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Canned evaporated milk — Determination of tin content — Method using graphite furnace atomic absorption spectrometry

Lait concentré en boîte — Détermination de la teneur en étain — Méthode par spectrométrique d'absorption atomique à four graphite

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Foreword

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The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this International Standard may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

International Standard ISO 14377|IDF 168 was prepared by Technical Committee ISO/TC 34, *Food products*, Subcommittee SC 5, *Milk and milk products*, and the International Dairy Federation (IDF), in collaboration with AOAC International. It is being published jointly by ISO and IDF and separately by AOAC International.

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Foreword

IDF (the International Dairy Federation) is a worldwide federation of the dairy sector with a National Committee in every member country. Every National Committee has the right to be represented on the IDF Standing Committees carrying out the technical work. IDF collaborates with ISO and AOAC International in the development of standard methods of analysis and sampling for milk and milk products.

Draft International Standards adopted by the Action Teams and Standing Committees are circulated to the National Committees for voting. Publication as an International Standard requires approval by at least 50 % of IDF National Committees casting a vote.

International Standard ISO 14377|IDF 168 was prepared by Technical Committee ISO/TC 34*, Food products,* Subcommittee SC 5*, Milk and milk products,* and the International Dairy Federation (IDF), in collaboration with AOAC International. It is being published jointly by ISO and IDF and separately by AOAC International.

All work was carried out by the Joint ISO/IDF/AOAC Action Team, *Elements in milk and milk products*, of the Standing Committee on *Minor components and characterization of physical properties*, under the aegis of its project leader, Dr G. Ellen (NL).

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Canned evaporated milk — Determination of tin content — Method using graphite furnace atomic absorption spectrometry

1 Scope

This International Standard specifies a graphite furnace atomic absorption spectrometric method for the determination of the tin content of (sterilized) canned evaporated milk. It is applicable to samples with tin contents of more than 5 mg/kg.

2 Normative reference

The following normative document contains provisions which, through reference in this text, constitute provisions of this International Standard. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent edition of the normative document indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

ISO 3696, *Water for analytical laboratory use — Specification and test methods*

3 Term and definition

For the purposes of this International Standard, the following term and definition applies.

3.1
tin content of canned evaporated milk
mass fraction of substances determined by the procedure specified in this International Standard

NOTE The tin content is expressed in milligrams per kilogram.

4 Principle

A test portion is diluted 100-fold with water, then further diluted (1:1) with 15 % ascorbic acid solution (matrix modifier). The atomic absorption is measured at a wavelength of 286,3 nm with an electrothermal (graphite furnace, atomization from the wall of the tube) atomic absorption spectrometer. The results are quantified by means of a calibration graph obtained by measuring calibration solutions prepared in 100-fold diluted (evaporated) milk with a very low tin content [bottled (evaporated) milk], further diluted 1:1 with 15 % ascorbic acid solution. As an alternative, platform atomization may be used, with $NH_4H_2PO_4/Mg(NO_3)_2$ as matrix modifier.

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5 Reagents

Use only reagents of recognized analytical grade, containing only a trace amount of tin.

5.1 Water, complying with grade 2 of ISO 3696.

5.2 Hydrochloric acid (HCl), concentrated, ρ_{20}(HCl) = 1,15 g/ml (Merck "Suprapur"[1)] or equivalent).

5.3 Tin standard solutions

5.3.1 Tin stock solution, having a tin (Sn) content of 1 000 mg/l.

Use a commercially available preparation (Baker No. 6943[1)] or equivalent).

5.3.2 Tin standard working solution, having a tin (Sn) content of 100 mg/l.

Pipette 10 ml of the tin stock solution (5.3.1) into a 100 ml volumetric flask (6.3). Add 30 ml of hydrochloric acid (5.2). Dilute to the mark with water (5.1) and mix.

5.3.3 Tin standard working solution in diluted (evaporated) milk

Use bottled evaporated milk that matches as closely as possible the canned milk samples to be analysed as regards fat content and dry matter content. Homogenize the bottled (evaporated) milk well before use.

Pipette 1 ml of bottled evaporated milk into each of five 100 ml volumetric flasks (6.3). Add about 80 ml of water (5.1). Then pipette into the five volumetric flasks 0 µl, 100 µl, 200 µl, 500 µl and 1 000 µl, respectively, of the tin standard working solution (5.3.2). Dilute to the mark with the water and mix by gently swirling.

Prepare fresh daily the tin standard working solutions in diluted evaporated milk.

If bottled evaporated milk is not available, take such an amount of regular milk that the concentration of milk solids in the tin standard working solutions and test solutions is almost the same.

NOTE 1 Assuming that the amount of evaporated milk in each of the five one-mark volumetric flasks is 1,00 g, the amounts of tin in the standard working solutions correspond to a tin content in the original, undiluted product of 0 mg/kg, 10 mg/kg, 20 mg/kg, 50 mg/kg and 100 mg/kg, respectively.

NOTE 2 See also 6.5, if platform atomization is to be used.

5.4 Matrix modifier solution I, having an ascorbic acid ($C_6H_8O_6$) content of 150 g/l.

Dissolve 15 g of ascorbic acid (Merck No. 127 [1)] or equivalent) in water (5.1) in a volumetric flask (6.3). Dilute to the mark with the water and mix.

5.5 Matrix modifier solution II, having an ammonium dihydrogen phosphate ($NH_4H_2PO_4$) content of 0,2 mg and a magnesium nitrate [$Mg(NO_3)_2$] content of 0,01 mg per 10 µl of solution.

NOTE This is used as an alternative in the case of platform atomization.

Dissolve 2,0 g of $NH_4H_2PO_4$ (Aldrich No. 20400-5 [1)] or equivalent) and 0,173 g of $Mg(NO_3)_2{\cdot}6H_2O$ (Merck No. 5855 [1)] or equivalent) in a 100 ml volumetric flask (6.3). Dilute to the mark with water (5.1) and mix.

1) Merck Suprapur, No. 127 and No. 5855, Baker No. 6943 and Aldrich No. 20400-5 are examples of suitable products available commercially. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of these products.

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6 Apparatus

Keep the clean glassware in a 10 % (mass fraction) nitric acid (HNO_3) solution. Before use, rinse the glassware three times with double-distilled water and allow to dry. Store the glassware in a dust-free environment.

Usual laboratory equipment and, in particular, the following.

6.1 Balance, capable of weighing to the nearest 1 mg.

6.2 Water bath, capable of being maintained at between 40 °C and 60 °C.

6.3 One-mark volumetric flasks, of capacity 100 ml.

6.4 Dosing pipettes, with adjustable volumes of 50 µl to 200 µl and 200 µl to 1 000 µl, with plastic pipette tips.

6.5 Atomic absorption spectrometer, equipped with

— an electrothermal atomizer (graphite furnace),

— an autosampler with sample cups (about 2 ml),

— a tin hollow cathode lamp or an electrode-less discharge lamp,

— a background correction system,

— pyrolytic-coated graphite tubes,

— argon,

— a facility to measure peak areas, and

— a recorder or printer.

The use of pyrolytic-coated graphite tubes gives slightly higher signals than untreated tubes. Instead of atomization from the wall of the tube, platform atomization may be employed. In that case, ascorbic acid cannot be used as matrix modifier because of build-up of carbon residues on the platform. Instead, use 10 µl of a solution of $NH_4H_2PO_4$ and $Mg(NO_3)_2$ (5.5) as matrix modifier. If the platform technique is chosen, the test and standard solutions are not diluted 1:1 with 15 % ascorbic acid solution (see 9.3). Therefore, the tin standard working solutions in 5.3.3 have to contain about 0,5 g of evaporated milk per 100 ml, meaning that 0,5 ml of evaporated milk instead of 1 ml has to be pipetted. Moreover, add amounts of 0 µl, 50 µl, 100 µl, 250 µl and 500 µl of the tin standard working solution (5.3.2) to the five 100 ml volumetric flasks (6.3) to prepare the tin standard working solutions in diluted evaporated milk as in 5.3.3.

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7 Sampling

Sampling is not part of the method specified in this International Standard. A recommended sampling method is given in ISO 707.

It is important that the laboratory receive a sample which is truly representative and has not been damaged or changed during transport or storage.

Store the sample in such a way that deterioration and change in its composition are prevented. Avoid contamination by tin.

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8 Preparation of test sample

8.1 Shake the container thoroughly with frequent inversion. Open it and pour the contents into another container (made of glass or plastic and provided with an airtight lid) which has been well cleaned before use. Take care to incorporate all fat or other constituents adhering to the wall of the original container in the sample. Mix thoroughly by stirring with a spoon or spatula and close the container.

8.2 Heat the closed container in the water bath (6.2) set at a temperature between 40 °C and 60 °C. Remove and shake the container every 15 min. Remove the container after 2 h and cool to ambient temperature. Remove the lid and mix thoroughly by stirring with a spoon or spatula. Do not use tin-containing spoons or spatulas for mixing.

Avoid leaving the sample in the original container after it has been opened because this can lead to a rapid increase of the tin content.

NOTE If the fat separates out, correct results cannot be expected.

9 Procedure

9.1 Test portion

Weigh, to the nearest 1 mg, 1,0 g ± 0,1 g of the test sample into a 100 ml volumetric flask (6.3). Dilute to the mark with water (5.1) and homogenize by gently swirling.

If platform atomization is to be used, weigh, to the nearest 1 mg, 0,5 g ± 0,05 g of the test sample into a 100 ml volumetric flask (6.3). Make up and homogenize as before.

9.2 Start-up and settings of the measuring equipment

Switch on the power of the atomic absorption spectrometer at least 30 min before starting the measurements. Adjust instrumental parameters in accordance with the manufacturer's instructions. As a guide, settings for a Perkin Elmer Zeeman/3030 Atomic Absorption Spectrometer [2)], equipped with a HGA-600 graphite furnace atomizer, a tin electrode-less discharge lamp and an AS-60 autosampler are as follows:

lamp energy:	8 W
wavelength:	286,3 nm
slit width:	0,7 nm
sheath gas:	argon

The injection volume is 20 µl. Measure all standard and test solutions three times. During atomization (step 4 of Table 1), the peak area of the absorbance signal (corrected for background absorption) is measured.

NOTE 1 The reduced gas flow of 50 ml/min in step 4 is a compromise between sensitivity and linear range.

NOTE 2 The programme of the graphite furnace atomizer might need adjustment if another type of instrumentation is used.

If platform atomization is used, use the same programme as in Table 1 except that, after each injection of the test or standard solution, 10 µl of the matrix modifier solution II (5.5) (see 6.5) is added.

2) This is an example of suitable equipment available commercially. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of this equipment.

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Table 1 — Programme of the graphite furnace atomizer

Step number	Furnace temperature °C	Time s		Internal gas flow ml/min	Reading
		Ramp	Hold		
1	90	20	10	300	–
2	120	20	10	300	–
3	800	15	15	300	–
4	2 200	0	3	50	+
5	2 650	1	5	300	–

9.3 Preparation of calibrating solutions and test solution

Pipette 0,75 ml of the matrix modifier solution I (5.4) into an autosampler cup. Use the pipette with the same plastic tip to add 0,75 ml of the tin standard working solution (5.3.3) containing 0 µl of the tin standard.

Mix by taking 0,75 ml out of the cup using again the pipette with the same plastic tip and injecting this back into the cup. Repeat this procedure twice. This is the zero solution of the calibration solutions.

Prepare in the same manner the calibration solutions of the remaining tin standard working solutions (5.3.3) in diluted evaporated milk and the test solution from the test portion (9.1).

If autosampler cups of capacity less or more than 2 ml are used, adjust the volumes of the standard, the test and ascorbic acid solutions as it is essential to obtain 1:1 mixtures of the standard or the test solutions with the ascorbic acid solution. Mix these mixtures well.

If platform atomization is employed, the addition of ascorbic acid solution is omitted. Bring about 1,5 ml of each of the standard solutions and of the test solution into the autosampler cups. Fill one more cup with the alternative matrix modifier solution II (5.5).

If the atomic absorption spectrometer is also equipped with an autosampler having facilities for automatic adding of matrix modifier solution and performing standard additions, use these facilities for diluting the test solution 1:1 with ascorbic acid solution in the graphite tube as well as for calibration by the method of standard additions. (Instead of preparing a calibration graph by means of measuring standard solutions in the diluted tin-free evaporated milk.) In the latter case it should be checked that the linear range of the calibration graph is not exceeded.

9.4 Measuring procedure

9.4.1 Place the cups containing the prepared solutions (9.3) in the autosampler in such a way that first the zero solution is measured, then the other four calibration solutions, followed by the test solution. Measure all solutions three times and record the peak areas of the absorbance signals, corrected for background absorption. Then measure the four calibration solutions once more.

The calibration graph is linear up to tin contents of 100 mg/kg in the original undiluted samples. Samples giving rise to absorbance signals more than 10 % higher than that of the highest standard shall be diluted two-fold and measured again. Be sure that the diluted test solution contains 75 g/l of ascorbic acid. In this case also adjust the amount of evaporated milk in the diluted test solution by adding an appropriate volume of the bottled evaporated milk used for preparation of the standard solutions.

The presence of ascorbic acid in the solutions leads to build-up of residual carbon in the graphite tube. After a series of 50 to 100 firings, clean the inside of the tube carefully with a small spatula.

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9.4.2 Due to low absorbance signals, the precision of results for samples containing $\leqslant$ 20 mg/kg of tin is not very good. If more precise results are required for such samples, use a somewhat different procedure, briefly outlined as follows.

Weigh, to the nearest 1 mg, 2 g $\pm$ 0,2 g of test sample instead of the 1 g as given in 9.1. If platform atomization is used, weigh 1 g $\pm$ 0,1 g instead of an amount of 0,5 g. Employ gas stop (no internal gas flow) during the atomization step. Prepare a separate calibration graph for the samples with low tin contents by using diluted solutions of bottled evaporated milk spiked with tin corresponding to contents of 0 mg/kg, 5 mg/kg, 10 mg/kg and 20 mg/kg in the undiluted sample.

9.5 Preparation of calibration graph

Subtract the mean value of the peak area of the zero calibration solution (9.3) from the mean values of the peak areas for the calibrating solutions measured before and after the test solution.

NOTE The peak area for the zero calibration solution should be virtually zero.

Calculate the mean values of the peak areas, corrected for the zero calibration solution value, measured for the calibration solutions before and after the test solutions.

Plot the mean values against the corresponding tin contents in the undiluted sample (10 mg/kg, 20 mg/kg, 50 mg/kg and 100 mg/kg) or, alternatively, calculate the regression line by the method of linear least-squares analysis.

10 Calculation and expression of results

10.1 Calculation

Convert the mean peak-area values for the test solution to a test portion of 1,000 g (for platform atomization 0,500 g) by means of the following equation:

$$A_c = \frac{A_s - A_{bl}}{m}$$

where

A_c is the converted mean peak area, expressed in absorbance $\times$ seconds, for the test solution;

A_s is the mean peak area, expressed in absorbance $\times$ seconds, found for the three measurements of the test solution;

A_{bl} is the mean peak area, expressed in absorbance $\times$ seconds, found for the three measurements of the zero calibrating solution;

m is the mass, in grams, of the test portion (9.1). Multiply m by 2 when using the platform atomization procedure.

Calculate the tin content of the test sample, expressed in milligrams per kilogram, by reading directly from the calibration graph using A_c, or calculate the tin content directly from the regression line equation.

10.2 Expression of results

Round the results to the first decimal place.

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11 Precision

11.1 Interlaboratory test

The values for the repeatability and reproducibility limits were derived from the results of an interlaboratory test carried out in accordance with ISO 5725-1 and ISO 5725-2. Details of the interlaboratory test on the precision and accuracy of the method are summarized in reference [5]. The values derived from this interlaboratory test may not be applicable to concentration ranges and matrices other than those given.

NOTE IDF 135 provides specific guidance for interlaboratory tests on methods of analysis and milk products. It is based on ISO 5725.

11.2 Repeatability

The absolute difference between two independent single test results, obtained using 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 cases be greater than 7 % of the arithmetic mean of the two results.

11.3 Reproducibility

The absolute difference between two single test results, obtained using the same method on identical test material in different laboratories with different operators using different equipment, will in not more than 5 % of cases be greater than 19 % of the arithmetic mean of the two results.

12 Test report

The test report shall specify:

— all information necessary for the complete identification of the sample;

— the sampling method used, if known;

— the test method used, with reference to this International Standard;

— all operational details not specified in this International Standard, or regarded as optional, together with details of any incidents which may have influenced the test result(s);

— the test result(s) obtained;

— if the repeatability has been checked, the final quoted result obtained.

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