INTERNATIONAL STANDARD

ISO 21422

IDF 242:2018

First edition
2018-09

Corrected version
2021-03

Milk, milk products, infant formula and adult nutritionals — Determination of chloride — Potentiometric titration method

Lait, produits laitiers, formules infantiles et produits nutritionnels pour adultes — Détermination de la teneur en chlorures — Méthode par titrage potentiométrique

Reference numbers
ISO 21422:2018(E)
IDF 242:2018:2018(E)

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Published in Switzerland

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see www.iso.org/iso/foreword.html.

This document 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 and separately by AOAC INTERNATIONAL. The method described in this International Standard is equivalent to the AOAC Official Method 2016.03: Chloride in Milk, Milk Products, Whey Powder, Infant Formula and Adult Nutritionals Potentiometric titration.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

This corrected version of ISO 21422 | FIL 242:2018 incorporates the following corrections:

— in 5.1, the sentence has been revised to "[...] less than 0,056 mS/cm (more than 18 MΩ) [...]";

— in Clause 12, the description of "V_1" in Formulae (1) and (2) has been revised to "V_1 is the volume of 0,1 mol/l or 0,025 mol/l $AgNO_3$ solution [...]".

IDF (the International Dairy Federation) is a non-profit private sector organization representing the interests of various stakeholders in dairying at the global level. IDF members are organized in National Committees, which are national associations composed of representatives of dairy-related national interest groups including dairy farmers, dairy processing industry, dairy suppliers, academics and governments/food control authorities.

ISO and IDF collaborate closely on all matters of standardization relating to methods of analysis and sampling for milk and milk products. Since 2001, ISO and IDF jointly publish their International Standards using the logos and reference numbers of both organizations.

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This document was prepared by the IDF Standing Committee on Analytical Methods for Composition and ISO Technical Committee ISO/TC 34, Food products, Subcommittee SC 5, Milk and milk products. It is being published jointly by ISO and IDF.

The work was carried out by the ISO/IDF Project Group C39 of the Standing Committee on Analytical Methods for Composition under the aegis of its project leader, Mr E. Konings (CH).

Milk, milk products, infant formula and adult nutritionals — Determination of chloride — Potentiometric titration method

1 Scope

This document specifies a method for the determination of chloride in milk, milk products, infant formula and adult nutritionals by potentiometry[1][2][3][4] with an analytical range of 0,35 mg chloride/100 g to 711,6 mg chloride/100 g product, or ready-to-feed products.

2 Normative references

There are no normative references in this document.

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

4 Principle

Chloride is extracted from samples by mixing in warm water, or directly from ready-to-feed (RTF) products. After (optional) precipitation of proteins, chloride ions are titrated with standardized $AgNO_3$ solution potentiometrically, using a silver electrode to detect the end point.

5 Reagents

5.1 Water, purified, less than 0,056 mS/cm (more than 18 MΩ) (EMD Millipore[1)] Corp., Billerica, MA, USA, or equivalent).

5.2 Sodium chloride (NaCl), purity ≥ 99,5 %, certified reference material for titrimetry, Sigma Aldrich #71387[1)] or equivalent.

5.3 Silver nitrate ($AgNO_3$), meeting analytical specification of European Pharmacopoeia (Ph. Eur), British Pharmacopoeia (BP), United States Pharmacopeia (USP), assay 99,8 % to 100,5 %, Sigma-Aldrich 10220[1)], or equivalent.

5.4 Potassium ferrocyanide trihydrate ($K_4Fe(CN)_6 \cdot 3H_2O$), puriss, p.a., American Chemical Society (ACS) reagent, reag. ISO, reag. Ph. Eur., ≥ 99 %, Sigma-Aldrich # 31524[1)] or equivalent.

1) This is an example of a suitable product available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO or IDF of the product named. Equivalent products may be used if they can be shown to lead to the same results.

5.5 Zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$), ACS reagent puriss p.a., ≥ 99,0 %, Sigma Aldrich # 96459[1)] or equivalent.

5.6 Nitric acid (HNO_3), minimum 65 % p.a., Merck #100452[1)] or equivalent.

5.7 Standardized $AgNO_3$ solution, substance concentration c = 0,1 mol/l, Titripur® Reag. Ph. Eur. Reag. USP. # 1,09081,1000 or EM3214-1, or ready-to-use standardized titrant prepared according to GB/T 601[5][1)], or equivalent.

5.8 NaCl standard solution, c = 0,1000 0 mol/l, Alfa Aesar[1)], # 35616, (Ward Hill, MA, USA), or equivalent.

5.9 Glacial acetic acid, 100 %, p.a., MERCK, # 100063[1)] or equivalent.

5.10 Potassium nitrate, (KNO_3), p.a., MERCK, # 105063[1)] or equivalent.

5.11 Acetone.

5.12 Dimethylpolysiloxane, defoaming agent, Sigma-Aldrich, #DMPS2C[1)] or equivalent.

6 Preparation of solutions

6.1 Standardized $AgNO_3$ solution, c = 0,1 mol/l.

If ready-to-use $AgNO_3$ (5.7) standard solution is not available, weigh 16,989 0 g ± 0,000 5 g $AgNO_3$ (5.3) previously dried for 2 h at 120 °C ± 2 °C. Dissolve in water (5.1) and make up to the mark in a 1 000 ml volumetric flask. Store in a brown reagent bottle.

After preparation, check the titre by titration of 5,0 ml with exactly 0,1 mol/l NaCl solution. For either commercial or in-house solution verify the titre on a regular basis. Store the standardized $AgNO_3$ solution so it is protected from light for up to two months.

6.2 NaCl solution, c = 0,1 mol/l.

If ready-to-use NaCl (5.8) standard solution is not available, weigh 5,844 0 g ± 0,000 5 g NaCl (5.2), previously dried for 2 h at 110 °C ± 2 °C. Dissolve in water (5.1) and make up to the mark in a 1 000 ml volumetric flask. This solution is stable for up to one month.

6.3 Precipitating solution (Carrez) I.

Weigh 106 g potassium ferrocyanide trihydrate (5.4), and transfer into a 1 000 ml volumetric flask. Dissolve with an appropriate amount of water (5.1). Make up to the mark using water (5.1). Mix well.

6.4 Precipitating solution (Carrez) II.

Weigh 220 g zinc acetate dihydrate (5.5) and transfer into a 1 000 ml volumetric flask. Dissolve in an appropriate amount of water (5.1) and add 30 ml glacial acetic acid (5.9). Make up to the mark with water (5.1). Mix well.

6.5 HNO_3 solution, c = 4 mol/l.

Carefully add 100 ml concentrated HNO_3 (5.6) to 300 ml water (5.1). Mix well.

In accordance with the autosampler/titrator manufacturer's instructions, this may be used as the wash solution (e.g. acetone, nitric acid solution or other).

6.6 $AgNO_3$ solution, c = 0,025 mol/l (optional).

Pipet 25 ml $AgNO_3$ solution, 0,1 mol/l (5.7 or 6.1) into a 100 ml volumetric flask. Make up to the mark with water (5.1). Prepare freshly before use. Then check the titre by titration of 25 ml against 0,025 mol/l NaCl solution.

6.7 NaCl solution, c = 0,025 mol/l (optional).

Pipet 25 ml NaCl solution, 0,1 mol/l (5.8 or 6.2) into a 100 ml volumetric flask. Make up to the mark with water (5.1). Prepare freshly before use.

6.8 KNO_3 solution, c = 1 mol/l.

Weigh 10,11 g KNO_3 (5.10) into a 100 ml volumetric flask. Add about 80 ml of water (5.1) and place it in an ultrasonic cleaner (7.13) until completely dissolved. Cool down to room temperature and make up to the mark with water (5.1). Filter using a disposable syringe with a 0,45 µm membrane filter (7.14) before use.

7 Apparatus

Usual laboratory equipment and, in particular, the following.

7.1 Analytical balances, precision 0,01 mg and 0,1 mg.

7.2 Centrifuge, table-top with rotor for 50 ml conical tubes, capable of operating at 4 °C and ≥ 12 000*g*.

7.3 Centrifuge tubes, 50 ml, conical, polypropylene.

7.4 Pipettes, 1 ml, 10 ml, 20 ml, 50 ml and 100 ml, volumetric or automatic, Class A in accordance with ISO 1042[6].

7.5 One-mark volumetric flasks, 50 ml, 100 ml, 500 ml, and 1 000 ml, Class A in accordance with ISO 1042[6].

7.6 Graduated cylinders, 25 ml, 100 ml and 500 ml, glass.

7.7 Autosampler beaker, e.g. 120 ml, depending on the titrator used.

7.8 pH-meter or mV-meter, with a scale covering ±700 mV.

7.9 Automatic titrator, autosampler, motorized piston burette, with remote-control dispensing and filling, or glass burette 20 ml or 25 ml.

Mettler T50, Roundo Tower autosampler, MettlerLabX 3.1 software or Metrohm 862 Compact Titrosampler, 800 Dosino, 10 ml Exchange Unit, or equivalent. Alternatively, a semi-automated titrator (e.g. MetrohmTitrando 905/907, with MetrohmTiamo™ software[2)] or equivalent or a manual titrator (using a burette with a readability of 0,01 ml) may be used.

7.10 Combined ring silver electrode, e.g. Mettler DM 141 or DMi145-SC, Metrohm Ag Titrode 6.0430.100[2)] or equivalent. Alternatively, a silver electrode with reference electrode may be used.

2) These are examples of suitable products available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO or IDF of the products named. Equivalent products may be used if they can be shown to lead to the same results.

7.11 Magnetic stirrer.

7.12 Water bath.

7.13 Ultrasonic cleaner.

7.14 Disposable syringe, 3 ml, with handspike and 0,45 µm disposable syringe filter.

7.15 Blender, capable to hold and blend 100 ml volume.

8 Sample preparation

8.1 Powders, for milk, milk products and infant formula

Mix well to ensure that the sample is homogeneous, Reconstitute powder samples by dissolving 25 g sample in 200 ml warm water of 40 °C.

8.2 Cheese, for hard or rinded cheese

Prior to analysis, remove the rind or smear or mouldy surface layer of the cheese in such a way as to provide a sample representative of the cheese as it is usually consumed. Grind or grate the sample by means of an appropriate device. Mix the ground or grated mass quickly, and if possible grind or grate a second time and again mix thoroughly. If the sample cannot be ground or grated, mix it thoroughly by intensive stirring and kneading.

Transfer the sample to an airtight container to await analysis, which should be carried out as soon as possible after grinding. If delay is unavoidable, take all precautions to ensure proper preservation of the sample and to prevent condensation of moisture on the inside surface of the container. The storage temperature should be 10 °C to 12 °C.

8.3 Butter

If the sample is visibly inhomogeneous, or if the history of the sample (age, storage conditions) is such that inhomogeneity is expected, homogenize the sample as follows.

Warm the sample in the original unopened container, which should be from one-half to two-thirds full, to a temperature at which the sample will be soft enough to facilitate thorough mixing to a homogeneous state (either by a mechanical shaker or by hand). Take care that the mixing temperature does not exceed 30 °C.

Cool the sample to ambient temperature with constant mixing until cooling is complete. As soon as possible thereafter, open the sample container and stir briefly (no longer than 10 s) with a suitable device, for example a spoon or spatula, before weighing.

9 Extraction

9.1 Cheese

Weigh 2 g to 5 g of the prepared sample (8.2) into the titration vessel. For processed cheese, weigh 2,5 g. Add 30 ml of water (5.1) at about 55 °C. Suspend the sample using a blender (7.15). Rinse the blender with approximately 10 ml of water, collecting the rinsing in the titration vessel. Add 2 ml to 3 ml of the HNO_3 solution of c = 4 mol/l (6.5). Proceed with 9.4.4.

9.2 Butter

Weigh 2 g to 4 g of the prepared sample (8.3) into the titration vessel. For salted butter, weigh 2,5 g. Carefully add 100 ml of boiling water and heat to boiling to suspend the test portion. Cool the obtained suspension to below 55 °C. Proceed with 9.4.4.

9.3 Milk, milk products, infant formula and adult nutritional products

Proceed with 9.4.3 unless it is determined that additional protein precipitation is required to achieve acceptable performance. Protein precipitation is accomplished by following 9.4.1 to 9.4.2.

NOTE Validation data from the collaborative trial for infant formula and adult nutritional products (Annex B) showed no difference in results for samples treated with and without additional protein precipitation. See Annex C.

9.4 Procedure

9.4.1 Weigh an appropriate well mixed aliquot of RTF product or reconstituted powder (8.1) (e.g. 25 g accurate to 1 mg) into a 50 ml centrifuge tube. For samples with a high chloride content, weigh a smaller test portion (e.g. 5 g of RTF or reconstituted powder).

Transfer 2,5 ml precipitating solution I (6.3) and 2,5 ml precipitating solution II (6.4) into the tube. Dilute to 50 ml with water. Mix well. If foam impacts the constant volume, add one or two drops of defoaming agent (5.12).

9.4.2 Centrifuge at 12 000*g* for 5 min at 4 °C. Then equilibrate to room temperature.

9.4.3 Accurately transfer either 10 ml supernatant from steps 9.4.1 to 9.4.2 or weigh an appropriate aliquot of RTF or reconstituted powder (8.1) (e.g. 25 g ± 1 g accurately weighed to 1 mg). For samples with a high chloride content, weigh a smaller test portion (e.g. 5 g ± 1 g of RTF or reconstituted or powder) into a 120 ml sample beaker or autosampler cup.

Add 5 ml HNO_3 solution (6.5) and 50 ml of water before titration. Add a magnetic stirring bar (if the titrator does not have a built-in rod stirrer). Place the autosampler cup or beaker onto a magnetic stirrer and stir until dissolved or finely suspended.

9.4.4 The pH of the test solution shall be below 1,5. In case of any doubt, check by means of a pH-meter and, if necessary, add a little more HNO_3 solution (6.5).

10 Instrument operating conditions

10.1 Check and maintenance of the combined silver electrode

Rinse the electrode with deionized water and wipe before use. Renew the electrolyte c = 1 mol/l KNO_3 (6.8) periodically as per the manufacturer's recommendations. If fat sticks to the electrodes during a series of analyses, then remove it by briefly immersing the electrode in acetone (5.11). Store the silver electrode in KNO_3 solution (6.8) after appropriate cleaning.

NOTE Instead of the combined silver electrode, separate silver and reference electrodes can be used.

10.2 Titration

Connect the combined silver electrode to the titration apparatus, according to the manufacturer's instructions. Ensure that the titration vessels are correctly placed on the autosampler and that there are sufficient reagents, both HNO_3 solution (6.5), if added automatically, and standardized $AgNO_3$ solution (6.1). If no autosampler is available, place the sample solutions manually under the titration equipment.