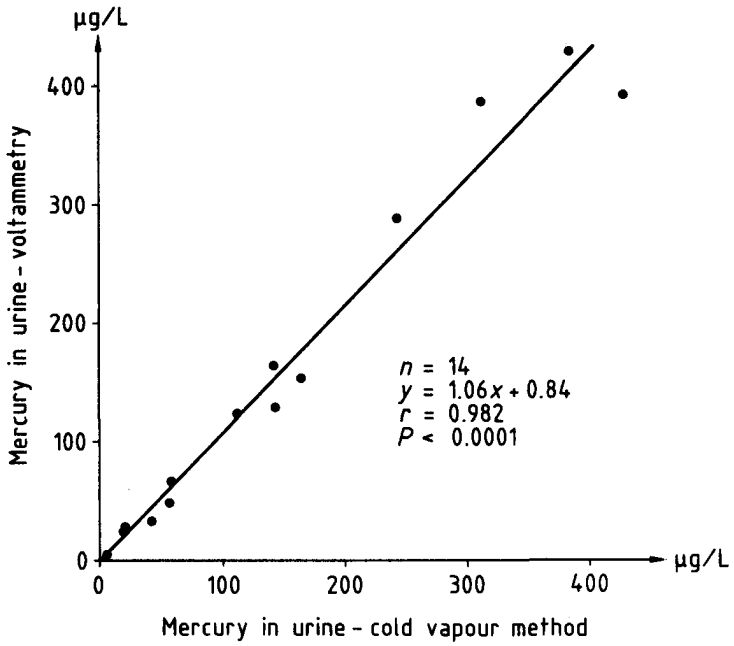

Fig. 3. Correlation curve for the parallel analysis of urine samples from persons occupationally exposed to mercury using the cold vapour method described here and an independent voltammetric method.

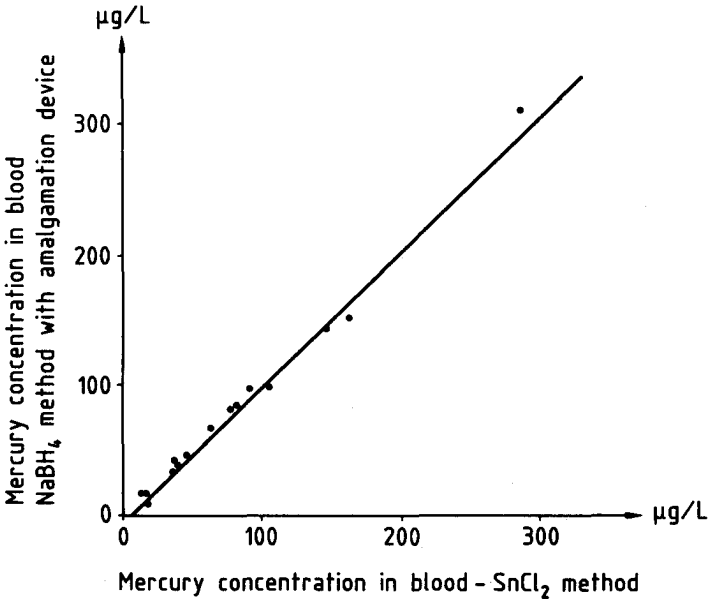

Fig. 4. Correlation curve for the parallel analysis of blood samples from persons occupationally exposed to mercury using the cold vapour method described here and a similar procedure in which the decomposition was carried out with a sulfuric acid-permanganate solution and with a hydride system of a type which is not commercially available [12].