

Analysis of formulated detergents —

Part 3: Quantitative test methods —

Section 3.25 Methods for determination of water and volatile matter content

NOTE It is recommended that this Section be read in conjunction with the information in the “General introduction”, published separately as BS 3762-0.

UDC 661.185:543

Confirmed January 2011

Foreword

This Section of BS 3762 has been prepared under the direction of the Chemicals Standards Policy Committee and supersedes method D14 of BS 3762:1964, which is withdrawn.

This Section describes methods of test only and should not be referred to as a specification defining limits of purity. Reference to the standard should indicate that the method of test used is in conformity with BS 3762-3.25.

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Summary of pages

This document comprises a front cover, an inside front cover, pages i and ii, pages 1 to 4, an inside back cover and a back cover.

This standard has been updated (see copyright date) and may have had amendments incorporated. This will be indicated in the amendment table on the inside front cover.

Amendments issued since publication

Amd. No.	Date of issue	Comments

This British Standard, having been prepared under the direction of the Chemicals Standards Policy Committee, was published under the authority of the Board of BSI and comes into effect on 29 September 1989

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The committees responsible for this British Standard are shown in Part 0.
The following BSI references relate to the work on this standard:
Committee reference CIC/34
Draft for comment 88/52266 DC

ISBN 0 580 17368 2

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1 Scope

This Section of BS 3762 describes methods for determining the content of water or volatile matter in formulated detergents.

NOTE 1 The water determined may include water of crystallization.

Method 1 is for determination of water in samples that do not contain volatile compounds that are miscible with water, for example, low molecular mass alcohols. Method 2 is for determination of the loss in mass on heating at 150 °C, which indicates the volatile matter content; the result will be the water content if water is the only volatile compound in the sample. Method 3 is for determination of water in liquids and in pastes and solids that release all their water during the titration of a solution or a dispersion in methanol; it is not applicable to samples that contain noticeable amounts of oxidizing agents, ketones, strong acids or strong bases.

NOTE 2 The titles of the publications referred to in this Section are listed on the inside back cover.

2 Method 1. Entrainment

2.1 Principle

The water present in a test portion is entrained by azeotropic distillation with xylene, and the volume of water collected is measured.

2.2 Reagents

The reagents shall be of a recognized analytical grade. Water complying with grade 3 of BS 3978 shall be used throughout.

2.2.1 Xylene

2.2.2 Calcium stearate, anhydrous.

NOTE Anhydrous sodium acetate may be substituted for anhydrous calcium stearate.

2.2.3 Ammonium hexanitratocerate(IV) solution. Dissolve 20 g of ammonium hexanitratocerate(IV) in about 60 mL of water. Add 25 mL of nitric acid solution [70 % (m/m) HNO₃] and dilute to 100 mL.

NOTE This solution may be prepared in proportionately smaller quantities if preferred.

2.3 Apparatus

Ordinary laboratory apparatus and the following are required.

2.3.1 Dean and Stark apparatus, complying with BS 756, type 1, having a distillation flask of 500 mL capacity and a 2 mL receiver (for solids) or a 7.5 mL receiver (for liquids and pastes).

2.3.2 Boiling aid, for example pumice stone fragments.

2.4 Procedure

Thoroughly dry the flask and the receiver, using an oven or a current of warm air. Weigh between 7 g and 20 g of sample, to the nearest 0.01 g, into the flask ensuring that the expected water content does not exceed the capacity of the receiver. Add 100 mL to 150 mL of the xylene (2.2.1) to the flask. Add 1 g to 2 g of the anhydrous calcium stearate or sodium acetate (2.2.2). Dry the inner surface of the condenser by pushing a plug of absorbent cotton through it, then connect it to the receiver and flask.

Heat the flask and contents using an electric heating mantle or an oil bath so that the contents boil and condensate falls from the condenser at a rate of 2 to 5 drops per second.

After at least 30 min and when the distilled xylene is clear and the volume of water in the receiver no longer increases, stop heating and allow the apparatus to stand long enough for the water to separate completely. If drops of water adhere to the tube or the condenser, use a long stout wire or a spray of xylene to dislodge them and combine them with the water in the receiver. Read the volume of water collected.

NOTE To test for the presence of volatile alcohols, transfer the water layer, or part of it, to a small test tube and place a similar quantity of distilled water, or water of equivalent purity, into a second tube for comparison. Add to each an equal volume of the ammonium hexanitratocerate(IV) solution (2.2.3) and mix. An orange colour in the sample tube, when compared with the yellow of the blank, indicates that alcohols are present and that method 1 is inapplicable.

2.5 Expression of results

The water content, expressed as a percentage by mass, is given by the following expression:

$$\frac{V \times 100}{m}$$

where

V is the volume of water collected in the receiver (in mL);

m is the mass of the test portion (in g).

NOTE It is assumed that the density of water, at the temperature when the volume is read, is exactly 1 g/mL within the accuracy of the determination.

2.6 Precision

No precision data are available.

3 Method 2. Oven drying

3.1 Principle

The loss of mass, on heating at 150 °C for 2 h, is determined.

3.2 Apparatus

Ordinary laboratory apparatus and the following are required.

3.2.1 Dish or beaker, of glass or porcelain, of capacity not exceeding 100 mL.

3.2.2 Oven, ventilated, capable of being controlled at 150 ± 5 °C.

3.3 Procedure

Ensure that the dish or beaker (**3.2.1**) is dry, then weigh to the nearest 0.001 g.

NOTE 1 Some dry, coarse sand or other stable material may be contained in the dish or beaker to accelerate the subsequent drying operation.

Add 2 g to 3 g of sample and reweigh to the nearest 0.001 g. Place the dish or beaker in the oven (**3.2.2**) at 150 ± 5 °C for 2 h

NOTE 2 If desired the dish or beaker may first be heated on a steam-bath under a stream of air until most of the water has evaporated.

Allow the dish or beaker and contents to cool in a desiccator and then reweigh to the nearest 0.001 g.

3.4 Expression of results

The loss in mass on heating at 150 °C, expressed as a percentage by mass, is given by the following expression:

$$\frac{m_2 - m_3}{m_2 - m_1} \times 100$$

where

m_1 is the mass of the empty dish or beaker (in g);

m_2 is the mass of the dish or beaker plus sample (in g);

m_3 is the mass of the dish or beaker plus dried contents (in g).

NOTE If water is the only volatile compound liable to be present, the result may be expressed as "water content".

3.5 Precision

Intralaboratory studies have given the following values for liquid detergents (see BS 5497-1):

Water content	Repeatability
Lower than 30 %	0.3 % absolute
Not lower than 30 %	1 % relative

4 Method 3. Karl Fischer

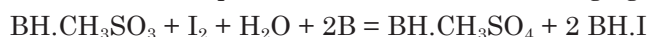
4.1 Principle

A solution or dispersion of the detergent is titrated with Karl Fischer reagent using an electrometric method to determine the end point. Karl Fischer reagent is a solution containing a methosulphite and iodine, the former being created by mixing the components:



(B is a base, typically pyridine.)

In the presence of water, the methosulphite ion is oxidized to methosulphate, the reaction being quantitative in the presence of a suitable buffering agent, for example pyridine plus 1-ethyl piperidine:



At the end-point a slight excess of iodine will depolarize an electrode pair placed in the solution and allow a current to flow and move a galvanometer needle, or some other detector.

4.2 Reagents

The reagents shall be of a recognized grade for the determination of water using Karl Fischer reagent.

4.2.1 Karl Fischer reagent, of concentration such that 1 mL is equivalent to about 5 mg of water.

NOTE Various Karl Fischer reagents, some of which are pyridine-free, are available commercially and may be used. Alternatively, Karl Fischer reagent may be prepared as described in 2.4 of BS 2511:1970.

4.2.2 Methanol, water content $\leq 0.02\%$ (m/m).

NOTE Methanol specially dried for use with Karl Fischer reagent is available commercially.

4.2.3 Sample solvent for pyridine-free Karl Fischer reagent, as recommended by the supplier of the pyridine-free Karl Fischer reagent.

4.2.4 Water, complying with grade 3 of BS 3978.

4.3 Apparatus

4.3.1 Manual or semi-automatic Karl Fischer apparatus, comprising a burette of size 10 mL to 50 mL, a Karl Fischer reagent reservoir, a titration vessel, a stirrer, and an electrical circuit to detect the end-point. The titration vessel shall have a stoppered side inlet for introducing samples and a stopcock for drainage. The apparatus shall be fitted with seals and guard tubes of desiccant to prevent the ingress of atmospheric moisture.

4.3.2 Syringe, or Lunge-Rey pipette, of minimum capacity 0.25 mL.

4.3.3 Tube, or other container, for weighing a solid sample and permitting easy transference to the titration vessel.

4.4 Standardization of the Karl Fischer reagent

4.4.1 Standardize the Karl Fischer reagent daily before use. Follow the same standardization procedure for the pyridine-containing titrant/solvent system and the pyridine-free titrant/solvent system.

4.4.2 Add enough of the appropriate solvent (4.2.2 or 4.2.3) to the clean, dry titration vessel to cover the electrodes.

NOTE The volume of solvent depends on the size of the titration vessel.

Seal all openings to the vessel, start the magnetic stirrer and adjust for a smooth stirring action. Turn on the indication circuit and add the Karl Fischer reagent (4.2.1) from the burette until the end point is reached. Swirl the contents of the titration vessel to remove any water from the inside walls of the vessel. If necessary, run off excess liquid. Carefully add more of the Karl Fischer reagent if needed until a steady end point is just reached and maintained for at least 30 s.

4.4.3 Into the syringe or pipette (4.3.2) place an amount of the water (4.2.4) equivalent to about half the contents of the Karl Fischer reagent burette, and weigh. Add the contents of the syringe or pipette to the sample solvent in the titration vessel which has been adjusted to the end point. Reseal the vessel immediately, then reweigh the syringe or pipette. Titrate with Karl Fischer reagent until a steady end point is reached and maintained for at least 30 s. Record to the nearest 0.01 mL the volume of titrant needed to reach the end point.

4.4.4 Calculate the water equivalent of the Karl Fischer reagent using the expression:

$$F = M/T$$

where

F is the water equivalent of the Karl Fischer reagent (in mg/mL);

M is the mass of water added (in mg);

T is the volume of reagent required for titration of the added water (in mL).

4.4.5 Run off sufficient of the contents of the titration vessel to leave the electrodes just covered, then repeat the operations of 4.4.3 and 4.4.4.

4.4.6 If the two values of F differ by more than 2 % of their mean, then discard the contents of the titration vessel and repeat steps 4.4.2 to 4.4.5.

NOTE If there is difficulty in obtaining results within 2 % then it is likely that the Karl Fischer reagent or the solvent has deteriorated and fresh supplies should be used.

When two values of F agreeing to within 2 % have been obtained, record the mean as F_2 .

4.5 Determination

4.5.1 Add the solvent to the titration vessel and adjust to the end point by proceeding as in 4.4.2.

NOTE If the previous titration was for standardization or analysis of a liquid detergent and did not overshoot the end-point, it is sufficient to run out excess liquid until the electrodes are just covered.

4.5.2 Proceed as in 4.4.3 using the sample to be analysed and taking sufficient to yield a titration of between 30 % and 150 % of the volume used in standardization. In the case of a solid sample, use the tube (4.3.3) in place of the syringe or pipette (4.3.2).

4.6 Expression of results

The water content, expressed as a percentage by mass, is given by the expression:

$$\frac{T \times F_2}{m \times 10}$$

where

T is the titration from 4.5 (in mL);

F_2 is the mean water equivalent of the Karl Fischer reagent (in mg/mL);

m is the mass of sample (in g).

4.7 Precision

No precision data are available.

5 Test report

The test report shall include the following information:

- a reference to this British Standard, i.e. BS 3726-3.25:1989;
- a reference to the test method used, i.e. method 1, method 2 or method 3;
- the results expressed in accordance with 2.5, 3.4 or 4.6;
- a complete identification of the sample.

Publications referred to

BS 756, *Specification for Dean and Stark apparatus.*

BS 2511, *Methods for the determination of water (Karl Fischer method).*

BS 3978, *Specification for water for laboratory use.*

BS 5497, *Precision of test methods.*

BS 5497-1, *Guide for the determination of repeatability and reproducibility for a standard test method by inter-laboratory tests.*

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