BRITISH STANDARD

BS EN
13268:2001
Incorporating
Corrigendum No. 1

Surface active agents — Determination of ethylene oxide and propylene oxide groups in ethylene oxide and propylene oxide adducts

The European Standard EN 13268:2001 has the status of a British Standard

ICS 71.100.40

BSI
British Standards

National foreword

This British Standard is the official English language version of EN 13268:2001, including Corrigendum July 2002.

The UK participation in its preparation was entrusted to Technical Committee CII/34, Methods of test for surface active agents, which has the responsibility to:

— aid enquirers to understand the text;

— present to the responsible European committee any enquiries on the interpretation, or proposals for change, and keep the UK interests informed;

— monitor related international and European developments and promulgate them in the UK.

A list of organizations represented on this committee can be obtained on request to its secretary.

Additional information

Some textual errors were discovered when the English language version of EN 13268:2001 was adopted as the national standard. Some of the chemical names are not consistently presented and do not conform to IUPAC recommendations.These textual errors have been reported to CEN in a proposal to amend the text of the European Standard.

Cross-references

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This British Standard, having been prepared under the direction of the Sector Committee for Materials and Chemicals, was published under the authority of the Standards Committee and comes into effect on 15 June 2001

Summary of pages

This document comprises a front cover, an inside front cover, the EN title page, pages 2 to 15 and a back cover.

The BSI copyright date displayed in this document indicates when the document was last issued.

Amendments issued since publication

Amd. No.	Date	Comments
14888 Corrigendum No. 1	9 January 2004	Correction to Clause **8**

ISBN 0 580 37403 3

EUROPEAN STANDARD

NORME EUROPÉENNE

EUROPÄISCHE NORM

EN 13268

April 2001

ICS 71.100.40

Incorporating corrigendum July 2002

English version

Surface active agents — Determination of ethylene oxide and propylene oxide groups in ethylene oxide and propylene oxide adducts

Agents de surface — Détermination de la teneur en oxyde d'éthylène et en oxyde de propylène dans les condensats à base d'oxyde d'éthylène et d'oxyde de propylène

Grenzflächenaktive Stoffe — Bestimmung von Ethylenoxid- und Propylenoxid-Gruppen in Ethylenoxid- und Propylenoxid-Addukten

This European Standard was approved by CEN on 19 January 2001.

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This European Standard exists in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the Management Centre has the same status as the official versions.

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Ref. No. EN 13268:2001 E

Contents

Foreword

This European Standard has been prepared by Technical Committee CEN/TC 276, Surface active agents, the Secretariat of which is held by AFNOR.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by October 2001, and conflicting national standards shall be withdrawn at the latest by October 2001.

Annex A is informative.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Czech Republic, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and the United Kingdom.

Introduction

Under the specified reaction conditions, ethylene oxide groups convert stoichiometrically into ethyl iodide. However, the conversion of propylene oxide groups to isopropyl iodide is not stoichiometric.

1 Scope

This European Standard specifies a method for the qualitative and quantitative determination of ethylene oxide and propylene oxide groups in ethylene oxide (EO) and propylene oxide (PO) adducts, polyethers and polyglycol esters.

NOTE If a suitable calibration is performed, methoxy groups can also be determined.

2 Normative references

This European Standard incorporates by dated or undated reference, provisions from other publications. These normative references are cited at the appropriate places in the text and the publications are listed hereafter. For dated references, subsequent amendments to or revisions of any of these publications apply to this European Standard only when incorporated in it by amendment or revision. For undated references the latest edition of the publication referred to applies (including amendments).

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

ISO 607, *Surface active agents and detergents — Methods of sample division.*

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*.

3 Principle

Hydroiodic acid and nonane are added to the sample to be analysed and the mixture is heated in a closed vessel for 1 h at 150 °C. Upon conversion, ethylene oxide groups form stoichiometric amounts of ethyl iodide, and propylene oxide groups form [74 % to 77 % (*m*/*m*)] of propyl iodide (mainly the iso-form, less frequently the n-form). These compounds are extracted by the nonane present and thus removed from the reaction medium.

Under the specified digestion conditions, ethyl iodide is formed from all compounds containing ethoxy groups (ethers and esters) and ethylene glycol derivatives; and isopropyl iodide is formed from all compounds containing isopropoxy groups, propylene glycol and glycerol derivatives.

The alkyl iodides are determined directly from the nonane solution by means of gas chromatography using toluene as internal standard.

Substances that contain isobutyl groups give isobutyl iodide when cleavage takes place. Isobutyl iodide cannot be exactly separated from the internal standard, toluene, in the chromatogram.

4 Reagents

During the analysis, use only reagents of recognized analytical grade and water complying with grade 3 as defined in EN ISO 3696.

4.1 **Hydroiodic acid**, HI, $w(HI) \geq 6{,}7$ %.

4.2 **Adipic acid**, $C_8H_6O_4$, $w(C_8H_6O_4) \geq 98$ %.

4.3 **Toluene**, C_7H_8, $w(C_7H_8) \geq 99$ %.

4.4 **Nonane**, C_9H_{20}, $wC_9H_{20}) \geq 99$ %, GC quality.

4.5 Ethyl iodide, C_2H_5I, $w(C_2H_5I) \geq 99$ %, GC quality.

4.6 Propyl iodide, C_3H_7I, $w(C_3H_7I) \geq 98$ %.

4.7 Isopropyl iodide, C_3H_7I, $w(C_3H_7I) \geq 98$ %.

4.8 Internal standard solution. Fill a 1 000 ml volumetric flask with about 200 ml nonane (4.4). Add approximately 2 g of toluene (4.3), weighed to nearest 0,01 g. Fill the flask up to the mark with nonane.

4.9 2-phenoxyethanol, $C_8H_{10}O_2$, $w(C_8H_{10}O_2) \geq 98$ %.

4.10 1,2-propanediol, $C_3H_8O_2$, $w(C_3H_8O_2) \geq 99$ %.

5 Apparatus

Ordinary laboratory apparatus and the following:

5.1 Metal heating block, thermostatically controlled, to fit the pressure resistant digestion vial (5.2), capable of maintaining a temperature of (150 ± 5) °C, or **drying cupboard**, capable of maintaining a temperature of (150 ± 5) °C.

5.2 Pressure resistant digestion vial for hydroiodic cleavage, for example as shown in Figure 1, with a screw top lined with a rubber septum onto which a protective polytetrafluorethylene foil is glued.

5.3 Syringes, with capacities of 1 µl and 50 µl.

5.4 Gas chromatograph, equipped with on-column injector and flame ionization detector (FID) or thermal conductivity detector (TCD).

5.5 Integrator, or **computer-based chromatography data system**.

5.6 Laboratory shaker, or magnetic stirrer suitable for the metal heating block (5.1).

6 Sampling and preparation of the test sample

6.1 General

The sample shall be taken in accordance with ISO 607 and prepared as specified in 6.2.

6.2 Digestion

Weigh approximately 50 mg of the test sample to the nearest 0,1 mg and transfer it into the pressure resistant digestion vial (5.2). Add approximately 150 mg of adipic acid (4.2), 2 ml of hydroiodic acid (4.1) and 2 ml of internal standard solution (4.8). Add a stirring bar if the laboratory shaker or the magnetic stirrer (5.6) is used.

Immediately seal the pressure resistant digestion vial tightly and either place it into the metal heating block (5.1) set at (150 ± 5) °C [(130 ± 5) °C if the laboratory shaker or the magnetic stirrer (5.6) is used] or in the drying cupboard (5.1) set at (150 ± 5) °C. Maintain the corresponding temperature for 1,5 h ± 5 min [1 h ± 5 min in case of the metal heating block (5.1) without the laboratory shaker or the magnetic stirrer (5.6)].

Cool to room temperature.

Shake vigorously in order to obtain a phase separation.

Inject with the 1 μl syringe (5.3) 0,3 μl of nonane phase into the gas chromatograph for the analysis.

NOTE 1 Strict adherence to the specified conditions is important because the digestion is relatively sensitive to temperature variations.

NOTE 2 The fully digested samples can be kept sealed up to 38 h at 4 °C. Older or tapped test samples give misleading results.

7 Procedure

7.1 Chromatography conditions

Detector:	FID or TCD;
Injector:	on-column;
Carrier gas:	helium;
Column:	fused silica capillary column, coated with a stationary phase of 3 % volume units of cyanopropylpolysiloxane/3 % volume units of phenylpolysiloxane/94 % volume unit of methyl polysiloxane;
	length: 30 m;
	internal diameter: 0,25 mm;
	film thickness: 1 μm;
Temperature programme:	60 °C, 3 min isothermal;
	60 °C to 130 °C, 6 °C/min;
	130 °C to 280 °C, 15 °C/min;
	280 °C, 20 min isothermal.
Injector temperature:	130 °C;
Detector temperature:	200 °C.

NOTE If the separation is comparable to that demonstrated by the chromatogram as shown in Figure 2, different instruments, columns and conditions can also be used for the GC analysis.

7.2 Calibration

Add the following substances in sequence to the pressure resistant digestion vial (5.2):

— about 50 mg of adipic acid (4.2);

— 2,00 ml of internal standard solution (4.8);

— 2 ml of hydroiodic acid (4.1).

Use the 50 µl syringe (5.3) to introduce 50 µl of isopropyl iodide (4.7) or 45 µl of ethyl iodide (4.5) (about 100 mg) through the septum. Weigh the vial, then shake vigorously.

NOTE Phase separation is allowed to occur.

7.3 Determination

Chromatograph the test samples and calculate the response factors as specified in 7.4.

NOTE Daily recalibration is unnecessary. The accuracy of the response factors can be monitored with the help of test samples prepared from defined amounts of 2-phenoxyethanol and 1,2-propanediol. For the determination of methoxy groups, methyl iodide should be used for calibration and test samples prepared from defined amounts of vanillin [minimum purity of 99 % (*m*/*m*)] for monitoring the accuracy of the response factors.

7.4 Calculation

The results are calculated using the internal standard method to derive the relative response factors.

Calculate the relative response factors (f_i) from the equation (1):

$$f_i = \frac{m_i / F_i}{m_o / F_o} \qquad (1)$$

where:

m_i is the mass of alkyl iodide in the calibrating solution, in grams;

m_o is the mass of the internal standard in the calibrating solution, in grams;

F_i is the peak area of the alkyl iodide in the calibrating solution, in peak area units;

F_o is the peak area of the internal standard, in peak area units.

The factors shall be determined with pure alkyl iodides.

8 Expression of results

Calculate the content of ethylene oxide *w*(EO) and propylene oxide *w*(PO), expressed as percent by mass, using the equations (2) to (4) as follows:

$$m_i = f_i \frac{F_i}{F_o} m_o \qquad (2)$$

$$w(\mathrm{EO}) = \frac{m_i}{m} \times \frac{M_{\mathrm{EO}}}{M_{\mathrm{C_2H_5I}}} \times 100 \qquad (3)$$

$$w(\mathrm{PO}) = \frac{m_i}{m} \times \frac{M_{\mathrm{PO}}}{M_{\mathrm{C_3H_7I}}} \times 100 \times 1{,}33 \qquad (4)$$

where:

m_i is the mass of alkyl iodide in the calibrating solution, in grams;

m_o is the mass of the internal standard in the calibrating solution, in grams;

m is the initial mass of the test sample, in grams;

M_{EO} is the molar mass of EO, in grams per mol (M_{EO} = 44,05 g/mol);

$M_{C_2H_5I}$ is the molar mass of C_2H_5I, in grams per mol ($M_{C_2H_5I}$ = 155,97 g/mol);

M_{PO} is the molar mass of PO, in grams per mol (M_{PO} = 58,08 g/mol);

$M_{C_3H_7I}$ is the molar mass of C_3H_7I, in grams per mol ($M_{C_3H_7I}$ = 169,99 g/mol);

1,33 is a correction factor.

Calculate the sum of n- and isopropyl iodide.

Express the results to one decimal place.

NOTE 1 The correction factor accounts for the incomplete transformation of the propylene oxide groups. It is a constant and does not depend on the particular reaction conditions used.

NOTE 2 Under the given conditions, a baseline separation of the alkyl iodides is observed so that there is no need for involving correction calculations.

9 Precision

9.1 Repeatability limit

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 not exceed the repeatability limit, r, in more than 5 % of cases.

For the compounds used in the ring test, two determinations shall not differ more than the corresponding repeatability limit, r, given in annex A. Precision data from ring tests evaluated in accordance with ISO 5725-2 are shown in annex A.

9.2 Reproducibility limit

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 not exceed the reproducibility limit, R, in more than 5 % of cases.

For the compounds used in the ring test, two determinations shall not differ more than the corresponding reproducibility limit, R, given in annex A. Precision data from ring tests evaluated in accordance with ISO 5725-2 are shown in annex A.

10 Test report

The test report shall include the following information:

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

b) a reference to this European Standard;

c) any details of the gas chromatograph (5.4) used, including chromatography conditions (7.1);

d) the results calculated according to 7.4 and clause 8;

e) any unusual features noted during the determination;

f) details of any operations not specified in this European Standard or the European Standards to which reference is made, and any operations regarded as optional, as well as any incidents likely to have affected the results.

Annex A
(informative)

Ring test results
(CESIO/AISE Ring test 408-1-92)

A.1 Test sample 1 (long-chain alcohol-ethoxylate-propoxylate), EO

Number of collaborative laboratories	8
Number of outliers	-
Total number of values	36
Total mean value ($\overline{w}$)	37,3 % (*m*/*m*)
Repeatability standard deviation, s_r	3,96 % (*m*/*m*)
Repeatability limit, r : ($r = 2{,}8 \times s_r$)	11,09 % (*m*/*m*)
Repeatability coefficient of variation	10,6 %
Reproducibility standard deviation, s_R	4,65 % (*m*/*m*)
Reproducibility limit, R : ($R = 2{,}8 \times S_R$)	13,02 % (*m*/*m*)
Reproducibility coefficient of variation	12,5 %

A.2 Test sample 1 (long-chain alcohol-ethoxylate-propoxylate), PO

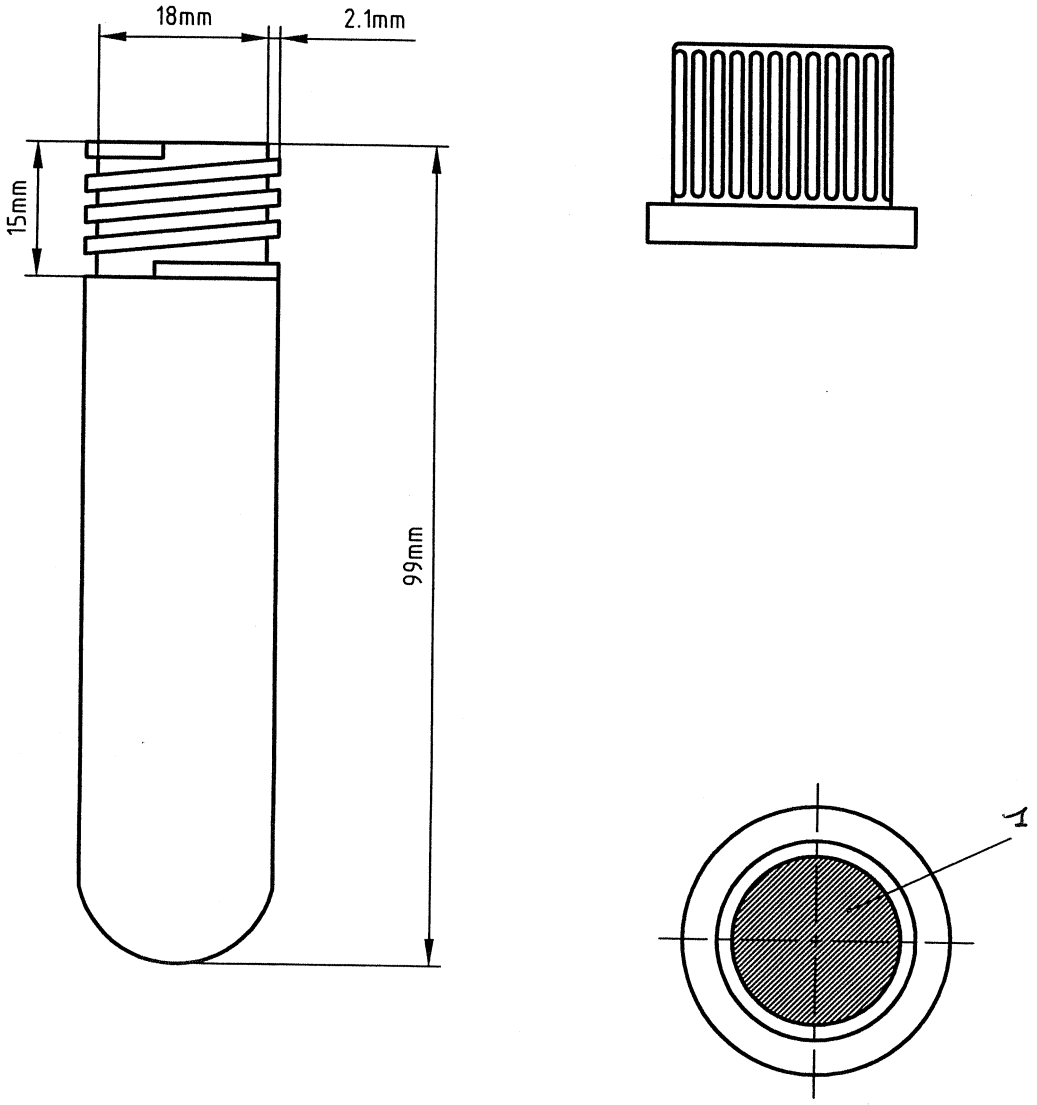
Number of collaborative laboratories	8
Number of outliers	1
Total number of values	22
Mean value ($\overline{w}$)	31,2 % (*m*/*m*)
Repeatability standard deviation, s_r	0,75 % (*m*/*m*)
Repeatability limit, r : ($r = 2{,}8 \times s_r$)	2,09 % (*m*/*m*)
Repeatability coefficient of variation	2,4 %
Reproducibility standard deviation, s_R	1,37 % (*m*/*m*)
Reproducibility limit, R : ($R = 2{,}8 \times S_R$)	3,85 % (*m*/*m*)
Reproducibility coefficient of variation	4,4 %

A.3 Test sample 2 (ethoxylate-propoxylate), EO

Number of collaborative laboratories	7
Number of outliers	1
Total number of values	21
Mean value ($\overline{w}$)	78,5 % (*m*/*m*)
Repeatability standard deviation, s_r	2,34 % (*m*/*m*)
Repeatability limit, r : (r = 2,8 × s_r)	6,54 % (*m*/*m*)
Repeatability coefficient of variation	3,0 %
Reproducibility standard deviation, s_R	3,85 % (*m*/*m*)
Reproducibility limit, R : (R = 2,8 × S_R)	10,77 % (*m*/*m*)
Reproducibility coefficient of variation	4,9 %

A.4 Test sample 2 (ethoxylate-propoxylate), PO

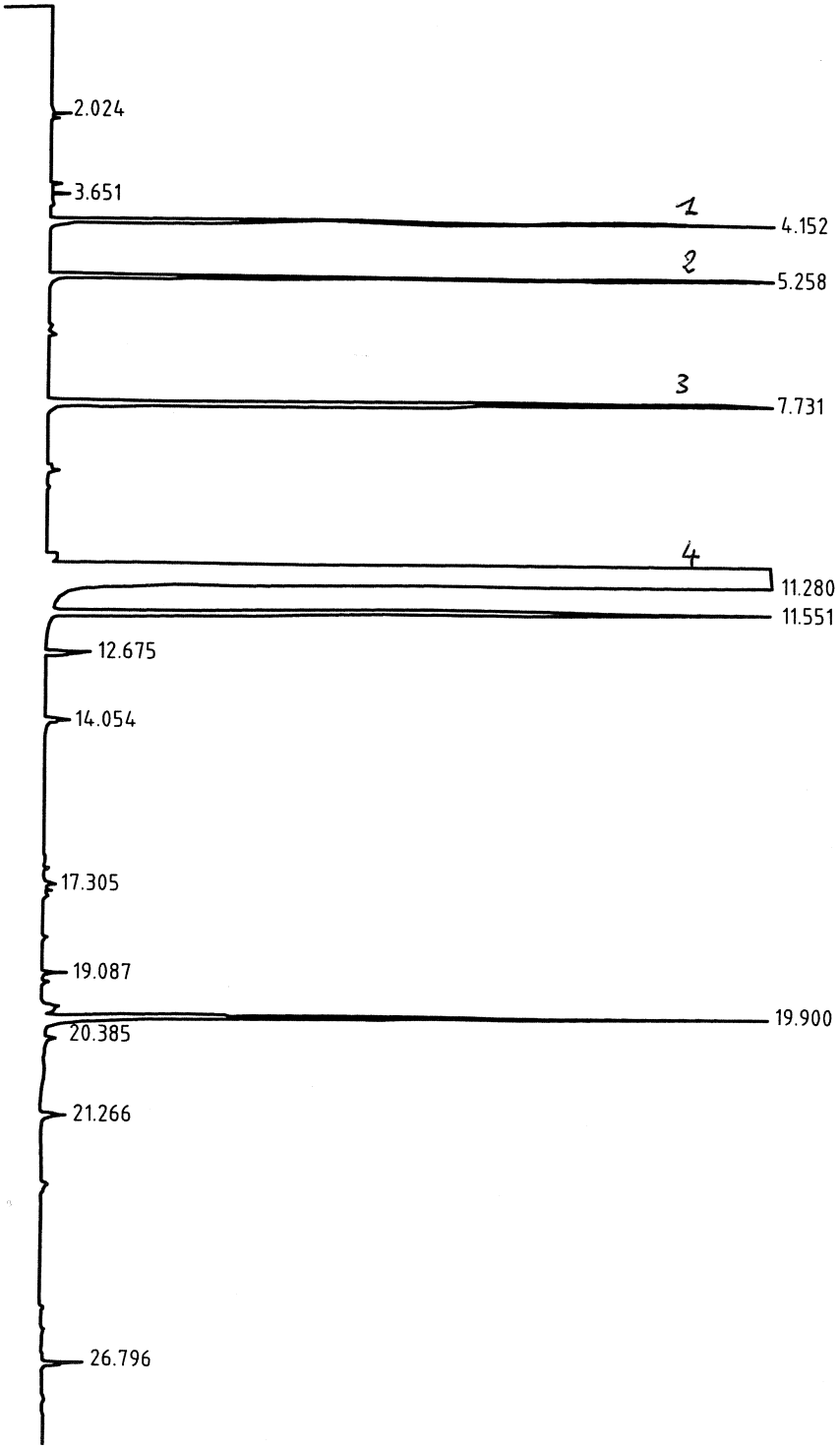
Number of collaborative laboratories	7
Number of outliers	1
Total number of value	21
Mean value ($\overline{w}$)	21,2 % (*m*/*m*)
Repeatability standard deviation, s_r	0,47 % (*m*/*m*)
Repeatability limit, r : (r = 2,8 × s_r)	1,31 % (*m*/*m*)
Repeatability coefficient of variation	2,2 %
Reproducibility standard deviation, s_R	1,00 % (*m*/*m*)
Reproducibility limit, R : (R = 2,8 × S_R)	2,81 % (*m*/*m*)
Reproducibility coefficient of variation	4,7 %



Key

1 Rubber seal with foil of polytetrafluorethylene (PTFE)

Figure 1 — Example of a glass digestion vial



Key

1 Ethyl iodide
2 Isopropyl iodide
3 Toluene (internal standard)
4 Solvent

Figure 2 — Typical chromatogram

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