BRITISH STANDARD

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Foodstuffs — Determination of trace elements — Determination of mercury by cold-vapour atomic absorption spectrometry (CVAAS) after pressure digestion

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ICS 67.050

National foreword

This British Standard is the official English language version of EN 13806:2002

The UK participation in its preparation was entrusted to Technical Committee AW/-/3, Horizontal analysis, which has the responsibility to:

— aid enquirers to understand the text;

— present to the responsible international/European committee any enquiries on the interpretation, or proposals for change, and keep the UK interests informed;

— monitor related international and European developments and promulgate them in the UK.

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English version

Foodstuffs - Determination of trace elements - Determination of mercury by cold-vapour atomic absorption spectrometry (CVAAS) after pressure digestion

Produits alimentaires - Dosage des éléments-traces - Dosage du mercure par spectrométrie d'absorption atomique par génération de vapeurs froides après digestion sous pression

Lebensmittel - Bestimmung von Elementspuren - Bestimmung von Quecksilber mit Atomabsorptionsspektrometrie (AAS)-Kaltdampftechnik nach Druckaufschluss

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Foreword

This European Standard has been prepared by Technical Committee CEN/TC 275 "Food analysis - Horizontal methods", the secretariat of which is held by DIN.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by February 2003, and conflicting national standards shall be withdrawn at the latest by February 2003.

Annex A is informative.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Czech Republic, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Malta, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and the United Kingdom.

1 Scope

This European Standard specifies a method for the determination of mercury in foodstuffs by cold-vapour atomic absorption spectrometry (CVAAS) after pressure digestion.

Specific foodstuffs for which European Standards exist are excluded from the scope of this horizontal European Standard. It is the task of the analyst to review if vertical standards exist.

2 Normative references

This European Standard incorporates by dated or undated reference, provisions from other publications. These normative references are cited at the appropriate places in the text, and the publications are listed hereafter. For dated references, subsequent amendments to or revisions of any of these publications apply to this European Standard only when incorporated in it by amendment or revision. For undated references the latest edition of the publication referred to applies (including amendments).

EN 13804, *Foodstuffs — Determination of trace elements — Performance criteria, general considerations and sample preparation.*

EN 13805, *Foodstuffs — Determination of trace elements — Pressure digestion.*

3 Principle

Determination of mercury in the test solution by cold-vapour atomic absorption spectrometry (CVAAS) after pressure digestion according to EN 13805.

The test solution is transferred to the reaction vessel of the mercury analysis unit, and the mercury is reduced with divalent tin or sodium borohydride and flushed into the cuvette of the AAS instrument using a carrier gas stream. The absorption at 253,7 nm (mercury line) is used as a measure of the mercury concentration in the cuvette. If the amounts of mercury in the test solution are very small, it is advisable to enrich the mercury expelled on a gold/platinum gauze (amalgam technique) prior to determination in the cuvette.

WARNING — The use of this standard can involve hazardous materials, operations and equipment. This standard does not purport to address all the safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

4 Reagents

4.1 General

The concentration of the trace elements in the reagents and water used shall be low enough not to affect the results of the determination.

4.2 Hydrochloric acid, not less than 30 % (mass fraction), of approximately ρ (HCl) = 1,15 g/ml.

4.3 Nitric acid, not less than 65 % (mass fraction), of approximately ρ (HNO_3) = 1,4 g/ml.

4.4 Diluted nitric acid.

Mix nitric acid (4.3) and water in a proportion of 1 + 9 parts by volume as a minimum.

4.5 Reducing agent

4.5.1 General

Tin(II) chloride or sodium borohydride may be used as the reducing agent, but it is not advisable to use the two reagents alternately. Observe the instructions of the manufacturers of the apparatus.

4.5.2 Tin(II) chloride solution with a concentration of 100 g/l.

Dissolve 50 g of tin(II) chloride, $SnCl_2 \cdot 2H_2O$ in approximately 100 ml of hydrochloric acid (4.2) in a 500 ml volumetric flask and dilute to the mark with water. Prepare a fresh solution.

4.5.3 Sodium borohydride solution with a concentration of 30 g/l.

Dissolve 3 g of sodium borohydride together with 1 g of sodium hydroxide pellets in water and dilute to 100 ml. Prepare a fresh solution daily and, when necessary, filter it before use.

The concentration by mass of the reducing agent solutions may be varied to suit the system and the relevant information provided by the manufacturer of the apparatus shall be observed.

WARNING — It is essential to observe the safety instructions for working with sodium borohydride. Sodium borohydride forms hydrogen with acids and this can result in an explosive air/hydrogen mixture. A permanent extraction system shall be provided at the point where measurements are carried out.

4.6 Potassium permanganate solution with a concentration of 40 g/l.

Dissolve 0,4 g of potassium permanganate solution in water and dilute to 10 ml. Prepare a fresh solution daily.

4.7 Potassium dichromate solution with a concentration of 5 g/l.

Dissolve 5 g of potassium dichromate in 500 ml of nitric acid (4.3) and dilute to 1 l with water.

4.8 Mercury stock solution with a mercury concentration of 1 000 mg/l.

Dissolve 1,080 g of mercury(II) oxide in 10 ml of potassium dichromate solution (4.7) and dilute to 1 l with water. The stock solution is also commercially available. It is advisable to use certified stock solutions.

4.9 Mercury calibration solutions.

Dilute the stock solutions to the concentrations needed for calibration, with 10 ml of potassium dichromate solution (4.7) per litre in each solution. Choose the concentrations so as not to exceed the linear range of the calibration function. It is recommended to use a minimum of 3 calibration solutions with different concentrations.

The concentration of acid in the calibration solutions shall be equal to that in the test solution. Mercury solutions are not stable for a long time, even at fairly high concentrations and shall therefore be made up daily.

4.10 Zero member compensation solution.

The zero member compensation solution shall contain water, 10 ml/l of potassium dichromate (4.7) and an amount of nitric acid (4.3) which is equal to the acid concentration in the test solution.

5 Apparatus and equipment

5.1 General

To minimise the contamination, all apparatus which come into direct contact with the sample and the solutions should be carefully pre-treated according to EN 13804.

5.2 Atomic absorption spectrometer, optionally with background correction, and with the accessories used for the cold-vapour and optionally amalgam techniques and with a measurement and recording system. As an alternative to the manual method, a flow injection system may be used.

5.3 Element-specific lamp for mercury.

6 Procedure

6.1 Cold-vapour atomic absorption spectrometry (CVAAS)

6.1.1 Spectrometer settings

To devise a test schedule, first adjust the apparatus as specified in the operating manual of the manufacturer, then optimise the settings, paying particular attention to gas flow times and the amounts of tin(II) chloride or sodium borohydride introduced.

6.1.2 Example of CVAAS determination

Adjust the zero of the instrument using the zero member compensation solution described in 4.10 when necessary.

Use the appropriate calibration solutions to obtain the calibration function. If possible, calibrate the measurement reading directly in concentration using the calibration solutions. Check the linear range of the calibration function regularly.

After the calibration function has been established, the test solution may be used for the determination, either without further treatment or, if the concentration is outside the linear range, after suitable dilution. When carrying out prolonged series of measurements, it is advisable to check the zero and the calibration at intervals.

In order to avoid absorption of mercury on the walls of the measuring vessels and to enhance stability of calibration and sample solutions during long runs, it may be advisable to add a few drops of potassium permanganate solution (4.6) to the sample solution in the measuring vessel until the red coloration is permanent. Allow the solution to stand for ten minutes before connecting it to the reaction unit for the determination.

Although a correction is seldom necessary in the case of the cold-vapour technique, whether the background correction is necessary or not shall be checked for every type of sample. As an analytical quality control, reference samples having reliably known mercury contents shall be analysed in parallel with all the series of samples analysed, the reference samples being subjected to all the steps in the method starting from digestion. Blank solutions prepared by subjecting them to all the steps in the method shall also be determined.

7 Calculation

Calculate the mass fraction of mercury, *w*, in milligrams per kilogram of sample, using the following equation:

$$w = \frac{a \cdot V}{V_1 \cdot m \cdot 1000} \quad (1)$$

where

a is the absolute mass of mercury, in nanogram, found in the test solution used;

V is the volume of the digestion solution after being made up, in millilitre;

V_1 is the volume of test solution used, in millilitre;

m is the initial sample mass, in gram.

If necessary, subtract the result of the blank solution from the content, *a*, of mercury.

8 Limit of quantification

The limit of quantification according to EN 13804 of the measuring solution depends on the following parameters:

— principle of release of mercury (batch- or flow system);

— enrichment (amalgam) or no enrichment;

— in the case of flow systems:

  — continuous/discontinuous release of Hg;

  — amount of digestion solution used;

  — construction of the equipment;

  — influences of the matrix.

The limit of quantification is regularly in the range between 0,05 µg/l and 5 µg/l, regarded to the measuring solution.

With a test portion of 0,5 g and a final digestion volume of 20 ml the limit of quantification for the foodstuff will be calculated between 0,002 mg/kg and 0,2 mg/kg.

9 Precision

9.1 General

Details of an interlaboratory test on the precision of the method are summarised in annex A. The values derived from this interlaboratory test may not be applicable to concentration ranges and matrices other than those given.

9.2 Repeatability

The absolute difference between two independent single test results, obtained with the same method on identical test material in the same laboratory by the same operator using the same equipment within a short interval of time, will in not more than 5 % of the cases exceed the values of *r* given in Table 1.

Table 1 – Repeatability

Sample	$\bar{x}$ mg/kg	***r*** mg/kg
Bovine Liver, lyophilised	0,042	0,007
Salt-Water Fish, homogenised	0,36	0,04
Lobster, homogenised	0,020	0,005
Trout, lyophilised	0,12	0,04
Apple Powder, lyophilised	0,015	0,003
Wheat Flour	0,017	0,003

9.3 Reproducibility

The absolute difference between two single test results, obtained with the same method on identical test material in different laboratories by different operators using different equipment, will in not more than 5 % of the cases exceed the values of *R* given in Table 2.

Table 2 – Reproducibility

Sample	$\bar{x}$ mg/kg	***R*** mg/kg
Bovine Liver, lyophilised	0,042	0,020
Salt-Water Fish, homogenised	0,36	0,13
Lobster, homogenised	0,020	0,011
Trout, lyophilised	0,12	0,08
Apple Powder, lyophilised	0,015	0,022
Wheat Flour	0,017	0,023

10 Test report

The test report shall specify at least the following:

a) all information necessary for the complete identification of the sample;

b) the test method used, with reference to this European Standard;

c) the test results obtained and the units in which they are specified;

d) date of sampling and sampling procedure (if known);

e) date when the analysis was finished;

f) whether the requirement of the repeatability limit has been fulfilled;

g) all operating details not specified in this European Standard, or regarded as optional, together with details of any incidents occurred when performing the method which may have influenced the test result(s).

Annex A
(informative)

Results of the interlaboratory tests

The precision of the method was established by the Working Group "Balanced diets - Trace element analysis" of the Commission of the German Federal Health Board for implementing Article 35 of the German Federal Foods Act and by the Working Group "Inorganic Constituents" of the study group of the Foodstuffs Chemistry Society of the German Chemists Society and has been verified in an interlaboratory test evaluated in accordance with ISO 5725 [3]. The results are given in Table A.1.

Table A.1 – Precision data

Parameter	Sample					
	Bovine Liver lyophilised	**Salt-Water Fish homogenised**	**Lobster homogenised**	**Trout lyophilised**	**Apple Powder lyophilised**	**Wheat Flour**
Year of test	1993	1993	1993	1994	1994	1994
Number of laboratories	10	12	11	12	8	8
Number of laboratories after elimination of outliers	9	12	10	12	8	8
Number of outliers	1	0	1	0	0	0
Number of accepted results	45	60	20	24	16	16
Mean value $\bar{x}$ (mg/kg)	0,042	0,36	0,020	0,12	0,015	0,017
Repeatability-standard deviation s_r (mg/kg)	0,002	0,01	0,002	0,02	0,001	0,001
RSD - *r* (%)	5,7	4,1	8,8	12,9	7,2	6,7
Repeatability limit *r* (mg/kg)	0,007	0,04	0,005	0,04	0,003	0,003
Horwitz value *r*	17	13	19	15	20	19
Horrat *r* index	0,34	0,32	0,46	0,89	0,37	0,35
Reproducibility-standard deviation S_R (mg/kg)	0,007	0,04	0,004	0,03	0,008	0,008
RSD - R (%)	16,6	12,3	19,7	23,0	51,0	47
Reproducibility limit *R* (mg/kg)	0,020	0,13	0,011	0,08	0,022	0,023
Horwitz value *R*	26	19	29	22	30	29
Horrat *R* index	0,64	0,65	0,68	1,05	1,69	1,58

The certified values of some of the samples analysed in the interlaboratory tests are given in Table A.2.The certified values of some of the samples analysed in the interlaboratory tests are given in Table A.2 [4].

Table A.2 – Certified values

Sample	Certified value mg/kg	Confidence interval (95 %)	Mean value mg/kg
Bovine Liver, lyophilised	0,044	0,003	0,042
Lobster, homogenised	0,017	0,002	0,020
Trout, lyophilised	0,116	0,018	0,121

Bibliography

[1] Hatch, W. R.; Ott, W. L. Analytical Chemistry, 1968: 40, No. 14, S. 2085 - 2087.

[2] Welz, B., Sperling, M.: Atomabsorptionsspektrometrie, Weinheim, Wiley-VCH-Verlag 1997.

[3] ISO 5725:1986, *Precision of test methods – Determination of repeatability and reproducibility for a standard test method by inter-laboratory tests (now withdrawn),* (was used to obtain the precision data).

[4] NMKL procedure No. 9, 2001. Evaluation of results derived from the analysis of certified reference materials. NMKL c/o National Veterinary Institute, Box 8156 Dep., 0033 Oslo, Norway.

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