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Modified starch — Determination of hydroxypropyl content — Method using proton nuclear magnetic resonance (NMR) spectrometry

Amidon modifié — Détermination de la teneur en hydroxypropyle — Méthode spectrométrique de résonance magnétique nucléaire du proton

Reference number
ISO 11543:2000(E)

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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 3.

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 11543 was prepared by Technical Committee ISO/TC 93, *Starch (including derivatives and by-products)*.

Annex A of this International Standard is for information only.

Modified starch — Determination of hydroxypropyl content — Method using proton nuclear magnetic resonance (NMR) spectrometry

1 Scope

This International Standard specifies a proton NMR spectrometric method for the determination of the hydroxypropyl content of granular modified starch.

2 Normative references

The following normative documents contain 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 editions of the normative documents 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 1666:1996, *Starch — Determination of moisture content — Oven-drying method*.

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

3 Principle

The modified starch is dissolved by partial hydrolysis in a solution of deuterium chloride in deuterium oxide.

The signal coming from the three protons of the methyl group in the hydroxypropyl function is measured.

An internal standard, 3-trimethylsilyl-1-propane sulfonic acid, sodium salt, is used.

4 Reagents and materials

Use only reagents of recognized analytical grade.

4.1 Water, complying with at least grade 3 in accordance with ISO 3696. The water shall be free from carbon dioxide.

4.2 Deuterium oxide, at least 99,8 % purity, in 25 ml screw-cap bottles.

4.3 Deuterium oxide, at least 99,95 % purity, in 0,75 ml sealed ampoules.

4.4 Deuterium chloride solution, c(DCl) ≈ 2 mol/l.

Dilute 1 ml of concentrated deuterium chloride [commercial form, w(DCl) ≈ 38 % (by mass)] with 5 ml of deuterium oxide (4.2).

4.5 Internal standard solution.

The internal standard is prepared by weighing at the same time the standard and the solvent.

Dissolve about 50 mg of 3-trimethylsilyl-1-propane sulfonic acid (TSPSA), sodium salt (CAS No. 2039-96-51), weighed to the nearest 0,1 mg, in about 5 g of deuterium oxide (4.2), weighed to the nearest 0,1 mg. Store in a sealed bottle.

5 Apparatus

Usual laboratory apparatus and, in particular, the following.

5.1 Analytical balance, capable of weighing to the nearest 0,1 mg.

5.2 Beaker, of 400 ml capacity.

5.3 Büchner flask and **funnel.**

5.4 Vacuum oven, equipped with a pump that can maintain a pressure not in excess of 10 kPa.

5.5 Tube, 5 mm, for NMR, equipped with a spinner in order to record the spectrum in rotation.

5.6 Micropipettes, of 5 ml capacity accurate to 0,05 ml, and micropipettes of capacities 0,1 ml and 0,05 ml accurate to 0,001 ml.

5.7 Boiling water bath.

5.8 Nuclear magnetic resonance spectrometer, of minimum power 60 MHz, capable of performing a proton spectrum, and of carrying out quantitative analyses.

5.9 Sieve, 800 μm.

5.10 Blade mill.

6 Sampling

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

Sampling is not part of the method specified in this International Standard.

7 Preparation of test sample

Sieve the laboratory sample through the 800 μm sieve (5.9). If the material does not pass through the sieve, then grind the sample with a blade mill (5.10) untill it passes completely through the 800 μm sieve. Homogenize the sample.

8 Procedure

8.1 Sample washing

8.1.1 Weigh about 20 g of the prepared test sample into the beaker (5.2). Add 200 ml of water (4.1) at room temperature and agitate for 15 min.

If problems of poor dispersibility or slow filtration are encountered, then repeat 8.1.1 with refrigerated water (4.1).

8.1.2 Filter the starch on the Büchner flask (5.3) under vacuum.

8.1.3 Repeat steps 8.1.1 and 8.1.2 twice.

8.1.4 Dry the washed starch for at least 4 h in the vacuum oven (5.4) at a temperature of (30 ± 5) °C.

8.2 Moisture content

Using a test portion of 5 g, determine the moisture content of the washed and dried test sample (8.1.4) in accordance with ISO 1666.

8.3 Preparation of test solution

8.3.1 Weigh, to the nearest 0,1 mg, about 12 mg (dry basis) of the washed and dried test sample (8.1.4) in the tube (5.5).

8.3.2 Add the contents of an ampoule of deuterium oxide (4.3) to the tube (5.5) and 0,1 ml of deuterium chloride solution (4.4) using a micropipette (5.6).

8.3.3 Cap the tube, mix, and then place it in a boiling water bath (5.7).

8.3.4 After 3 min, if a clear solution is obtained, remove and allow it to cool to room temperature. If not clear, continue the treatment in the water bath (5.7) for up to a maximum of 1 h to achieve a clear solution.

8.3.5 Dry the exterior of the tube (5.5) and weigh it to the nearest 0,1 mg. Using a micropipette (5.6), add 0,05 ml of internal standard solution (4.5) to the tube. Weigh, to the nearest 0,1 mg, to determine the mass of the internal standard solution (4.5) introduced into the tube (5.5).

8.3.6 Mix thoroughly, adjust the spinner and place the tube (5.5) in the instrument (5.8). Start the rotation of the tube (5.5).

8.4 Recording of spectrum

8.4.1 Make the appropriate instrument settings so as to obtain a suitable spectrum. A relaxation delay of at least 15 s is recommended for a Fourier Transform (FT) instrument.

8.4.2 Use a spectral window of between –0,5 ppm and +6 ppm, referring to the methyl signal of TSPSA at 0 ppm.

8.4.3 For FT-NMR, transform the FID (Free Induction Decay) to a spectrum and start the integration sub-routine after phase corrections.

8.4.4 Measure the peak areas of the doublet coming from the methyl group of the hydroxypropyl function, at +1,2 ppm, and of the methyl groups of TSPSA at 0 ppm, after baseline correction.

9 Calculation and expression of results

Calculate the hydroxypropyl content, w_h, of the dry test sample by the equation:

$$w_h = \frac{3A_h}{A_{is}} \times \frac{w_{is} \times m_{is}}{M_{is}} \times M_h \times \frac{100\ \%}{m} \times \frac{100\ \%}{100\ \% - w_m}$$

where

w_h is the hydroxypropyl content, as a percentage by mass, of the dry test sample;

A_h is the area, in units of area, of the methyl group of hydroxypropyl;

A_{is} is the area, in units of area, of the methyl groups in the internal standard (TSPSA);

3 is a numerical value representing the three methyl groups in TSPSA;

w_{is} is the mass fraction, in milligrams per gram, of TSPSA in the internal standard solution (4.5);

m_{is} is the mass, in grams, of the internal standard solution (4.5) in the NMR tube (see 8.3.5);

M_{is} is the molar mass, in grams per mole, of TSPSA (M_{is} = 218 g/mol);

M_h is the molar mass, in grams per mole, of the hydroxypropyl group (M_h = 59 g/mol);

m is the mass, in milligrams, of the washed and dried test sample in the NMR tube (see 8.3.1);

w_m is the moisture content, as a percentage by mass, of the washed and dried test sample (see 8.2).

Report the result to the nearest 0,1 % (by mass).

10 Precision

10.1 Interlaboratory test

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

10.2 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 exceed the repeatability limit r given in or derived from Table 1.

10.3 Reproducibility

The absolute difference between two single test results, obtained using the same method on identical test material in different laboratories by different operators using different equipment, will in not more than 5 % of cases exceed the reproducibility limit R given in or derived from Table 1.

Table 1 – Repeatability limit (r) and reproducibility limit (R)

Mean hydroxypropyl content % (by mass)	r % (by mass)	R % (by mass)
0,82	0,31	0,48
3,35	0,98	0,98
3,60	0,76	0,95
5,80	0,70	1,72
6,40	2,33	2,59

11 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;

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

— the test result obtained, or the two test results obtained if the repeatability was checked.

Annex A
(informative)

Results of an interlaboratory test

An international collaborative test involving ten laboratories was carried out on five different samples of potato starch, waxy maize starch, cross-bonded native corn starch and cross-bonded waxy maize starch.

The results obtained were subjected to statistical analysis in accordance with ISO 5725 [1)] to give the precision data shown in Table A.1.

Table A.1 — Statistical results of the interlaboratory test

Parameter	Sample [a]				
	1	**2**	**3**	**4**	**5**
Number of laboratories retained after eliminating outliers	9	9	9	9	9
Number of outliers (laboratories)	1	1	1	1	1
Number of accepted results	18	18	18	18	18
Mean total hydroxypropyl content, % (by mass)	5,8	3,35	0,82	3,60	6,40
Repeatability standard deviation, s_r, % (by mass)	0,25	0,34	0,11	0,27	0,82
Repeatability coefficient of variability, %	4,3	10,3	13,4	7,45	12,9
Repeatability limit, r [$r = 2{,}8 \times s_r$], % (by mass)	0,70	0,98	0,31	0,76	2,33
Reproducibility standard deviation, s_R, % (by mass)	0,61	0,34	0,17	0,34	0,91
Reproducibility coefficient of variability, %	10,4	10,3	21,0	9,36	14,3
Reproducibility limit, R [$R = 2{,}8 \times s_R$], % (by mass)	1,72	0,98	0,48	0,95	2,59

[a] 1: waxy starch ether and hybrids;
2: potato starch ether;
3: maize starch ether, thinned;
4: waxy starch ether and hybrids;
5: waxy starch ether and hybrids.

1) ISO 5725:1986 (now withdrawn) was used to obtain the precision data.

Bibliography

[1] ISO 5725:1986, *Precision of test methods — Determination of repeatability and reproducibility for a standard test method by inter-laboratory tests.*

[2] ISO 5725-1:1994, *Accuracy (trueness and precision) of measurement methods and results — Part 1: General principles and definitions.*

[3] ISO 5725-2:1994, *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.*

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