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Milk and canned evaporated milk — Determination of tin content — Spectrometric method

Lait et lait concentré non sucré en boîte — Détermination de la teneur en étain — Méthode spectrométrique

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Foreword

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International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

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.

In other circumstances, particularly when there is an urgent market requirement for such documents, a technical committee may decide to publish other types of normative document:

— an ISO Publicly Available Specification (ISO/PAS) represents an agreement between technical experts in an ISO working group and is accepted for publication if it is approved by more than 50 % of the members of the parent committee casting a vote;

— an ISO Technical Specification (ISO/TS) represents an agreement between the members of a technical committee and is accepted for publication if it is approved by 2/3 of the members of the committee casting a vote.

An ISO/PAS or ISO/TS is reviewed after three years in order to decide whether it will be confirmed for a further three years, revised to become an International Standard, or withdrawn. If the ISO/PAS or ISO/TS is confirmed, it is reviewed again after a further three years, at which time it must either be transformed into an International Standard or be withdrawn.

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

ISO/TS 9941|IDF/RM 160 was prepared by Technical Committee ISO/TC 34, *Food products*, Subcommittee SC 5, *Milk and milk products*, and the International Dairy Federation (IDF). It is being published jointly by ISO and IDF.

This second edition cancels and replaces the first edition (ISO/TS 9941|IDF/RM 160:2003), which has been technically revised.

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.

The main task of technical committees is to prepare International Standards. 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.

In other circumstances, particularly when there is an urgent market requirement for such documents, a Standing Committee may decide to publish an other type of normative document which is called by IDF: *Reviewed method*. Such a method represents an agreement between the members of a Standing Committee and is accepted for publication if it is approved by at least 50 % of the committee members casting a vote. A *Reviewed method* is equal to an ISO/PAS or ISO/TS and will, therefore, also be published jointly under ISO conditions.

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

ISO/TS 9941|IDF/RM 160 was prepared by Technical Committee ISO/TC 34, *Food products*, Subcommittee SC 5, *Milk and milk products*, and the International Dairy Federation (IDF). It is being published jointly by ISO and IDF.

All work was carried out by the Joint ISO/IDF Action Team on *Minor compounds*, of the Standing Committee on *Minor components and characterization of physical properties*, under the aegis of its project leaders, Dr M. Carl (DE) and Dr G. Ellen (NL).

This second edition cancels and replaces the first edition (ISO/TS 9941|IDF/RM 160:2003), which has been technically revised.

Introduction

This Technical Specification (Reviewed Method for IDF) specifies a spectrometric method for the determination of tin content in canned evaporated milk. Its limit of determination is 5 mg of tin per kilogram.

Despite several attempts, the Joint IDF-ISO Action Team (JAT) on *Minor compounds* could not organize a collaborative study with a sufficient number of participating laboratories to be in accordance with ISO 5725-2. Thus no precision figures for repeatability and reproducibility could be established. However, the method has been proven to be reliable by at least three experienced laboratories and particularly with respect to its accuracy.

The method was therefore adopted as a Technical Specification rather than as an International Standard.

Milk and canned evaporated milk — Determination of tin content — Spectrometric method

1 Scope

This Technical Specification (Reviewed Method for IDF) specifies a spectrometric method for the determination of the tin content in canned evaporated milk. The limit of determination of the method is 5 mg/kg.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 3696:1987, *Water for analytical laboratory use — Specification and test methods*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1
tin content
mass fraction of substances determined by the procedure specified in this Technical Specification

NOTE The tin content is expressed in milligrams per kilogram of sample.

4 Principle

The organic material is mineralized with a mixture of nitric acid and sulfuric acid. Water, hydrochloric acid and sodium carbonate solution are added. Interfering iron(III) ions are masked with thiourea solution and the tin(IV) is complexed with quercetin. The absorbance of the yellow solution is measured spectrometrically at the wavelength of maximum absorption (437 nm).

5 Reagents

Use only reagents of very pure analytical grade which, with the exception of the tin standard solution (5.11), are free from tin.

5.1 Water, double distilled or of equivalent quality, complying with the requirements of ISO 3696:1987, grade 2.

5.2 Ethanol (CH_3CH_2OH), with volume fraction of about 96 %.

5.3 Diethyl ether [$(C_2H_5)_2O$].

5.4 Sulfuric acid, concentrated, $\rho_{20}(H_2SO_4) = 1,84$ g/ml.

5.5 Nitric acid, concentrated, $\rho_{20}(HNO_3) = 1,42$ g/ml.

5.6 Hydrogen peroxide solution, $\rho_{20}(H_2O_2) = (1,099$ to $1,103)$ g/ml.

Store the hydrogen peroxide solution in a refrigerator.

5.7 Hydrochloric acid, dilute, $c(HCl) = 2,5$ mol/l.

Dilute 221 ml of concentrated hydrochloric acid [$\rho_{20}(HCl) = (1,17$ to $1,18)$ g/ml] with water to 1 000 ml and mix.

5.8 Sodium carbonate solution, $c(Na_2CO_3) = 200$ g/l.

Dissolve 200 g of anhydrous sodium carbonate in water. Dilute with water to 1 000 ml and mix.

5.9 Thiourea solution, $c[CS(NH_2)_2] = 90$ g/l.

Dissolve 45 g of thiourea in water. Dilute with water to 500 ml and mix.

5.10 Quercetin solution, $c(C_{15}H_{10}O_7) = 0,75$ g/l.

Dissolve 750 mg of quercetin (3,3',4',5,7-pentahydroxyflavone) in ethanol (5.2). Dilute with ethanol (5.2) to 1 000 ml and mix. Filter the quercetin solution through a filter paper. Store the solution in the dark for no longer than one week.

5.11 Tin standard solution, $c(Sn) = 1,000$ g/l.

Dilute a commercially available preparation that contains exactly 1,000 g of Sn (e.g. Sn(IV), Titrisol No. 9929 [1] is suitable) with the dilute hydrochloric acid (5.7) to 1 000 ml and mix well.

5.12 Milk, with low tin content, e.g. bottled evaporated milk or whole pasteurised milk.

5.13 Sodium chloride solution (NaCl), containing 0,5 % sodium chloride (mass fraction).

6 Apparatus

Keep the clean glassware, including the glass (or quartz) beads (6.5), in 10 % (mass fraction) nitric acid. Rinse the glassware and the beads three times before use with distilled water and then three times with double-distilled water. Dry, if necessary, by successively rinsing with ethanol (5.2) and diethyl ether (5.3).

Usual laboratory equipment and, in particular, the following.

6.1 Analytical balance, capable of weighing to the nearest 1 mg.

6.2 Water baths, capable of operating at 20 °C ± 2 °C, at 40 °C ± 2 °C, and at between 40 °C and 60 °C.

6.3 Micro gas burners, which do not emit tin-containing particles, or **electric heaters**.

6.4 Mineralization flasks, (Kjeldahl flasks), of capacity approximately 70 ml, with ground-glass joints (NS 19, with matching glass stoppers), calibrated with a mark on the lower part of the neck at 50 ml.

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[1] Titrisol No. 9929 is an example of a suitable product available commercially. This information is given for the convenience of users of this Technical Specification and does not constitute an endorsement by either ISO or IDF of this product.

6.5 **Beads**, made of glass or quartz.

6.6 **One-mark volumetric flasks**, of capacities 50 ml, 500 ml and 1 000 ml.

6.7 **Graduated pipettes**, of capacities 1 ml, 2 ml and 5 ml, with 0,1 ml graduations.

6.8 **One-mark pipettes**, capable of delivering 3 ml, 10 ml and 20 ml.

6.9 **Micro-pipettes**, capable of delivering 10 µl, 20 µl, 50 µl, 100 µl and 150 µl.

6.10 **Spectrometer**, capable of measuring absorbance at 437 nm, equipped with glass or quartz cells of 10 mm optical path length, with polytetrafluoroethylene stoppers.

7 Sampling

A representative sample should have been sent to the laboratory. It should not have been damaged or changed during transport or storage.

Sampling is not part of the method specified in this Technical Specification. A recommended sampling method is given in ISO 707|IDF 50.

Care should be taken to avoid contamination by tin during sampling. Store glass sampling jars in 10 % (mass fraction) nitric acid. Rinse them thoroughly and dry before use.

8 Preparation of test sample

8.1 Shake the container thoroughly with frequent inversion. Taking care to avoid contamination by tin, open the container and pour out its contents slowly into another pre-cleaned container made of glass and provided with an airtight lid. Incorporate in the test sample any fat or other constituents adhering to the wall of the original container. Stir vigorously and close the glass container.

8.2 Heat the closed glass container in a water bath (6.2) set at between 40 °C and 60 °C. Remove and shake the container vigorously every 15 min. After 2 h, remove the container and cool in another water bath (6.2) to 20 °C. Remove the lid and mix thoroughly by stirring the test sample with a spoon or spatula.

8.3 Correct results cannot be expected if the fat separates out.

9 Procedure

9.1 Test portion and pretreatment

Take precautions to avoid contamination by tin during the procedure. Weigh, to the nearest 1 mg, 0,5 g ± 0,1 g of prepared test sample (8.2) into a mineralization flask (6.4). While swirling, add 0,5 ml of water, 0,50 ml of concentrated sulfuric acid (5.4) and 0,5 ml of concentrated nitric acid (5.5).

9.2 Mineralization

9.2.1 Add three glass (or quartz) beads (6.5) to the contents of the mineralization flask (9.1). Leave the flask at room temperature for 30 min. Operating under a well-ventilated fume hood, place the flask in an inclined position and heat it with a micro gas burner or electric heater (6.3). Limit production of foam in the flask by controlling the height of the burner flame or the power position of the electric heater. Foaming is allowed into the neck of the flask but no foam shall escape. Keep the flask contents gently boiling. Avoid local overheating. Do not directly heat the flask above the surface level of the contents (see also 9.6).

9.2.2 When the solution starts to turn brown, carefully add 3 to 5 drops of nitric acid (5.5) to the mineralization flask. Avoid charring, which might cause loss of tin. Swirl the flask occasionally to remove any material adhering to the wall. If the solution remains brown, continue heating and add 5 to 20 drops of nitric acid (5.5) until it becomes virtually colourless. Then heat the colourless solution vigorously for 15 min. Cool to room temperature.

9.2.3 Carefully add 2 ml of water (5.1) and 1 ml of hydrogen peroxide solution (5.6) to the contents of the mineralization flask, while swirling. Heat again until white fumes are emitted. Prevent evaporation losses by allowing the sulfuric acid fumes to reflux in the neck of the flask.

If the solution becomes yellow, cool to room temperature and add a further 0,5 ml of hydrogen peroxide solution (5.6). Continue vigorous heating for 15 min after the beginning of the emission of white fumes. Cool to room temperature again. At this stage, the solution should be completely colourless.

9.3 Colour development

Slowly add, swirling after each addition, 10 ml of water (5.1), 4,5 ml of hydrochloric acid (5.7), 4,5 ml of sodium carbonate solution (5.8), 3 ml of thiourea solution (5.9) and 20 ml of quercetin solution (5.10) to the cooled solution in the mineralization flask (9.2.3). Dilute to the 50 ml mark with water. Keep the flask in the water bath (6.2) set at 40 °C for 1 h. Cool the flask in another water bath (6.2) to 20 °C and adjust its contents again with water to the 50 ml mark. Keep the flask at 20 °C for 30 min.

9.4 Blank test

Simultaneously with the procedure for the test portion (see 9.1 and 9.2), carry out a blank test by using all reagents but 0,5 ml of water (5.1) instead of the test portion (9.1). During the mineralization period, use the same amount of nitric acid (5.5) and hydrogen peroxide solution (5.6) as was needed to mineralize the test portion.

9.5 Preparation of the calibration graph

9.5.1 Using the micro-pipettes (6.9), transfer into a series of six mineralization flasks (6.4), each containing 0,5 g of bottled evaporated milk or 1,0 g of whole milk (5.12), the following amounts of tin standard solution (5.11):

0 µl (zero member), 10 µl, 20 µl, 50 µl, 100 µl and 150 µl.

The pipetted amounts correspond to 0 µg, 10 µg, 20 µg, 50 µg, 100 µg and 150 µg of tin respectively.

Add, swirling after each addition, 0,5 ml of water, 0,50 ml of sulfuric acid (5.4) and 0,5 ml of nitric acid (5.5).

9.5.2 Carry out the mineralization and colour development as specified in 9.2 and 9.3.

9.5.3 Use a pipette to transfer each solution to the 10 mm optical cell of the spectrometer (6.10).

Measure the absorbance of each of the six tin standard solutions against that of water at a wavelength of 437 nm. Subtract the zero member value from the values obtained for the other five solutions.

9.5.4 Plot the net obtained absorbance values against the amount of the tin standard solution added to the mineralization flask (see 9.5.1) (specific molar absorbance coefficient approximately 3,38 × 10^3 l mol^{-1} cm^{-1}). Draw the best-fitting straight line through the points to obtain the calibration graph, or calculate the regression line by using the method of least squares.

9.5.5 Check the thus-obtained calibration graph weekly.

9.6 Check on tin losses

Due to the high volatility of tin(IV) tetrachloride, losses of tin can occur during the mineralization step. In case of doubts, it is recommended to carry out mineralization by the same procedure as described in 9.5.1 to 9.5.5 but replacing the amount of milk (5.12) used in 9.5.1 with 1 ml of water (5.1) and, in parallel, with 1 ml of sodium chloride solution (5.13). The mineralization has correctly been performed when both calibration curves coincide.

9.7 Spectrometric measurements

Use a pipette to transfer the test solution (9.3) to the 10 mm optical cell of the spectrometer (6.10). Measure the absorbance of the test solution (9.3) and that of the blank test solution (9.4) against that of water (5.1) at a wavelength of 437 nm. Subtract the absorbance value obtained for the blank test solution from the value obtained for the test solution. Use the thus-corrected value to read the amount of tin content from the calibration graph, or calculate the amount of tin from the regression line obtained by using the method of least squares.

9.8 Number of determinations

Carry out all determinations, including the blank test (9.4), in duplicate.

10 Calculation and expression of results

10.1 Calculation

Calculate the tin content of the sample, w, expressed in milligrams per kilogram, by using the following equation:

$$w = \frac{m_1}{m_0}$$

where

m_0 is the mass of the test portion, in grams (9.1);

m_1 is the mass of tin, read from the calibration graph (or calculated from the regression line obtained by the method of least squares), in micrograms (9.7).

10.2 Expression of results

Express the test results as the arithmetic mean of the obtained values to one decimal place.

11 Test report

The test report shall specify

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

b) the sampling method used, if known;

c) the test method used, with reference to this Technical Specification;

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

e) the test result(s) obtained.

Bibliography

[1] ISO 707|IDF 50, *Milk and milk products — Guidance on sampling*

[2] ISO 5725-1, *Accuracy (trueness and precision) of measurement methods and results — Part 1: General principles and definitions*

[3] ISO 5725-2, *Accuracy (trueness and precision) of measurement methods and results — Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method*

[4] KOOPS, J., KLOMP, H. and WESTERBEEK, D. *Neth. Milk Dairy J.* 1984, pp. 1-17

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