# British Standard

BRITISH STANDARD

BS EN
13628-2:2002

# Packaging — Flexible packaging material — Determination of residual solvents by static headspace gas chromatography —

## Part 2: Industrial methods

The European Standard EN 13628-2:2002 has the status of a British Standard

ICS 55.040



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British Standards

# National foreword

This British Standard is the official English language version of EN 13628-2:2002.

The UK participation in its preparation was entrusted by Technical Committee PKW/5, Primary and transport packaging, to Subcommittee PKW/5/26, Packaging made from flexible materials, which has the responsibility to:

— aid enquirers to understand the text;

— present to the responsible international/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 subcommittee can be obtained on request to its secretary.

**Cross-references**

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This British Standard, having been prepared under the direction of the Consumer Products and Services Sector Policy and Strategy Committee, was published under the authority of the Standards Policy and Strategy Committee on 21 October 2002

**Summary of pages**

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EUROPEAN STANDARD

NORME EUROPÉENNE

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# EN 13628-2

October 2002

ICS 55.040

English version

# Packaging - Flexible packaging material - Determination of residual solvents by static headspace gas chromatography - Part 2: Industrial methods

Emballage - Matériaux d'emballages souples - Détermination des solvants résiduels par chromatographie en phase gazeuse et espace de tête statique - Partie 2: Méthodes industrielles

Verpackung - Flexible Packstoffe - Bestimmung der Restlösemittel durch statische Dampfraumanalyse mittels Gaschromatographie - Teil 2: Industrielle Verfahren

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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 13628-2:2002 E

# Contents

## Foreword

This document EN 13628-2:2002 has been prepared by Technical Committee CEN/TC 261 "Packaging", 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 April 2003, and conflicting national standards shall be withdrawn at the latest by April 2003.

This standard is part of a standard for determination of residual solvents by static headspace gas chromatography, which is published in two parts:

- *Part 1: Absolute methods*

- *Part 2: Industrial methods*

This part of EN 13628 should be read in conjunction with EN 13628-1.

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, Malta, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and the United Kingdom.

## 1 Scope

This part of this European Standard specifies rapid methods as commonly used in quality control for monitoring the level of residual solvents used in the production of flexible packaging by static headspace chromatography. The procedures described in this part involve one single injection of the headspace which implies an incomplete extraction of the solvent. The values obtained may be lower than the absolute content which should be determined according to Part 1. Residues from thermal decomposition products are not within the scope of this standard.

The method is applicable to flexible packaging materials that may consist of mono- or multilayer plastic films, paper or board, foil or combinations thereof.

This method does not apply to residual solvents with amounts lower than 0,5 mg/m².

## 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).

ISO 2859-1, *Sampling procedures for inspection by attributes - Part 1: Sampling schemes indexed by acceptance quality limit (AQL) for lot-by-lot inspection*.

ISO 2859-2, *Sampling procedures for inspection by attributes - Part 2: Sampling plans indexed by limiting quality (LQ) for isolated lot inspection*.

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

Specimens of the flexible packaging material are placed in a hermetically closed vial and heated under closely controlled conditions of time and temperature to vaporize solvents into the headspace. The amount of solvent released into the headspace is determined by transferring an aliquot of the headspace into a gas chromatograph for analysis. The transfer may be performed:

a) by specific semi-automatic or automatic systems which allow pressurization of the heated vials;

b) manually or automatically by using a heated gastight syringe or a loop without pressurization of the heated vials.

The relative amount of residual solvent is determined by single headspace extraction using external or internal standards.

NOTE For reproducibility the same incubation conditions should be used for each single analysis. During the analysis, there could be interferences from possible products of thermal decomposition. Additional peaks due to these products should not be considered for evaluation of residual solvents.

# 4 Reagents

## 4.1 General

All reagents shall be of a recognized analytical reagent grade.

NOTE Grades stated as being suitable for chromatography can be commercially available and are recommended for use as reference for standard calibration solutions. Appropiate safety precautions should be used when handling toxic and/or flammable solvents.

**4.2 Reference solvents,** for the preparation of standard calibration solutions.

**4.3 Dilution solvent,** with a retention time different from those of residual solvents in the sample.

NOTE Solvents such as hexane, cyclohexanaone, acid amides and glycerol triacetate (triacetin) are appropriate.

# 5 Apparatus

**5.1 Glass vials,** of capacity 6 ml, 8 ml, 20 ml, 50 ml or 100 ml depending upon the specific requirements of accessory equipment, for example, the headspace sampler, fitted with an inert septum seal and aluminium crimp tops. The septum seal shall neither absorb nor release volatile components, shall be gas tight during incubation and shall permit samples of the headspace gas to be withdrawn by syringe for subsequent analysis.

NOTE Elastomers lined with polytetrafluoroethylene (PTFE) are suitable materials for septum seals.

**5.2 Crimping tool,** for sealing the vials with the aluminium crimp tops.

**5.3 Seal removing tool.**

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

**5.5 Template,** for cutting samples. The dimensions of this template shall be matched to the vial volume used.

**5.6 Scalpel, or sharp knife.**

**5.7 Syringes** (e.g. 1 µl, 10 µl)

**5.8 Gas chromatograph,** having a flame ionization detector or equivalent for the solvents to be determined.

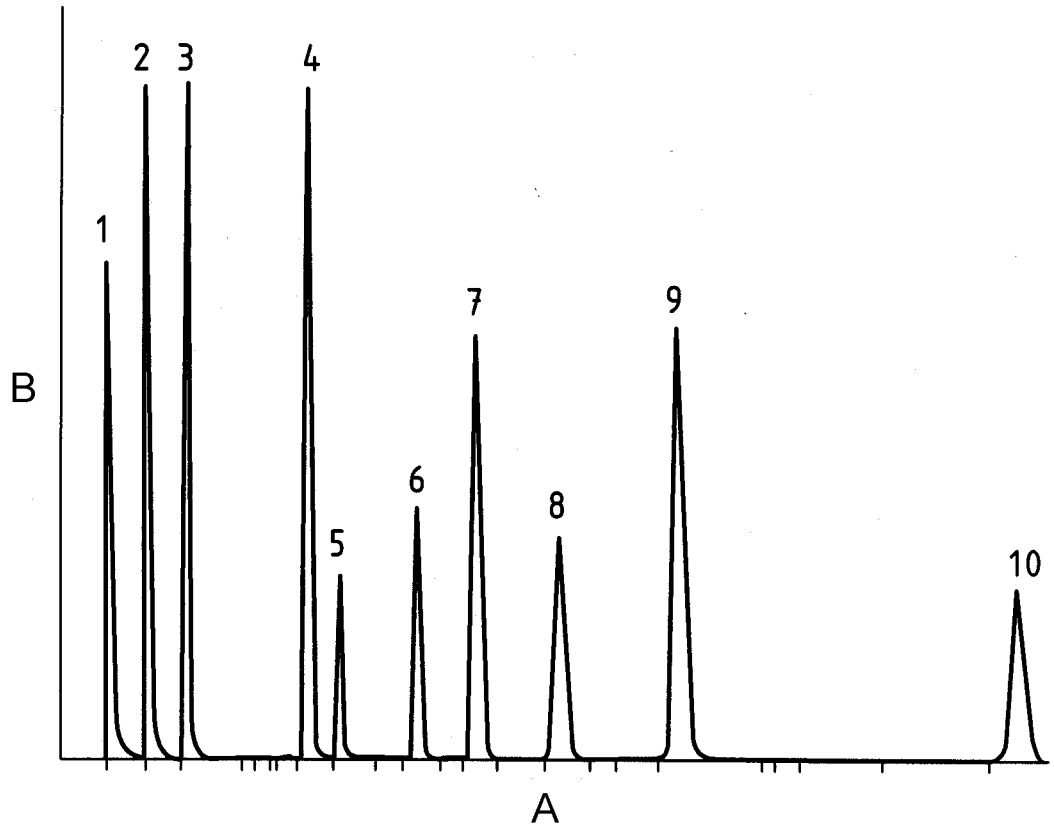
**5.9 Gas chromatographic column,** either packed or capillary, that will give good resolution of the solvents to be determined from any other components that might be injected with the specimen of the headspace.

Examples for suitable columns and operation conditions are:

a) Packed column

length: 3 m;
internal diameter: 3,2 mm;
column filling: 80/120 mesh graphitised carbon, deactivated with polyethyleneglycol;
carrier gas: $N_2$, 20 ml/min;
injector temperature: 220 °C;
temperature programme: 80 °C; raised to 160 °C at 6 °C/min; raised to 225 °C at 1,5 °C/min; held for 16 min

NOTE 1 A corresponding chromatogram obtained for a mixture of solvents is shown in Figure 1.




**Key**

1 4,23 methanol
2 6,67 ethanol
3 9,25 acetone
4 17, 06 ethyl acetate
5 19,1 butanol
6 23,34 trichloroethylene
7 28,4 isobutyl acetate
8 33,87 methyl isobutyl ketone
9 41,86 toluene
10 64.06 xylene

A Retention time (min)
B Peak height

**Figure 1 — Example of chromatogram obtained with a packed column**

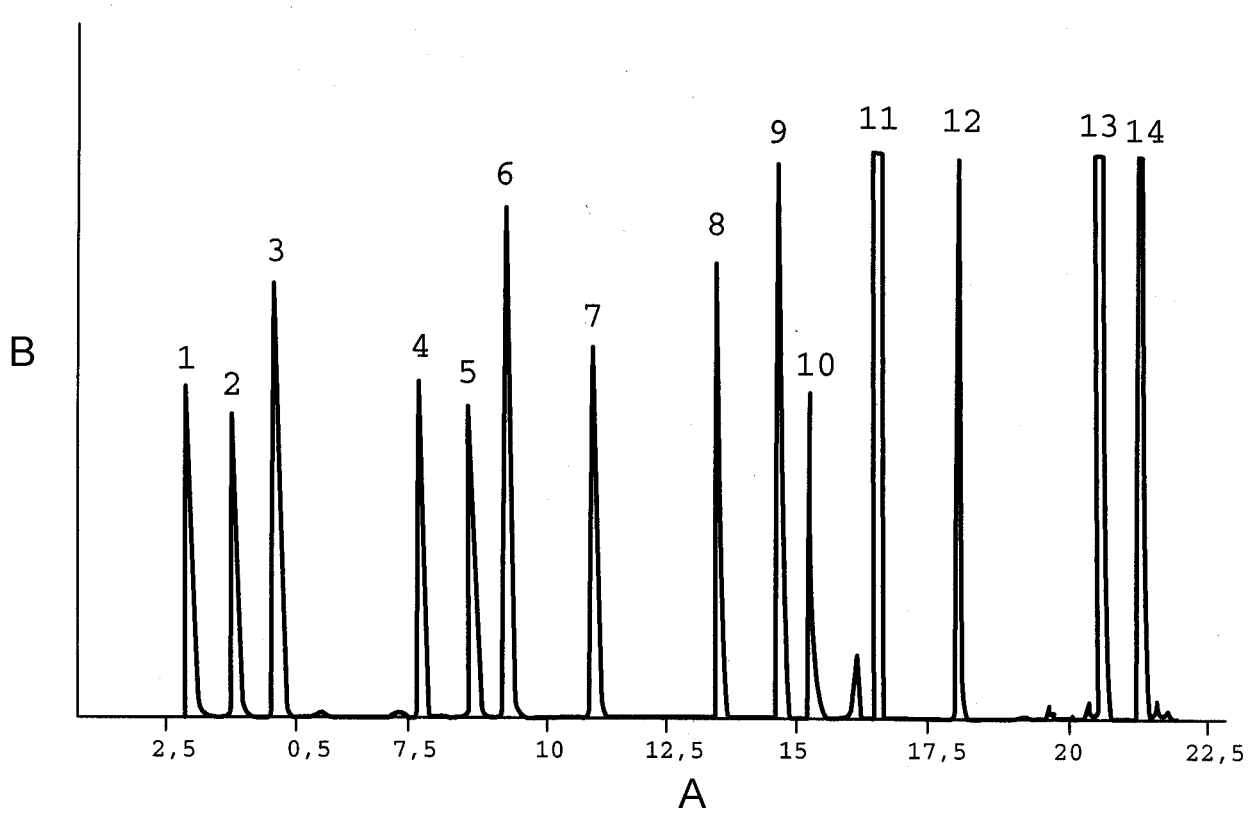
or

b) Capillary column: (fused silica):

length : 30 m;
internal diameter : 0,32 mm;
stationary phase : Poly(dimethylsiloxane) film thickness 3µm;
carrier gas : He 1,7ml/min;
carrier gas split ratio : 1:20;
injector temperature : 230 °C;
detector (flame ionisation) temperature : 280 °C;

temperature programme: 50 °C held for 5 min; raised to 100 °C at 5 °C/min; raised to 250 °C at 10 °C/min.

NOTE 2 A corresponding chromatogram is shown in Figure 2.




**Key**

1 Methanol
2 Ethanol
3 Isopropanol
4 Methyl ethyl ketone
5 Ethyl acetate
6 Isobutanol
7 Isopropyl acetate
8 n-propyl acetate
9 Methyl isobutyl ketone
10 Etoxypropanol
11 Toluene
12 n-butyl acetate
13 Xylene
14 Butyl cellosolve

A Retention time (min)
B Peak height

**Figure 2 — Example of chromatogram obtained with a capillary column**

NOTE Other apparatus which is more specific to the alternative methods is identified under the relevant clauses.

# 6 Sampling

Sampling shall be in accordance with internal quality control procedures.

Sampling shall follow ISO 2859-1 and ISO 2859-2.

Samples of packaging materials that are to be analyzed shall be handled and stored so as to prevent either loss of volatile solvents or contamination by absorption of volatile solvents that may be present in the surrounding atmosphere. Sampling and analysis shall be done in a place where the air is solvent-free to reduce the problem of contamination from the surroundings due to the low concentration of residual solvents in the samples.

NOTE If samples need to be stored they should be in tightly packed roll form if possible.

Sheet samples may be prepared from the roll by cutting out a square window (several layers of sheets) with a knife.

When in form of sheets they should be stacked tightly together to form a compact “block” and wrapped tightly in a barrier material, preferably aluminium foil with a thickness of 30 μm to 40 μm. For storage periods of more than one hour the wrapped samples should be stored at temperatures below 5 °C and in an atmosphere free of volatile contaminants.

# 7 Test specimens

## 7.1 Specimen area in relation to vial volume

The specimen area to be cut out shall depend on the vial volume and the level of residual solvents to be determined in the material. Usually the ratio between the specimen area (in $cm^2$) and the vial volume (in ml) shall be between three and five. The specimens shall be cut out using an appropriate template (**5.5**).

NOTE As an example, for a vial with a volume of 6 ml to 9 ml a specimen of 30 $cm^2$ (2 cm × 15 cm) can be used or proportional dimensions for other volumes.

### 7.2 Test specimens

From a representative sample (see clause **6**) cut a specimen using a template (**5.5**). Coil the specimen rapidly and immediately put it into the vial. Crimp the vial immediately to seal it.

The following precautions shall be taken:

- the different steps of the preparation shall be done very rapidly to avoid evaporation of the solvents;

- the specimens shall always be cut at a defined place e.g. on the same drawing printed on the same place in the width and the template for cutting shall always be placed in the same manner.

# 8 Incubation of the test specimens

Incubation temperature and time shall be chosen to suit the materials being tested and the solvents likely to be present. Conditions used shall be included in the test report.

NOTE Incubation conditions of 110 °C for 20 min are recommended.

In order to compare residual solvent levels, incubation conditions used shall be the same. To ensure repeatability, the temperature shall be accurate to ± 2 °C and time shall be accurate to ± 0,5 min.

# 9 Procedure

## 9.1 General

Quantitative analysis of residual solvents shall be carried out using one of the two methods of static headspace chromatography described in this clause, as appropriate. The methods are:

- semi-automatic or automatic injection (see **9.2**); and

- manual injection (see **9.3**).

## 9.2 Semi-automatic or automatic injection

### 9.2.1 General

This method shall be used where a semi-automatic or automatic headspace sampler is available which has an integrated system to heat the sample vials before automatic withdrawal and injection of an aliquot of the headspace.

NOTE The advantage of this method is a high precision determination of residual solvents with a relatively low work load.

### 9.2.2 Apparatus (additional to clause 5)

#### 9.2.2.1 Automatic or semi-automatic headspace sampler.

#### 9.2.2.2 Syringe, 0,5 µl.

### 9.2.3 Preparation of standard solutions

Prepare a mix of reference solvents (**4.2**) of same quantities by mass.

NOTE If necessary the mixture can be diluted. Care should be taken when weighing solvents because of loss by evaporation.

### 9.2.4 Chromatographic parameters

Parameters shall be selected to suit the type of column and the specific equipment used for the determination.

NOTE Examples of suitable parameters are given in **5.9**.

### 9.2.5 Determination with an external standard

#### 9.2.5.1 Analysis of the standard solution

Incubate a vial containing 1,0 µl of standard solution at a time and temperature determined in accordance with clause **8**.

Withdraw a part of the headspace from the vial and inject into the chromatographic column.

NOTE For equipment using pressurization, a pressurization time of 3 min and an injection time of 0,1 min are typical settings.

#### 9.2.5.2 Determination with the specimen

With a vial containing the specimen prepared in accordance with clause **7**, perform the analysis described in **9.2.5.1**

### 9.2.6 Determination with an internal standard

#### 9.2.6.1 Determination of response factors

Using a syringe (**5.7**) inject 1,0 µl to 10 µl of standard solution (see **9.2.3**) in a crimped vial (**5.1**) and using another syringe (**9.2.2.2**) inject a volume of 0,2 µl to 0,5 µl of a solvent used as internal standard. Perform the analysis described in **9.2.5.1**.

NOTE Internal standard solvent should never be present in the tested sample. The volume injected should be completely volatilised under the conditions of the analysis. The chemical character of the internal standard should be the same as the solvent to be determined.

#### 9.2.6.2 Determination with the specimen

In a crimped vial containing the specimen prepared in accordance with clause **7**, inject through the septum, using a syringe, the same volume of internal standard as in **9.2.6.1** and proceed as in **9.2.5.1**.

### 9.2.7 Results

#### 9.2.7.1 External standard method

The quantity of one residual solvent *Q,* in the sample, expressed in milligrams per square metre (mg/m²), is given by the equation:

$$Q = \frac{a \cdot p}{e \cdot S} \qquad (1)$$

where

*a* is the peak area on the chromatogram for this solvent;

*p* is the mass of the same solvent in standard solution expressed in milligrams (mg);

*e* is the peak area of the same solvent in standard solution;

*S* is the area of specimen expressed in square metres (m²).

#### 9.2.7.2 Internal standard method

The response factor *C* of one solvent is given by the equation:

$$C = \frac{S_i \cdot y}{S_n \,.\, p_c} \qquad (2)$$

where

$S_n$ is the peak area on the chromatogram for the same solvent in the standard solution;

$y$ is the mass of the same solvent in the vial expressed in milligrams (mg);

$S_i$ is the peak area on the chromatogram for internal standard;

$p_C$ is the mass of internal standard injected in the vial expressed in milligrams (mg).

The quantity of one residual solvent $Q$, expressed in milligrams per square metre (mg/m$^2$) of packaging material, is given by the equation:

$$Q = \frac{a \cdot C \cdot p_q}{e \cdot S} \qquad (3)$$

where

$a$ is the peak area for this solvent on chromatogram;

$p_q$ is the mass of internal standard injected in the vial expressed in milligrams (mg);

$e$ is the peak area of the internal standard on the chromatogram;

$S$ is the surface area of specimen expressed in square metres (m²).

## 9.3 Manual injection

### 9.3.1 General

This method shall be applied when a semi-automatic or automatic headspace sampler with an integrated heating step is not available.

NOTE This method involves manual injection with a pre heated syringe from vials incubated in an oven or a metal heating block.

### 9.3.2 Apparatus (additional to clause 5)

Additional apparatus required is as follows.

**9.3.2.1 Thermostatically controlled oven,** capable of maintaining a constant temperature in the range of (50 to 150) ºC ± 2 °C or equivalent metal heating block thermostat, which is suitable to hold the vials tightly.

**9.3.2.2 2 ml syringe,** gas-tight, designed with minimum deadspace, and able to withstand the high pressure developed when injecting a sample, without leakage. The plunger tip shall be made from PTFE with an internal O-ring to prevent loosening of the seal caused by cold flow of the PTFE. Needles shall be non-coring and of side port type.

### 9.3.3 Preparation of standard solutions

Prepare a mix of standard solvents (**4.2**) of the same quantities by mass.

NOTE If necessary the mixture can be diluted. Care should be taken when weighing solvents because of loss by evaporation.

### 9.3.4 Chromatographic parameters

Chromatographic parameters shall be selected to suit the type of column and the specific equipment used for the determination.

NOTE Examples of suitable parameters are given in **5.9**.

#### 9.3.5 Determination

Sample the headspace using the gas tight syringe (**9.3.2.2**) preheated preferably to the vial temperature but to at least 50 °C in the oven (**9.3.2.1**). For handling the heated equipment use gloves.

To determine the level of residual solvents in the packaging material using this apparatus follow steps **9.2.4** to **9.2.5.2** as per automatic injection.

#### 9.3.6 Results

Calculate the quantity *Q* of each residual solvent in accordance with **9.2.6**.

## 10 Precision data

Repeatability and reproducibility shall be determined according to ISO 5725-2, within each laboratory.

NOTE Precision is not known because inter laboratory data is not available.

## 11 Test report

The test report shall include the following information:

a) the list of solvents and their amounts determined, ignoring amounts < 0,5 mg/m²;

b) reference to this standard and indication of the method used;

c) the date of the test;

d) type of instrument used and operating conditions;

e) a description of the material tested;

f) sample area and vial volume;

g) the time and temperature for incubation of test specimens;

h) the composition of standards used;

i) any unusual features noted during the determination;

j) any deviation from the method.

*blank*

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