BS EN 16453:2014

BSI Standards Publication

Pulp, paper and paperboard — Determination of phthalates in extracts from paper and paperboard

bsi.

...making excellence a habit.™

National foreword

This British Standard is the UK implementation of EN 16453:2014.

The UK participation in its preparation was entrusted to Technical Committee CW/47/3, Paper and board in contact with food.

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

This publication does not purport to include all the necessary provisions of a contract. Users are responsible for its correct application.

ISBN 978 0 580 79012 6

ICS 67.250; 85.060

Compliance with a British Standard cannot confer immunity from legal obligations.

This British Standard was published under the authority of the Standards Policy and Strategy Committee on 31 January 2014.

Amendments issued since publication

Date	Text affected

EUROPEAN STANDARD

NORME EUROPÉENNE

EUROPÄISCHE NORM

EN 16453

January 2014

ICS 67.250; 85.060

English Version

Pulp, paper and paperboard - Determination of phthalates in extracts from paper and paperboard

Pâtes, papier et carton - Dosage des phtalates dans des extraits de papier et carton

Zellstoff, Papier und Karton - Bestimmung von Phthalaten in Papier- und Kartonextrakten

This European Standard was approved by CEN on 9 November 2013.

CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration. Up-to-date lists and bibliographical references concerning such national standards may be obtained on application to the CEN-CENELEC Management Centre or to any CEN member.

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 CEN-CENELEC Management Centre has the same status as the official versions.

CEN members are the national standards bodies of Austria, Belgium, Bulgaria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, Former Yugoslav Republic of Macedonia, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland, Turkey and United Kingdom.

EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

CEN-CENELEC Management Centre: Avenue Marnix 17, B-1000 Brussels

Contents

Page

Foreword

This document (EN 16453:2014) has been prepared by Technical Committee CEN/TC 172 “Pulp, paper and board”, the secretariat of which is held by DIN.

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 July 2014, and conflicting national standards shall be withdrawn at the latest by July 2014.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. CEN [and/or CENELEC] shall not be held responsible for identifying any or all such patent rights.

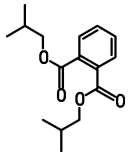
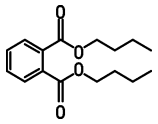
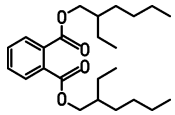
According to the CEN-CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Bulgaria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, Former Yugoslav Republic of Macedonia, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland, Turkey and the United Kingdom.

1 Scope

This European Standard specifies an analytical test method for the determination of phthalates in water, solvent and modified polyphenylene oxide (MPPO) extracts of paper and board materials and articles intended for food contact using gas chromatography coupled to mass spectrometry (GC-MS).

This method is applicable to the determination of phthalates in concentration ranging from 0,025 mg/l to 0,5 mg/l for water and solvent extracts and 0,002 mg/dm^2 to 0,040 mg/dm^2 for MPPO migration depending on the individual substance, the specified volume used for analysis and the value of the blank.

Table 1 — Phthlates determined by this method

Name	Abbreviation	Formula	CAS N°	Structure
Diisobutyl-phthalate	DIBP	$C_{16}H_{22}O_4$	84–69–5	
Dibutyl-phthalate	DBP	$C_{16}H_{22}O_4$	84–74–2	
Di-(-ethylhexyl)-phthalate	DEHP	$C_{24}H_{38}O_4$	117–81–7	

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

EN 645, *Paper and board intended to come into contact with foodstuffs - Preparation of a cold water extract*

EN 647, *Paper and board intended to come into contact with foodstuffs - Preparation of a hot water extract*

EN 14338, *Paper and board intended to come into contact with foodstuffs - Conditions for determination of migration from paper and board using modified polyphenylene oxide (MPPO) as a simulant*

EN 15519, *Paper and board intended to come into contact with foodstuffs - Preparation of an organic solvent extract*

EN 27213, *Pulps - Sampling for testing (ISO 7213)*

EN ISO 186, *Paper and board - Sampling to determine average quality (ISO 186)*

EN ISO 536, *Paper and board - Determination of grammage (ISO 536)*

EN ISO 638, *Paper, board and pulps - Determination of dry matter content - Oven-drying method (ISO 638)*

EN ISO 18856, *Water quality - Determination of selected phthalates using gas chromatography/mass spectrometry (ISO 18856)*

3 Principle

3.1 General

Phthalates in the test extract from paper and board materials are determined by gas chromatography / mass spectrometry. The test extract is prepared from water, organic solvent and/or MPPO simulant according to respectively: EN 645, EN 647, EN 15519, EN 14338.

Other phthalates, as listed in Table 1, may also be analysed by this procedure but it is necessary to determine its applicability in each case.

3.2 Interferences

Due to their use as plasticizer agents, phthalates are ubiquitous. Therefore, pay special attention to avoid any contamination. In order to avoid interferences and cross contamination, do not use plastics materials (tubes etc.).

Cross contamination is likely to occur with laboratory air. Therefore, remove as far as possible, plastic materials from the laboratory. Cleaning agents often contain phthalates and may severely contaminate the laboratory air if in use regularly. Therefore, refrain from using these agents during application of this procedure.

Phthalates may bleed from the septa of the injector port into the gas chromatograph, therefore use septa that are not likely to contaminate the system.

Fittings of syringes or equipment and septa of the sampling bottles may as well contain phthalates.

4 Materials

4.1 General

Common laboratory glassware, rinsed with ethyl acetate before use. After rinsing the glassware with solvent, let residual solvent evaporate under a fume hood. In case of contamination, special attention should be paid to the volumetric flasks cleaning. For example the non-volumetric glassware could be cleaned in a furnace at 500°C for at least 6 h.

Glassware for volumetric purpose can change its properties due to the heating process and so should not be treated thus.

Phthalates are ubiquitous laboratory contaminants. Each lot of reagent used for this method should be checked for phthalates contamination.

4.2 Pasteur pipettes

4.3 Double mark glass pipette of 0,05 ml, 0,2 ml, 0,5 ml, 1 ml, 5 ml and 10 ml

4.4 Volumetric flasks of 5 ml, 10 ml, 50 ml and 100 ml

4.5 Screw-cap glass bottle PYREX[1)] of 250 ml with a Polytetrafluorethylene-septa cap

4.6 Graduated cylinder of 200 ml

4.7 Round flask of 50 ml and 250 ml

4.8 Glass funnel

4.9 Polytetrafluorethylene-screw-cap glass vial single use (capacity adapted to the volume of concentrate)

5 Apparatus

5.1 Balance: capable of accurately weighing 0,000 1 g

5.2 Round flask heater

5.3 Rotary vacuum evaporator

5.4 Gas chromatograph coupled to a mass spectrometer (GC-MS)

6 Reagents

6.1 General

Use as far as available reagents of analytical quality or better. Use only reagents with negligibly low concentrations of phthalates and verify by blank determinations.

6.2 Operating gases for gas chromatography/mass spectrometry, of high purity and in accordance with manufacturer's specifications

6.3 Ethyl acetate, $C_4H_8O_2$, CAS N° 141-78-6

6.4 Isooctane, C_8H_{18}, CAS N° 540-84-1

Store the following solutions in glass bottles at −18 °C, protected from light.

6.5 Internal standard stock solution: For example d4-ring-deuterated-dibutyl phthalate (D4-ring-DBP) at 10 g/l

6.5.1 General

Weigh for example, approximately 0,1 g with an accuracy of 0,001 g of d4-DBP in a 10 ml volumetric flask (4.4) and bring to volume with ethyl acetate (6.3).

1) PYREX is an example of a suitable product available commercially. This information is given for the convenience of users of this European Standard and does not constitute an endorsement by CEN of this product.

6.5.2 Solution A of internal standard at 100 mg/l in ethyl acetate

Transfer 1 ml of the solution (6.5.1) into a 100 ml volumetric flask (4.4) and dilute to the mark with the ethyl acetate (6.3).

6.5.3 Solution B of internal standard at 10 mg/l in ethyl acetate

Transfer 0,5 ml of the solution A (6.5.2) into a 5 ml volumetric flask (4.4) and dilute to the mark with the ethyl acetate (6.3).

6.5.4 Solution C of internal standard at 0,5 mg/l in ethyl acetate

Transfer 0,25 ml of the stock solution A (6.5.2) into a 50 ml volumetric flask (4.4) and dilute to the mark with the ethyl acetate (6.3).

6.6 Stock solutions of individual phthalate at 1 000 mg/l in ethyl acetate

6.6.1 General

In a 100 ml volumetric flask (4.4), weigh approximately 0,1 g with an accuracy of 0,001 g of each of the reference substances and bring to volume with ethyl acetate (6.3).

6.6.2 Intermediate solution of phthalates at 50 mg/l in ethyl acetate

Transfer 5 ml of each stock solution (6.6.1) into a 100 ml volumetric flask (4.4) and dilute to the mark with ethyl acetate (6.3).

6.6.3 Calibration standard solutions of phthalates in isooctane

Five standard solutions are prepared by transferring respectively: 0,05 ml, 0,1 ml, 0,2 ml, 0,5 ml and 1 ml of the Intermediate solution (6.6.2) in 10 ml volumetric flasks (4.4) and 0,5 ml of the solution B of internal standard (6.5.3) by adjusting the volume with the solvent used for the extract of paper and board, for the preparation of solution having respectively concentrations of about: 0,25 mg/l, 0,5 mg/l, 1 mg/l, 2,5 mg/l and 5 mg/l of phthalate, and 0,5 mg/l of Internal Standard stock solution in each calibration solution.

6.6.4 Individual solutions of phthalates in ethyl acetate à 1 mg/l for determination of GC retention times

Transfer 0,1 ml of stock solution (6.6.1) into a 100 ml volumetric flask (4.4) and dilute to the mark with ethyl acetate (6.3).

7 Sampling

If the analysis is being made to evaluate a lot of paper, board or pulp, the sample shall be selected in accordance with EN ISO 186 or EN 27213, as relevant. If the analysis is made on another type of sample, report the source of the sample, and, if possible, the sampling procedure. Select the specimens so that they are representative of the sample received.

If required, take a separate sample for the determination of the grammage in accordance with EN ISO 536 and/or for the determination of dry matter content with EN ISO 638.

For any storage or transport between sampling and analysis, protect the sample from contamination by using for example aluminium foil to over-wrap

8 Preparation of the test sample of water extract

The water extract of paper or board samples shall be carried out in accordance with EN 645 or EN 647. Every extraction test should be done in duplicate. In parallel, perform a blank analysis.

The determination of the phthalates in the water extract shall be carried out in accordance to EN ISO 18856.

9 Preparation of the test sample of the organic solvent extract

The organic solvent extract of paper or board samples shall be carried out in accordance with EN 15519. The preferred solvent is isooctane but other solvents can also be used. Every extraction test should be done in duplicate before the determination described here.

A specified volume of the solvent extract is taken[2)]. 2 ml of solution C of Internal Standard is added to the organic solvent extract. It is then concentrated in a rotary vacuum evaporator until a final volume of around 2 ml. Transfer the extract to a glass vial with a PTFE-lined screw-cap.

In parallel, perform a blank analysis using a portion of the same batch of (unexposed) organic solvent that was used to extract the paper or board sample.

10 Preparation of the test sample of the MPPO Extract

The MPPO extract of paper or board samples shall be prepared according to the standard method in EN 14338. The solvent used for the extraction of MPPO is ethyl acetate. 0,4 ml of solution B of Internal Standard solution is added to the MPPO before extraction.

Every MPPO extraction test should be done in duplicate before the determination described here.

A specified volume of the 12,5 ml ethyl acetate extract is taken[3)] The ethyl acetate extract is then concentrated in a rotary vacuum evaporator until a final volume of around 2 ml. Transfer the extract to a glass vial with a PTFE-lined screw-cap.

In parallel, perform a blank extraction using a portion of the same batch of (unexposed) MPPO simulant that was used to test the paper or board sample.

11 Procedure

11.1 GC conditions

11.1.1 Example of gas chromatographic conditions

— column: 100 % polydimethylsiloxane;

— 30 metres; 0,25 mm inner diameter; 0,25 µm film thickness;

— carrier gas: Helium;

— injector: 320°C (splitless injection);

— source: at 250°C;

— injection volume 1 µl;

2) For example with 2 ml taken; 0,025 mg/l to 0,5 mg/l of isooctane is in the calibration range

3) For example with 12,5 ml taken; 0,002 mg/dm^2 to 0,040 mg/dm^2 of paper is in the calibration range

— flow rate: 1 ml/min constant flow;

— temperature programme: 100°C (0 min); 10°C/min; 300°C (10 min).

11.1.2 MS conditions

— solvent delay: 5 min;

— total ion scan from 40 mu to 400 mu from 3 min to 20 min;

— single ion chromatogram at 149 mu from 5 min to 14 min for quantification, i. e. the molecular fragment common to the target phthalates;

— reconstructed ion chromatogram at 223 mu and 278 mu for identification of DIBP;

— reconstructed ion chromatogram at 223 mu and 278 mu for identification of DBP;

— reconstructed ion chromatogram at 167 mu and 279 mu for identification of DEHP.

For the internal standard, d4-DBP, the selected ion recording is at 153.

11.2 Calibration

Inject aliquots from the reference solutions. (6.6.3).

Establish the retention times for the individual phthalates and the internal standard using the individual solutions (6.6.4 and 6.5.3). Establish the ratios of main ion to the second ions of each substance.

Construct calibration graphs by plotting the ratio of Phthalate peak area / internal standard peak area versus the concentration of phthalates in the calibration solutions. From the experimental area data, create a linear regression through the standard points.

Use the series of measured values to establish the linear regression function.

11.3 Analysis of test samples

Inject aliquots of each of the duplicate test sample extracts. Inject aliquot of the blank control sample. Using the retention times established for the standards (11.2), locate any phthalate of interest in the chromatograms for the sample extracts.

Under the analytical conditions as described previously, calculate the area of each peak detected using the mass fragment 149 mu for phthalates and 153 mu for internal standard.

For a definite identification, the ratios of main ion to the second ions of each substance are examined. The criterion for correct identifications that this ion ratio for a putative phthalate in the sample extracts should agree to within ± 10 % of the ratio established for the standards.

Determine the concentration of individual substances (C_i) in the blank control sample and in the test samples from each linear equations of the calibration.

12 Expression of results

12.1 For organic solvent extract: Expression of results

Determine the concentration of individual compounds (C_s) in the extracts for each phthalates:

$$C_s = \frac{C_i \cdot V}{V_s} \quad (1)$$

where:

C_s is the concentration of phthalates in mg/l for organic solvent;

C_i is the concentration of phthalate in the reconcentrated extract in mg/l;

V is the volume of the reconcentrated test sample (0,002 l);

V_s is the specified volume of solvent reconcentrated in litre (for example 0,02 l in footnote 2).

12.2 For MPPO extract: Expression of results

Determine the concentration of individual substances (C_s) for each phthalates:

$$C_s = \frac{C_i \cdot V_r \cdot Vt}{V_s \cdot S} \quad (2)$$

where:

C_s is the concentration of phthalates in mg/dm^2;

C_i is the concentration of phthalate in the reconcentrated extract in mg/l;

V_r is the volume of the reconcentrated extract (0,002 l);

V_s is the specified volume of solvent reconcentrated (for example 0,002 l in footnote 3);

V_t it the total volume of the Tenax extraction (0,05 l);

S is the surface area in contact with MPPO (1 dm^2).

13 Test report

The test report shall include the following information:

a) a reference to this European Standard;

b) date and place of testing;

c) complete identification of the sample tested;

d) applied method;

e) results;

f) any deviation from the specified procedure or other circumstances that may have affected the results.

14 Precision data

From an interlaboratory test (n = 7) of isooctane extract of two different samples, prepared centrally and then distributed, the test method described here gave repeatability (r) and reproducibility (R) results as shown in Table 2.

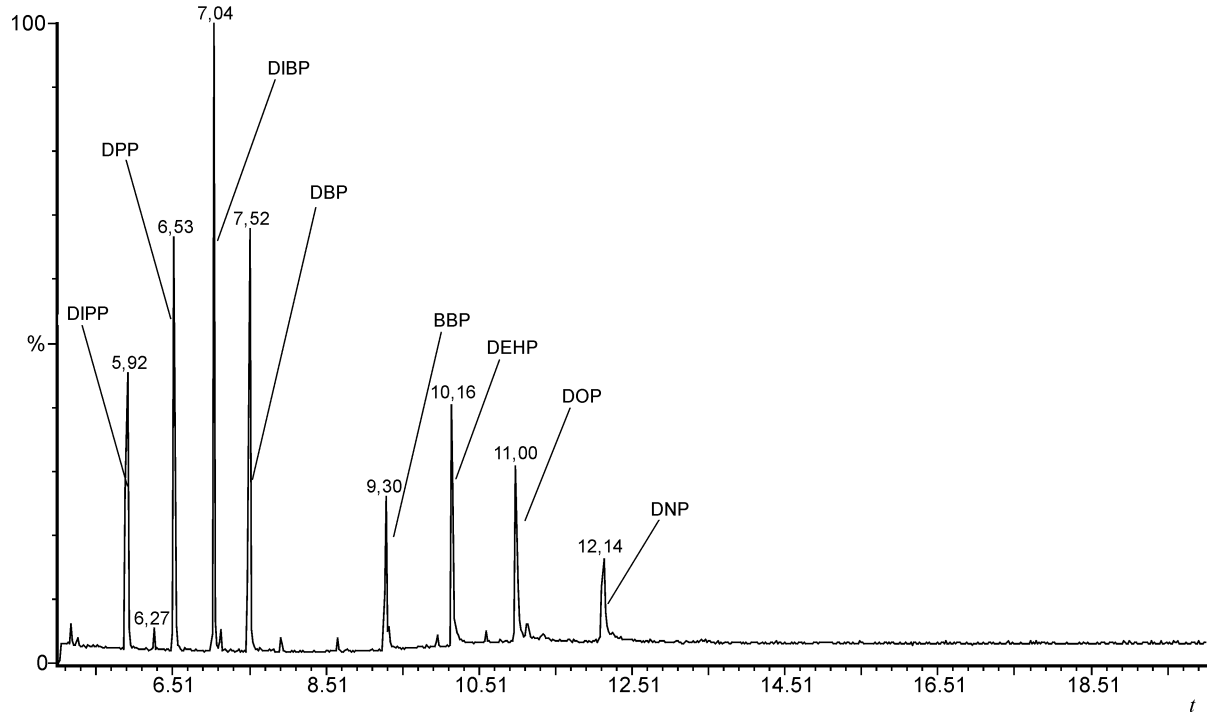
The repeatability (r) has been calculated as the mean coefficient of variation (CV_r) from the three replicates from each laboratory. The reproducibility (R) is given as the coefficient of variation (CV_R) between the means from the laboratories.

Table 2 — Precision data

Extract of sample 1	**Substance**	**Mean value in mg/l in isooctane**	**Repeatability** $C_{V,r}$ %	**Reproducibility** $C_{V,R}$ %
	DIBP	0,29	3,7	25
	DBP	0,04	7,1	49
	DEHP	0,21	7,8	25
Extract of sample 2	**Substance**	**Mean value in mg/l in isooctane**	**Repeatability** $C_{V,r}$ %	**Reproducibility** $C_{V,R}$ %
	DIBP	0,94	5,4	50
	DBP	0,17	5,6	56
	DEHP	0,57	9,0	31

Annex A
(informative)

GC-MS total ion chromatogram of a standard calibration solution of 2 mg/l of phthalates



Key:

DIPP: Diisopropylphthalate
DPP: Dipropylphthalate
DIBP: Diisobutylphthalate
DBP: Dibutylphthalate
BBP: Butylbenzylphthalate
DEHP: Di(2-ethylhexyl)phthalate
DOP: Dioctylphthalate
DNP: Dinonylphthalate

Figure A.1 — GC-MS Total Ion Chromatogram of a standard calibration solution at 2 mg/l of phthalates

This page deliberately left blank

British Standards Institution (BSI)

BSI is the national body responsible for preparing British Standards and other standards-related publications, information and services.

BSI is incorporated by Royal Charter. British Standards and other standardization products are published by BSI Standards Limited.

About us

We bring together business, industry, government, consumers, innovators and others to shape their combined experience and expertise into standards -based solutions.

The knowledge embodied in our standards has been carefully assembled in a dependable format and refined through our open consultation process. Organizations of all sizes and across all sectors choose standards to help them achieve their goals.

Information on standards

We can provide you with the knowledge that your organization needs to succeed. Find out more about British Standards by visiting our website at bsigroup.com/standards or contacting our Customer Services team or Knowledge Centre.

Buying standards

You can buy and download PDF versions of BSI publications, including British and adopted European and international standards, through our website at bsigroup.com/shop, where hard copies can also be purchased.

If you need international and foreign standards from other Standards Development Organizations, hard copies can be ordered from our Customer Services team.

Subscriptions

Our range of subscription services are designed to make using standards easier for you. For further information on our subscription products go to bsigroup.com/subscriptions.

With **British Standards Online (BSOL)** you'll have instant access to over 55,000 British and adopted European and international standards from your desktop. It's available 24/7 and is refreshed daily so you'll always be up to date.

You can keep in touch with standards developments and receive substantial discounts on the purchase price of standards, both in single copy and subscription format, by becoming a **BSI Subscribing Member**.

PLUS is an updating service exclusive to BSI Subscribing Members. You will automatically receive the latest hard copy of your standards when they're revised or replaced.

To find out more about becoming a BSI Subscribing Member and the benefits of membership, please visit bsigroup.com/shop.

With a **Multi-User Network Licence (MUNL)** you are able to host standards publications on your intranet. Licences can cover as few or as many users as you wish. With updates supplied as soon as they're available, you can be sure your documentation is current. For further information, email bsmusales@bsigroup.com.

BSI Group Headquarters

389 Chiswick High Road London W4 4AL UK

Revisions

Our British Standards and other publications are updated by amendment or revision.

We continually improve the quality of our products and services to benefit your business. If you find an inaccuracy or ambiguity within a British Standard or other BSI publication please inform the Knowledge Centre.

Copyright

Useful Contacts:

Customer Services
Tel: +44 845 086 9001
Email (orders): orders@bsigroup.com
Email (enquiries): cservices@bsigroup.com

Subscriptions
Tel: +44 845 086 9001
Email: subscriptions@bsigroup.com

Knowledge Centre
Tel: +44 20 8996 7004
Email: knowledgecentre@bsigroup.com

Copyright & Licensing
Tel: +44 20 8996 7070
Email: copyright@bsigroup.com

bsi.

...making excellence a habit.™