UMWELTPROBENBANK DES BUNDES

Guidelines for Chemical Analysis

Determination of Mercury in Environmental Samples by Direct Solid Analysis

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Contents

Guidelines for sampling, transport, storage and chemical characterisation of environmental and human samples
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1 German Environmental Specimen Bank

The German Environmental Specimen Bank (ESB) is an instrument for the monitoring of the environment. It is in the responsibility of the Federal Ministry for the Environment, Nature Protection and Reactor Safety (BMU) and technically and administratively coordinated by the Federal Environment Agency (Umweltbundesamt). The ESB collects ecologically representative environmental specimens as well as human samples, stores them and examines the archived material for environmental relevant substances.

The long-term storage is performed under conditions that exclude a change of state or a loss of chemical characteristics as far as possible during a period of several decades. By this means the archive provides specimens for a retrospective monitoring of such substances, whose hazard potential for the environment or human health are not yet known.

Comprehensive information on the German ESB is available at www.umweltprobenbank.de (English language pages available).

2 General information

This guideline describes a method for determining the mercury content in environmental samples by means of direct solid analysis. Previous digestion is not necessary, which means that preliminary sample preparation procedures with their risk of potential contamination of the sample, are kept to a minimum. For the test itself, a special device is required, the direct mercury analyzer (DMA) manufactured by MLS, Leutkirch.

This method replaces the cold-vapour atomic-absorption spectrometry method (CV-AAS) described in the procedural guidelines of the German Environmental Specimen Bank (ESB) (UMWELTBUNDESAMT 1996).

3 Area of application

This guideline is used for the routine testing of the following types of ESB samples: bladder wrack, mussels, eelpout (muscle tissue), herring gull egg, zebra mussels, bream (muscle tissue), spruce shoots, pine shoots, poplar leaves, beech leaves, earthworm, roe-deer liver, feral pigeon eggs.

In principle, the method described in this guideline can also be used for other types of biological sample. If samples are used for which no empirical data are available, a suitable validation of the method for the matrix in question should be carried out (see section 11).

The lower range of application for the process described is approx. 2-3 ng/g for solid samples and approx. 2-3 ng/mL for liquid samples.

4 Description of the method

The solid mercury analyser permits interference-free analysis of solid and liquid samples for mercury content. Automatic sample combustion is carried out at approx. 1000°C in a current of oxygen. Following combustion of the sample and catalytic conversion of the combustion gases, elemental mercury is selectively concentrated by amalgam formation and then measured by means of atomic-absorption spectrometry (AAS).

5 Apparatus

5.1 Solid-matter analyser

DMA-80 Direct Mercury Analyser with integrated autosampler, control system lab-TERMINAL 1024 and laboratory balance Precisa XT220 A (complete system from MLS, Leutkirch).

5.2 Accessories

Catalyst (DMA 8333);

Amalgamator (DMA 8134);

Sample crucible of metal (DMA 8142).

5.3 Oxygen supply

For the operation of the apparatus oxygen gas is required (e.g. pressurised oxygen from a cylinder).

Since mercury can also be introduced into the system by the oxygen flow, the gas used should be of 'analysis quality' at least (O_2 > 99.95 %).

Safety note: The safety measures to be observed when working with compressed gases must always be observed.

5.4 Vessels

Vessels of glass or plastic (FEP, PFA) may be used.

All vessels used for preparing and storing standard solutions or coming into contact with standard solutions, must be free of mercury. The vessels should be rinsed with diluted nitric acid (10%; quality supra or equivalent). After cleaning with acid, the vessels should be rinsed with high-purity water and then dried.

6 Reagents

6.1 Mercury stock solution

As stock solution commercially available solutions with e.g. 1000 mg Hg per litre (as single-element solution) should be used. These solutions have a shelf life of several years. The shelf life stated by the manufacturer should always be observed. Only certified standard solutions should be used.

6.2 Mercury calibration solutions

Suitable aqueous calibration solutions (normally in the range of 5 to 1000 µg/L Hg) should be prepared freshly using the mercury stock solution.

6.3 Carrier material

Standard quality wheat flour is generally used as carrier material for liquid solutions (amount per sample approx. 50 mg). The mercury blank value of the product used should be determined before use (normally less than 0.0010 ng Hg absolute).

6.4 Solid-matter reference material

As an alternative to the standard calibration with solutions generally carried out, a solid material can also be used for the calibration process. Certified reference materials (CRM) are suitable for this purpose, e.g. soil CRMs (e.g. 'light sandy soil BCR 142R') or dogfish liver ('DOLT-3').

7 Preparations before measurement

7.1 General notes

Before switching on the main unit, the oxygen supply has to be turned on (input pressure 500 kPa). When the main switch at the front is pressed, the control units 'lab-TERMINAL' and the DMA-80 software are started automatically. The automatic sample feeder moves into the starting position and all heating systems are heated up to starting temperature. After 15-20 minutes, the unit is ready for operation. The accompanying laboratory balance has to be switched on separately.

7.2 Check of blank values

To clean the system and check the catalyst and amalgam enrichment, the system blank values must first be verified. This is done by measuring the blank value without the sample crucible.

Set the program to '100°C - 0 s - 850°C - 180 s - 60 s' (drying temperature - drying time - incineration temperature - incineration time - flushing time) and then press the start button. When the measuring process is concluded, the result is indicated by the program.

The result should be < 0.0010 ng Hg absolute. If this value is not achieved, the measurement of the blank value should be repeated until the result is less than 0.0010 ng Hg absolute. Excessively high blank value readings may be caused by an exhausted catalyst or amalgamator.

7.3 Weighing samples

The samples for testing are weighed into special crucibles. The crucibles have a volume of approx. 700 µL corresponding to approx. 500 mg of solid matter (or less depending on the nature of the sample). To optimise the handling of the crucible, 500 µL volume should not be exceeded.

To obtain a high degree of accuracy, it is also advisable to weigh liquid samples into the crucible. In this way, evaluation is possible directly using the instrument software.

Liquid samples can also be applied to a carrier material with a low blank value (e.g. flour).

7.4 Loading the sample feeder

The sample crucibles are loaded into the automatic sample feeder on a turntable with 40 different positions. The turntable can be removed from the analyser for loading.

The crucibles (sample boats) are transferred from the balance to the turntable using tweezers. The crucibles have upwardly curving edges to make them easier to grip with the tweezers. The crucibles are positioned with this edge towards the centre of the turntable.

After placing the samples in the crucible, close the transparent cover of the instrument to prevent contamination with dust or other influences.

7.5 Cleaning the sample crucibles

After the test, the ash is removed manually from the crucibles. To clean the crucibles in the DMA-80, the sample changer is loaded with crucibles as for the test, and the empty crucibles cleaned using a similar program.

The program is set to '100°C - 0 s - 850°C -180 s - 60 s' ('drying temperature - drying time - incineration temperature - incineration time - rinsing time') and afterwards the start button is pressed.

During the program, the crucibles are fed into the system one after another and burned out. When burned-out crucibles are stored in a dust-free location, no further burning out is necessary.

Safety note: On conclusion of the cleaning program, the last crucibles processed are still hot. Before sample material is weighed into them they must be allowed to cool down to room temperature.

7.6 Measurement after installing a new catalyst

After installing a new catalyst several blank value tests have to be carried out first. At the start, dust and moisture in the catalyst may produce high blank-value readings.

In order to speed up the cleaning process, it is possible to test samples with a high organic content or slightly acidified aqueous samples. In this way, the blank value readings are reduced more quickly. The instrument is ready for use when the absolute blank value is less than 0.0010 ng Hg.

8 Measurement procedure

8.1 General notes

When testing ESB samples, the ratio of samples being tested to quality-assurance samples is always 2:1. A list of the reference materials used for elemental analysis of ESB samples is given in table 1.

8.2 Calibration

To carry out quantitative tests, the system first has to be calibrated by means of suitable standard samples (solid or liquid). The calibration then remains stable for a period of several months.

The validity of the calibration must be documented for each test (e.g. by testing certified reference materials). Before starting a new series of analyses, the instrument should be recalibrated if discrepancies appear during the measurement of quality assurance, if maintenance work has been carried out, the location of the instrument has been changed or if more than three months have elapsed since the last calibration.

Under normal circumstances the calibration function is linear. The coefficient of correlation r should be greater than 0.995. If r is less than 0.995, and the calibration is to be used in spite of this, the reason must be stated (e.g. calibration in the lowest application range of the method with consequently higher measurement uncertainty).

For calibration purposes, aqueous mercury standards of varying concentrations are used which are pipetted onto an organic carrier material (e.g. 50 mg of flour). As a rule, the following concentrations are used (freshly prepared in each case): 1000 µg/L, 500 µg/L, 250 µg/L, 200 µg/L, 100 µg/L, 50 µg/L, 25 µg/L, 10 µg/L, 5 µg/L. Normally 200 µL are used (in addition to 100 µL for the lowest concentrations). Alternatively, the calibration operation can also be carried out with suitably certified reference materials (solids). The differing mercury content for the individual calibration points is determined by means of different weighted quantities.

Table 1: Selection of available reference materials

Designation	Code	Certified by	Mercury content
Beech leaves	CRM 100	CRM	260 ± 10 ng/g (approx. value)
Spruce needles	CRM 101	BCR	70 ± 2 ng/g (approx. value)
Cod muscle tissue	CRM 422	BCR	559 ± 16 ng/g
Poplar leaves	NCS DC 73350	Institute of Geophysical and Geochemical Exploration (Langfang, China)	26 ± 3 ng/g
Mussel tissue	NIST 2976	NIST	61 ± 3,6 ng/g
Pig kidney	CRM 186	BCR	1970 ± 40 ng/g
Bovine liver	NIST 1577b	NIST	3 ng/g (approx. value)
Dogfish liver	DOLT-3	National Research Council Canada	3370 ± 140 ng/g
Pine needles	NIST 1575a	NIST	39.9 ± 0.7 ng/g
Sea lettuce (algae)	CRM 279	BCR	51.5 ± 2.9 ng/g
Dogfish muscle tissue	DORM-2	National Research Council Canada	4640 ± 260 ng/g

Standard program for calibration with solids (certified reference materials):

Setting: '100°C - 0 s - 850°C - 180 s - 60 s - 12 s - 30 s' ('drying temperature - drying time - incineration temperature - incineration time - rinsing time - amalgam heating – measurement time').

Standard program for liquid standards (with or without organic carrier):

Setting: '300°C - 300 s - 850°C - 240 s - 60 s - 12 s - 30 s' ('drying temperature - drying time - incineration temperature - incineration time - rinsing time - amalgam heating - measurement time').

8.3 Calibration check

When the control program is started, the previous calibration is automatically opened. If a different calibration is required, this must first be activated with the DMA-80 software under CALIBRATION.

To verify the calibration, a reference sample of known Hg concentration is first tested. The amount of sample material should be selected to obtain an absolute mercury quantity of approx. 10-20 ng Hg. For example, a standard solution with 0,1 mg/kg Hg (weighted quantity of 0,15 g = 150 µL) would be suitable.

The sample should be activated in the software as 'reference'. This ensures that the result of the test is compared automatically with the calibration and the deviation indicated. The mercury concentration of the tested reference material should also be entered. It should be ensured that the concentration is set correctly as mg/kg or µg/kg. Following measurement, the difference between the target and the actual values is indicated as sensitivity factor in the column 'Calibration Factor'.

The criterion of quality is a correspondence of 100 ± 10 % between the certified value and the value actually determined.

8.4 Limit of quantification

Following each re-calibration, it is necessary to re-calculate the limit of quantification of the process. The calculation is carried out using the blank value method (estimation of the limit of detection according to the standard DIN 32645, 1994; the limit of quantification is then taken to be three times the limit of detection).

8.5 Measurement of blank values

For each test, blank values are also measured (= empty test crucible; see 7.2). In order to compare the sample contents directly, a mass should be entered for the (theoretical) weight of the blank value which is equivalent to the weight of the samples being measured. Otherwise, the absolute Hg contents should be compared.

Corrections for blank values are not carried out. If the blank value is too high (> 5 - 10 % of the mercury content of the lowest sample), the system should be checked over (see also 13.1).

8.6 Mercury determination

The sample (approx. 10-200 mg or 50-500 µL) is weighted into the crucible on the integrated laboratory balance. The mass of the sample is then transmitted automatically to the test unit by pressing a button. The test process is started after weighing all the samples. The drying, incineration and oxidation times should be adapted to suit the sample material. This also applies for the drying and incineration temperatures as well as the duration of rinsing after incineration. The start button is then pressed to start the test.

<u>Standard program for freeze-dried biotic environmental samples (solids):</u>

Settings: '100°C - 0 s - 850°C - 180 s - 60 s - 12 s - 30 s' (drying temperature - drying time - incineration temperature - incineration time - rinsing time - amalgam heating – measurement time).

With dried or freeze-dried solid substances, no drying program is required because there is no risk of splashing caused by delay in boiling. The minimum incineration time is 120 sec. This time is necessary to heat the sample crucible up to the temperature required to release all the mercury. For samples with high organic content, a longer incineration time has to be selected. The general rule is that half the sample weight is equivalent to the incineration time in seconds. Samples with high organic contents often react by spontaneous ignition during incineration in the oxygen stream. It is therefore advisable to distribute these samples well over the bottom of the crucible (e.g. press down well to prevent excessive spontaneous reaction; see 13.1).

<u>Standard program for non-dried biological samples:</u>

Settings: '300°C - 60 s - 850°C - 180 s - 60 s - 12 s - 30 s' (drying temperature - drying time - incineration temperature - incineration time - rinsing time - amalgam heating – measurement time).

<u>Standard program for liquid samples:</u>

Settings: '300°C - 300 s - 850°C - 240 s - 60 s - 12 s - 30 s' (drying temperature - drying time - incineration temperature - incineration time - rinsing time - amalgam heating - measurement time).

For liquid samples, a drying operation is essential before the actual incineration operation. This is necessary to prevent the sample from splashing due to rapid rise in temperature and delay in boiling, and causing contamination in the system (quartz tube). For samples with a high water content, the temperature for drying should be set to 300°C. This temperature allows fast drying without causing the sample to splash. The length of the drying program depends on the amount of liquid weighted in. As a rule of thumb, the quantity of liquid in mg can be taken as equivalent to the length of the drying operation in seconds. If the sample contains only about 50% moisture, the time for drying is reduced accordingly. If a temperature of less than 300°C is set for water-based samples, the drying operation has to be prolonged. Even for liquid samples, a subsequent incineration program is essential to fully release all the mercury in the sample.

With liquid samples, suitable blank solutions must be tested (e.g. water, with acids, stabiliser etc.).

9 Evaluation

The data measured are evaluated by the software of the analyser unit. The automatic evaluation is checked for plausibility. For each calibration, a linear regression is carried out to calculate the slope, ordinate intercepts and coefficient of correlation (r) of the linear calibration lines. The concentrations of all the solutions tested (blind values, reference materials, samples) are calculated on the basis of these straight calibration lines.

10 Documentation

The following measurement parameters should be noted as raw data (or entered in a computer file):

- unique sample designation (e.g. ESB code),
- parameters of method (e.g. temperatures and analysis times set),
- calibration used,
- analysis results for mercury for samples and reference materials,
- any observations or comments.

Important note: All deviations from these guidelines must be documented in the raw data of the respective measurement.

11 Validation

Before using the DMA instrument for routine testing in the Environmental Specimen Bank program, extensive validation procedures were carried out. This involved testing a number of certified reference materials and ESB reference materials and then comparing the results with the target values. In this way it was possible to establish the suitability of the system for the analysis of ESB samples.

For all tests, suitable certified reference materials and (for analyses within the ESB program) suitable ESB reference materials are also tested in order to establish the correctness of the test results and to determine the uncertainty of the analytical data if necessary. The criterion of quality is a correspondence of 100 $\pm$ 15 % (or 100 $\pm$ 20% for concentrations close to the limit of quantification) between the certified value and the value actually determined.

For method validation for samples for which no validation data are available, the following process parameters should also be determined:

Selectivity / specificity: these are met if the concentration measured for the chemical blank value is less than the lowest validated concentration.

Reproducibility: the reproducibility is calculated from the correspondence data of the reference materials via the relative standard deviation (S_{rel}). This condition is fulfilled if the following applies: $S_{rel} < 10$ % ($n \geq 5$).

Limit of detection / limit of quantification: The limit of detection is calculated from blank value analyses (determined according to the standard DIN 32645: blank test method, quick estimate). The limit of quantification is produced by multiplying the limit of detection by a factor of 3.

12 Control charts

Control charts (as target-value charts) are maintained to document the long-term reproducibility of the process. These are prepared for the various reference materials and for blank values.

13 Interferences

13.1 High blank values

Excessively high blank values may be caused by contamination in the test system or an exhausted catalyst. If necessary, the system should be cleaned or the catalyst replaced.

13.2 Spontaneous reactions

Large quantities of gas are produced during a spontaneous reaction which may not be collected in the combustion chamber. The resulting pyrolysis products are then forced too quickly through the catalyst by a pressure wave. This means that the dwell time in the catalyst is too short for complete conversion to take place. These pyrolysis

products may cause damage to the subsequent gold carrier and the optical cell. The incompletely converted pyrolysis products may be deposited on the gold carrier and affect the actual mercury signal by additional non-specific absorption.

14 Statement of results

The results are related to the amount of solid matter used (to the fresh mass or, with freeze-dried samples, to the dry mass).

All results for mercury (Hg) should be stated to three significant places.

EXAMPLE: 123 ng/g; 34.5 ng/g; 0.678 µg/g.

Measurement results are subject to a degree of uncertainty. In the working range of a process, the measurement uncertainty increases as the concentration in the sample decreases. The degree of uncertainty of a measured value can be determined in a number of ways which are described in 'ISO Guide to the Expression of Uncertainty in Measurement (GUM)' (ISO, 1995) and guideline 'Quantifying Uncertainty in Analytical Measurement' (EURACHEM/CITAC, 2000). A practical means of determining uncertainty is the so-called Nordtest process (MAGNUSSON ET AL., 2003; calculation of uncertainty from duplicate measurements of certified reference materials and results of interlaboratory comparisons).

NOTE: For the analysis of Environment Specimen Bank samples, generally six sub-samples from one homogenate are used. The standard deviation of the average value is regarded as the measurement uncertainty of the result. The correctness of the results is verified with the help of certified reference materials. Representative data are given in the appendix

15 Analysis report

The following data should be documented in the analysis report:

- reference to this guideline,
- sample identity,
- concentration of mercury with reference to the sample dry weight,
- statement of measurement uncertainty if applicable,
- data on preliminary treatment of sample and digestion,
- any deviations from this guideline.

16 Representative analysis results

Representative results of analyses are given in the appendix:

a) Results of the analysis of certified reference materials,

b) Results of the analysis of reference materials from the Environmental Specimen Bank,

c) Results of the analysis of representative samples from the Environmental Specimen Bank

17 Bibliography

DIN 32645 (1994): Nachweis-, Erfassungs- und Bestimmungsgrenze - Ermittlung unter Wiederholbedingungen (Begriffe, Verfahren, Auswertung), Beuth Verlag, Berlin.

EURACHEM/CITAC (2000): Quantifying Uncertainty in Analytical Measurement, Ellison, S. L. R., Rosslein, M., Williams, A. (Editors), 2nd Edition.

ISO (1995): Guide to the expression of uncertainty in measurement (GUM), ISO, Genf.

MAGNUSSON, B.; NÄYKKI, T.; HOVIND, H.; KRYSELL, M. (2004): Handbook for calculation of measurement uncertainty in environmental laboratories, Nordtest report TR 537, edition 2, Espoo, Finnland. http://www.nordicinnovation.net/nordtestfiler/tec537.pdf

UMWELTBUNDESAMT (1996): "Analytische Vorschriften für Elemente und Spezies in Umweltproben, Matrixgruppe 1", Fassung vom Mai 1993, in: Umweltprobenbank des Bundes (UPB) - Verfahrensrichtlinien für Probenahme, Transport, Lagerung und chemische Charakterisierung von Umwelt- und Human-Organproben, Herausgeber: Umweltbundesamt, Berlin. Erich Schmidt Verlag, Berlin.

Appendix: Representative analysis results

a) Results of the analysis of certified reference materials

Table 2: Representative results for reference materials

Designation	Code	Correspondence ± standard deviation	Number (n)
Beech leaves	CRM 100	92.3 ± 0.6 %	8
Spruce needles	CRM 101	93.4 ± 2.4 %	12
Cod muscle tissue	CRM 422	94.5 ± 2.2 %	22
Poplar leaves	GBE 07604	120 ± 2 %	6
Mussel tissue	NIST 2976	102 ± 5 %	40
Pig kidney	CRM 186	109 ± 1 %	14
Bovine liver	NIST 1577b	95 ± 20 %	36
Dogfish muscle tissue	DORM-2	93.0 ± 0.6 %	18
Pine needles	NIST 1575a	107 ± 3 %	6
Sea lettuce (algae)	CRM 279	97.5 + 5.0 %	10

b) Results of the analysis of ESB reference materials
(IS UPB – Information system of Environmental Specimen Bank)

Table 3: Representative results of ESB reference materials

ESB reference material	ESB code	Content according to IS UPB	Recovery ± standard deviation (number)
Bream muscle, Güdingen 1992	3111/0/0892/02101/0	290 ± 6 ng/g	103 ± 3 % (n = 13)
Eelpout muscle, Meldorfer Bucht 1997	4210/0/0597/07202/0	347 ± 9 ng/g	103 ± 2 % (n = 9)
Spruce shoots, Warndt 1985	0110/0/0385/02201/0	50.1 ± 1.0 ng/g	87.8 ± 1.7 % (n = 6)
Bladder wrack, Eckwarderhörne 1989	4000/0/0089/07302/0	107 ± 5 ng/g	95.4 ± 6.8 % (n = 15)
Feral pigeon egg content, Saartal 1993	1211/0/0093/02100/0	2.05 ± 0.65 ng/g#	98 ± 35 % (n = 16)#
Herring gull egg content, Heuwiese 1993	4311/0/0693/06201/0	950 ± 39 ng/g	95.2 ± 0.8 % (n = 6)
Blue mussel, Königshafen 1992	4110/0/0092/07101/0	212 ± 9 ng/g	94.7 ± 5.4 % (n = 37)
Zebra mussels, Cumlosen 1998	3010/0/1198/10305/0	191 ± 8 ng/g	94.0 ± 5.4 % (n = 37)
Roe-deer liver, yearling, Dübener Heide 1998	1021/0/0098/11200/0	11.3 ± 0.3 ng/g	109 ± 12 % (n = 17)

Values show higher dispersion since in the range of the limit of quantification.

c) Examples of results from the analysis of representative ESB samples

Table 4: Representative results from ESB samples

Designation	ESB code	Content ± standard deviation	Number
Bream muscle, Saale/Wettin 2006	3111/0/0806/11001/0	1698 ± 15 ng/g	6
Bream muscle, Elbe/Blankenese 2005	3111/0/0806/10405/0	489 ± 2 ng/g	6
Eelpout muscle, Meldorfer Bucht 2006	4210/0/0506/07202/0	520 ± 3 ng/g	5
Beech leaves, Bayerischer Wald 2006	0410/0/0806/05102/0	33.5 ± 0.3 ng/g	5
Beech leaves, Scheyern 2006	0410/0/0806/16102/0	40.5 ± 0.9 ng/g	6
Poplar leaves, Leipzig 2006	0310/0/0806/11111/0	24.3 ± 0.5 ng/g	6
Spruce shoots, Warndt 2006	0110/0/0406/02201/0	22.6 ± 0.5 ng/g	6
Pine shoots, Dübener Heide 2006	0210/0/0306/11200/0	21.7 ± 0.4 ng/g	6
Bladder wrack, Varnkevitz 2006	4000/0/0006/06901/0	11.6 ± 0.9 ng/g	6
Earthworm, Saartal 2006	2211/0/1006/02100/0	277 ± 2 ng/g	5
Earthworm, Halle 2006	2211/0/1006/11107/0	2330 ± 20 ng/g	6
Feral pigeon egg content, Leipzig 2006	1211/0/0006/11111/0	< 1.4 ng/g#	6
Herring-gull egg content, Trischen 2006	4311/0/0506/07201/0	1500 ± 10 ng/g	6
Blue mussel, Darßer Ort 2006	4110/0/0006/06103/0	77.0 ± 1.4 ng/g	6
Zebra mussel, Saar/Güdingen 2005	3010/0/1105/02101/0	47.0 ± 6.6 ng/g	6
Roe-deer liver, yearling. Berchtesgaden 2006	1021/0/0506/01000/0	7.21 ± 0.1 ng/g	6

< limit of quantification