PD CEN/TS 16861:2015

BSI Standards Publication

# Plastics — Recycled plastics — Determination of selected marker compounds in food grade recycled polyethylene terephthalate (PET)

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## National foreword

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

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TECHNICAL SPECIFICATION

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# CEN/TS 16861

June 2015

ICS 13.030.50; 83.080.20

English Version

# Plastics - Recycled plastics - Determination of selected marker compounds in food grade recycled polyethylene terephthalate (PET)

Plastiques - Plastiques recyclés - Détermination de compositions de traceurs sélectionnés dans les poly(téréphtalate d'éthylène) (PET) recyclés de qualité alimentaire

Kunststoffe - Kunststoff-Rezyklate - Bestimmung von Markierungsstoffen in Polyethylenterephthalat (PET)-Rezyklaten für die Lebensmittelindustrie

This Technical Specification (CEN/TS) was approved by CEN on 19 April 2015 for provisional application.

The period of validity of this CEN/TS is limited initially to three years. After two years the members of CEN will be requested to submit their comments, particularly on the question whether the CEN/TS can be converted into a European Standard.

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# Foreword

This document (CEN/TS 16861:2015) has been prepared by Technical Committee CEN/TC 249 “Plastics”, the secretariat of which is held by NBN.

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.

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# Introduction

In addition to drivers such as the recycling targets in the EU waste packaging Directive (94/62/EC) and the economic cost of landfill taxes, there is a strong demand for recycled food grade plastic products from packaging end-users who are concerned about their corporate image and promoting their environmental responsibilities.

To ensure that recycling systems and plants used for recycling plastics from post-consumer waste for food contact use are fit for purpose, the EU Commission published Regulation (EC) 282/2008 in 27th March 2008 (Recycled plastic materials and articles intended to come into contact with foods). Two of the main purposes of Regulation (EC) 282/2008 are to define the conditions under which a recycling process should be run and managed and how an application to EFSA (European Food Safety Authority) to have the process authorized can be made. Even when plastics materials and articles are produced using a recycling process which has been authorized by EFSA, it is essential that they comply with the applicable food contact regulations, such as the Plastics Regulation (EU) 10/2011.

It can take a long time for validation to approve new recycling processes, and the “Challenge” test to demonstrate the effectiveness of recycling processes, which is described in Regulation (EC) 282/2008 and ultimately required by EFSA, can be relatively expensive and time consuming. The analytical method presented in this Technical Specification represents a novel, cost effective and relatively quick quality assurance tool that would support new process development and assist organisations to conform to the EC regulations on recycled plastics. Also, because of its flexibility with respect to sample geometry, and small scale nature, the method can also be used in an ad hoc way to assess the quality of a wide range of recycled PET samples and products, for example flake, pellets, and products such as bottles and trays. The chemical compounds (called Marker compounds) for which the method is validated fall into two categories: those that are representative of the PET plastic (e.g. residual monomers), and the common flavour compound limonene.

This Technical Specification is intended to serve two main purposes:

— to provide an analytical method to enable recyclers and end users of recycled food grade poly(ethyleneterephthalate) (PET) to identify and quantify the level of specific chemical compounds. As such, it provides a means of providing a cost-effective, comparative assessment of its quality in terms of the presence and level of these chemical contaminants;

— to provide a template for the development of analytical methods for the analysis of specific “marker compounds” in other types of recycled food contact materials and articles, for example high density polyethylene (HDPE).

This Technical Specification is intended to complement, but not to replace in any way, the existing chemical analysis tests, such as the EFSA “Challenge” test, used to assess the efficiency of PET recycling processes for food grade products, or the EU overall and specific migration tests on food grade PET materials and articles using food products and/or food simulants. It is not intended to be used as a pass or fail type method, but to enable changes in the level of specific chemical compounds to be detected. This information could then be used in a number of ways, depending upon the exact nature of the samples analysed, such as contributing to the information needed to justify a re-examination of a recycling process using the EFSA “Challenge” test.

This Technical Specification is based on FP7 Project SupercleanQ.

# 1 Scope

This Technical Specification specifies an analytical method for testing food grade, recycled polyethylene terephthalate (PET). This analytical method provides / is intended to be used as a quality control check. This test identifies and quantifies certain specified contaminants. Such contaminants are referred to as Marker Compounds.

The analytical method is applicable for use on PET samples and products at all stages in the recycling process and will therefore be useful to recycling companies producing commercial, recycled PET for food contact materials and articles, and the manufacturers of such articles.

This Technical Specification is without prejudice to any existing legislation.

NOTE Marker compounds are known to originate from two sources:

— from the PET material itself (i.e. residual monomers, degradation products or reaction/breakdown products);

— from food products that the PET has contacted during its “first use”.

**WARNING – The use of this Technical Specification might involve hazardous materials, operations and equipment.**

**Persons using this Technical Specification should be familiar with normal laboratory practise. This document does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practises and to ensure compliance with any national regulatory conditions.**

**IMPORTANT – It is absolutely essential that tests conducted according to this Technical Specification be carried out by suitably trained staff.**

# 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.

CEN/TS 16011, *Plastics - Recycled plastics - Sample preparation*

EN ISO 472, *Plastics - Vocabulary (ISO 472)*

# 3 Terms and definitions

For the purposes of this document, the terms and definitions given in EN ISO 472 and the following apply.

**3.1**
**analyte**
substance to be determined

Note 1 to entry: In the context of this standard 'analyte' refers to the selected marker compounds (3.4) in the PET sample.

**3.2**
**diagnostic ion**
selected fragment ion, molecular ion or other characteristic ion from the mass spectrum of the target compound, chosen to provide good specificity and sufficient sensitivity

**3.3**
**laboratory sample**
sample or subsample(s) sent to or received by the laboratory

Note 1 to entry: In the context of this standard 'laboratory sample' refers to sample of recycled PET, in the form or flakes or pellets, or recycled PET food grade products intended to be used for the laboratory tests and from which the test sample (3.9) will be removed.

Note 2 to entry: When the laboratory sample is further prepared (reduced) by subdividing, cutting, sawing, coring, or by combinations of these operations, the result is the test sample. When no preparation of the laboratory sample is required, the laboratory sample is the test sample. A test portion is removed from the test sample for the performance of the test or for analysis. The laboratory sample is the final sample from the point of view of sampling but it is the initial sample from the point of view of the laboratory.

Note 3 to entry: Several laboratory samples may be prepared and sent to different laboratories or to the same laboratory for different purposes. When sent to the same laboratory, the set is generally considered as a single laboratory sample and is documented as a single sample.

**3.4**
**marker compound**
chemical compound that is a typical contaminant present in post-consumer food grade PET and is the type of species that an approved recycling process is expected to remove to a safe level

Note 1 to entry: The marker compound can originate from either the PET itself or the food products that it has been in contact with during service.

**3.5**
**recycled food grade PET**
recycled PET in the form of flake or pellets from an extruder that has been recycled from post-consumer food grade PET waste using a recycling process that has passed a “Challenge” test and meets the requirements of the EU Regulation (EC) 282/2008

Note 1 to entry: Flake dimensions are typically 2 mm to 5 mm.

**3.6**
**recycled food grade PET products**
PET products, such as bottles and trays, which are intended for food use and have been manufactured from recycled PET that meets the requirements of EU Regulation (EC) 282/2008

**3.7**
**selected ion mode, SIM**
measuring the intensity of selected diagnostic ions only

**3.8**
**standard solution**
solution of accurately known concentration, prepared using standard substances in one or several ways

Note 1 to entry: In the context of this standard a 'standards solution is a solution containing a set of marker compounds (analytical standards) prepared at a known concentration.

**3.9**
**test sample**
sample, prepared from the laboratory sample, from which test portions are removed for testing or analysis

Note 1 to entry: In the context of this standard 'test sample' refers to aliquot of cryogenically ground and sieved laboratory sample (3.3) which will be analysed for the marker compounds.

## 4 Symbols and abbreviations

| | |
|---|---|
| CAS | Chemical abstracts service |
| GC-MS | Gas chromatography with mass spectrometric detection |
| HDPE | High density polyethylene |
| LOD | Limit of detection |
| LOQ | Limit of quantification |
| m/z | Mass [m] to charge [z] ratio i.e. modulus of the quotient of the particle mass in u and the particle charge in units of electronic charge |
| *n* | Number |
| PDMS | Polydimethyl siloxane |
| PET | Polyethylene terephthalate |
| RMS | Root mean square |
| RSD | Relative standard deviation, in % |
| $R^2$ | The square of the Pearson product moment correlation coefficient through data points in known y's and known x's |
| S/N | Signal to noise ratio |

## 5 Principle

The recycled PET sample is cryogenically ground using a laboratory-scale mill and sieved to a prescribed particle size and then accurately weighed into a headspace vial and sealed. The vial is heated and the headspace analysed by GC-MS using a capillary column of low polarity. Concentrations of specific analytes (selected marker compounds) are quantified using a standard addition headspace method. The specific analytes are listed in Table 1.

**Table 1 — Selected analytes – i.e. marker compounds**

| **Marker compound** | **CAS-number** |
|---|---|
| Acetaldehyde | 75–07–0 |
| 2-Methyl-1,3-dioxolane | 497–26–7 |
| Ethanol | 64–17–5 |
| Ethyl acetate | 141–78–6 |
| Hexanal | 66–25–1 |
| Limonene | 5989–27–5 |

## 6 Reagents

All reagents shall be of recognized analytical grade. Verify whether the reagents are applicable for this specific purpose and free of interfering compounds.

### 6.1 Carrier gases for gas chromatography

Carrier gas for gas chromatography shall be helium.

### 6.2 Solvent

Acetone for preparation of standard solutions (Propan-2-one, CAS 67-64-1).

### 6.3 Standard solutions

A mixed solution of the set of analytes listed in Table 1 shall be prepared at a known concentration of 4 mg/ml for each compound, in acetone (8.4).

## 7 Apparatus

### 7.1 Cryogenic mill

A cryogenically-cooled laboratory mill fitted with a 2 mm trapezoidal ring capable of operating at 16 000 r/min has been found suitable for this purpose.

### 7.2 Laboratory glassware

All glassware that comes into contact with the sample shall be free of the analytes and any interfering compounds. The following glassware will be used in practice:

— headspace vials fitted with inert septa;

— volumetric flasks;

— volumetric pipettes;

— inert septum-sealed glass vial – e.g. 7 ml capacity;

— microlitre syringes.

### 7.3 Headspace gas chromatograph-mass spectrometer

Gas chromatograph shall be equipped with:

— a capillary column (according to 7.4);

— a mass spectrometric detector;

— an automated headspace sampler.

### 7.4 Capillary column

A capillary column shall be appropriate for sufficient resolution of the analytes in Table 1.

NOTE An example of a capillary column which has been found to be satisfactory for this type of work is one that is 30 m long, has a diameter of 320 µm, and a 5 % phenyl 95 % PDMS stationary phase with a film thickness of 3 µm.

### 7.5 Refrigerator and freezer

A laboratory freezer shall be used capable of maintaining a temperature of −10 °C to −20 °C.

A laboratory refrigerator shall be used capable of maintaining a temperature of 2 °C to 8 °C.

### 7.6 Sieves

A fraction from the cryogenically ground PET is isolated for analysis by GC-MS by sieving the PET through two sieves:

— a sieve having an aperture size of 500 µm;

— a sieve having an aperture size of 1 mm.

### 7.7 Analytical balance

All sample and reference standard weighing shall be carried out using a calibrated and properly maintained balance capable of weighing to an accuracy of 0,01 mg.

## 8 Procedures

### 8.1 Introduction

The following instructions provide a standard addition sample with 4 µg/g of each marker compound added.

### 8.2 Sample conservation

The laboratory and test samples shall be stored in a freezer between −10 °C and −20 °C in a hermetically sealed container.

NOTE It is essential to store the PET samples in a freezer to maintain the stability and integrity of the sample. This is particularly important in the case of acetaldehyde due to its volatility.

Samples should be analysed 'as soon as possible' after they have been identified to avoid any loss of the marker compounds.

### 8.3 Grinding of the PET samples

#### 8.3.1 General

The laboratory samples shall be cryogenically ground and prepared for the next stage (8.6).

The laboratory sample shall be cut into pieces suitable for the mill before grinding (8.3.2). The cryogenically mill shall be cleaned before each use to prevent contamination (8.3.3). The grinding shall take place under controlled conditions (8.3.4). After grinding, the sample shall be sieved (8.3.5) as preparation for next stage (8.6).

#### 8.3.2 Initial preparation

The laboratory PET samples shall be taken in accordance with CEN/TS 16011.

The laboratory PET sample shall be cut into pieces smaller than 100 $mm^2$ prior to cryogenic milling.

#### 8.3.3 Cleaning of the cryogenic mill prior to use and in-between samples

To avoid contamination of the samples the mill shall be cleaned, before each use, in accordance with the following instruction:

Clean at least all interior parts of the mill, in particular the collection pan, the rotor blades, the sieve ring and any other parts such as the interior seals using a regime that includes both water based detergents and, finally, organic solvents.

#### 8.3.4 Cryogenic milling of the samples

The interior of the mill shall be cooled down prior to the addition of the sample, which itself shall have been cooled. The grinding shall be done as follows:

— Take approximately 50 g of the laboratory sample.

— Cool the laboratory sample by immersing into a liquid nitrogen bath for at least 10 min.

— Add the cooled laboratory sample slowly when the mill is up to speed (e.g. 16 000 r/min).

— Keep the mill at cryogenic temperatures during operation.

NOTE 1 Further quantities of liquid nitrogen may be added. However, for safety reasons, it is strongly advised that the mill is not rotating during addition of further nitrogen.

— Inspect the ground sample. Discard the ground sample if thermal degradation is visually apparent.

NOTE 2 In case of thermal degradation and when grinding further laboratory samples it is advised to take extra care to ensure both the sample and mill are sufficiently cooled.

#### 8.3.5 Sieving of ground samples

The ground sample (8.3.4) shall be sieved as follows:

— Sieve the ground sample through a series of laboratory test sieves of 1 mm and 500 µm apertures.

— Retain the portion with particles between 500 µm to 1 mm for analysis. This is the test sample.

If any storage is necessary prior to further preparation of samples (8.6) then store in accordance with 8.2.

### 8.4 Preparation of standard solutions

#### 8.4.1 General

A spiking solution of the six analytes at a suitable concentration in acetone shall be prepared.

— First prepare stock solution A (8.4.2). This solution contains all analytes with the exception of acetaldehyde. To prepare this solution the analytes shall be added in order of decreasing boiling point to minimize losses during preparation.

— Then prepare stock solution B (8.4.3.). This solution is made by adding acetaldehyde into stock solution A.

NOTE Because of its volatility, it is difficult to accurately and precisely transfer acetaldehyde in liquid form. Therefore, an excess amount is added, the exact mass added is determined and the solution is subsequently diluted to the required level using a further volume of stock solution A.

#### 8.4.2 Stock solution A

Prepare a solution containing all marker compounds, *with the exception of acetaldehyde*, as follows.

— Accurately weigh (0,4 g ± 0,1 g) of the following analytes into a single 100 ml volumetric flask: limonene, hexanal, ethanol, ethyl acetate and 2-methyl-1,3-dioxolane.

— Add the analytes in order of decreasing boiling point according to Table 2.

— Adjust to total volume using acetone.

**Table 2 — Order of analyte addition**

| **Order of addition** | **Analytes** | **Boiling point** °C |
|---|---|---|
| 1st | Limonene | 176,0 |
| 2nd | Hexanal | 130,5 |
| 3rd | 2-methyl-1,3-dioxolane | 81,0 |
| 4th | Ethanol | 78,4 |
| 5th | Ethyl acetate | 77,1 |

### 8.4.3 Stock solution B

Prepare a solution of acetaldehyde at approximately 8 mg/ml in stock solution A as follows.

— Accurately add 5 ml of stock solution A (8.4.2) into a septum-sealed glass vial with minimal headspace (e.g. 7 ml capacity). Close the vial and record the total mass of the vial, cap and contents. Record this value as $m_1$.

— Add approximately 0,04 g of cool acetaldehyde through the septum by transferring 50 µl directly from the refrigerator using a chilled microlitre syringe and immediately reweigh the vial, cap and contents. Record this as $m_2$. This forms stock solution B.

The exact concentration of acetaldehyde ($\rho_{ah}$) in stock solution B shall be calculated using Formula (1):

$$\rho_{ah} = \frac{m_2 - m_1}{V_a} \quad (1)$$

where

$\rho_{ah}$ is the concentration of acetaldehyde in the vial, in mg/ml;

$V_a$ is the volume of acetone in the vial, in ml;

$m_1$ is the total mass of vial, cap and contents of vial, in mg;

$m_2$ is the total mass of vial, cap and contents of vial after the addition of the acetaldehyde, in mg.

### 8.4.4 Spiking solution

Produce a spiking solution by accurately diluting appropriate volumes of stock solution B (8.4.3) in stock solution A (8.4.2) to bring the acetaldehyde level to approximately 4 mg/ml.

The volumes required to dilute stock solution B with stock solution A shall be derived from Formula (1).

Accurately calculate the concentration of each analyte in the spiking solution (mg/ml).

The spiking solution has been demonstrated to be stable for up to two weeks from preparation, if stored under refrigeration (7.5) in a hermetically sealed vessel with minimal headspace.

## 8.5 Blank determinations

Blank determinations shall be carried out to control the quality of the acetone in accordance with the following instructions:

— Prepare individual headspace vials, one containing 1 µl of the spiking solution (8.4.4) and the other containing 1 µl of the acetone used for the standard solutions.

— Carry out the analysis (8.7) on both vials.

— If the response (8.7.2.1) for any of the analytes in the blank vial is found to be equal to or greater than 5 % of the response obtained for the spiking solution, the analysis shall be repeated with a fresh source of acetone.

## 8.6 Preparation of sample vials

Two sample vials are prepared for each test sample as follows:

A (1 ± 0,05) g of test sample (8.3.5) shall be accurately weighed into two separate headspace vials. The weight of sample added to each vial is recorded.

Into one of the vials a 1 µl volume of spiking solution (8.4.4) shall be injected via a 10 µl syringe and the vial immediately hermetically sealed using an inert septum and crimp camp. This vial is the spiked sample.

Into the other vial a 1 µl volume of pure acetone solvent shall be injected via a 10 µl syringe and the vial is immediately sealed using an inert septum and a crimp camp. This vial is the unspiked sample.

## 8.7 Gas chromatographic analysis

### 8.7.1 General

The chromatographic analysis shall be done with the apparatus in accordance with 7.3.

The instrument settings listed in Annex B have found to be appropriate.

### 8.7.2 Identification and quantification of analytes using the standard addition method

#### 8.7.2.1 Measurement

Record the chromatograms of the vials from 8.6.

Identify and integrate the peaks that can be assigned to analytes considering the combination of

— the retention time;

— the characteristic diagnostic ion (Table B.3);

— an increased response detected in the spiked sample.

NOTE Refer to Annex A for guidance.

#### 8.7.2.2 Identification

An analyte is deemed to be present in a sample when the two criteria below are met. If one or both the criteria are not met, the analyte has not been identified and shall be reported as not detected.

— The signal for the diagnostic ions specified in Table B.3 shall be present in the mass chromatogram and its relative retention time shall be within ± 0,1 min.

— The signal to noise ratio (S/N) for a peak at the specific retention time in an unspiked sample (8.6) shall be greater than or equal to 10 for each analyte detected. This is calculated using RMS S/N. RMS S/N is typically derived using an automated function of the chromatographic data system.

#### 8.7.2.3 Quantification

To calculate amount of each specific analyte in the sample under test, carry out the following steps:

— Calculate the accurate concentration of each individual analyte in the spiking solution (8.4.4).

— Record the peak areas for each analyte detected in the spiked and unspiked sample vials (8.7.2.1).

— The amount of each specific analyte present in the sample under test ($m_M$) shall be calculated using Formula (2):

$$m_M = \frac{A_{smp}}{A_{std} - A_{smp}} \times m_{std} \quad (2)$$

where

$m_M$ is the amount of specific analyte in the sample under test, in µg/g

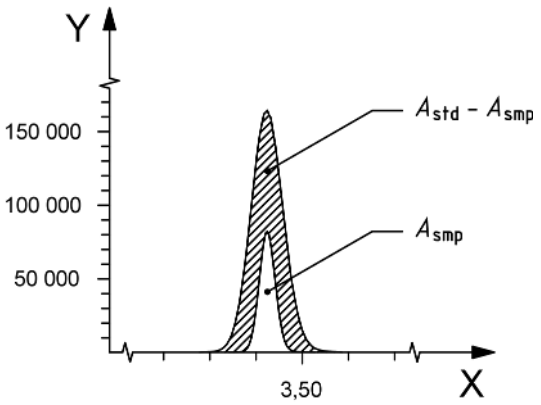
$A_{std}$ is the peak area in the spiked sample under test (8.6)

$A_{smp}$ is the peak area in the unspiked sample under test (8.6)

$m_{std}$ is the mass of specific analyte added to the spiked sample, in µg

NOTE $m_{std}$ (µg) is equivalent to the concentrations of the analytes calculated in 8.4.4 (mg/ml) due to the addition of 1 µl of spiking solution to the spiked sample vial (8.6).

See Figure 1.




**Key**

x-axis time (min)

y-axis abundance

**Figure 1 – Illustration of peak areas**

# 9 Interference

## 9.1 Interference during sampling and storage

Containers (including gaskets and closures) and transfer equipment shall be made up of materials that are not expected to contain any of the marker compounds, either by itself (e.g. non-PET plastic, metal or glass) or resulting from contamination from former uses, and would not be expected to react with the sample in any way.

## 9.2 Interference due to co-elution

The peak identified as being due to a specific analytes shall be examined for the presence of shoulders and other interferences.

Any observed interference should be noted in the final report.

NOTE Because the post-consumer PET samples have potential to come into contact with a wide range of chemical substances, there is a possibility of other compound(s) co-eluting with the analytes.

# 10 Test report

The test report shall contain at least the following information:

a) reference to this document: CEN/TS 16861:2015;

b) complete identification of the sample;

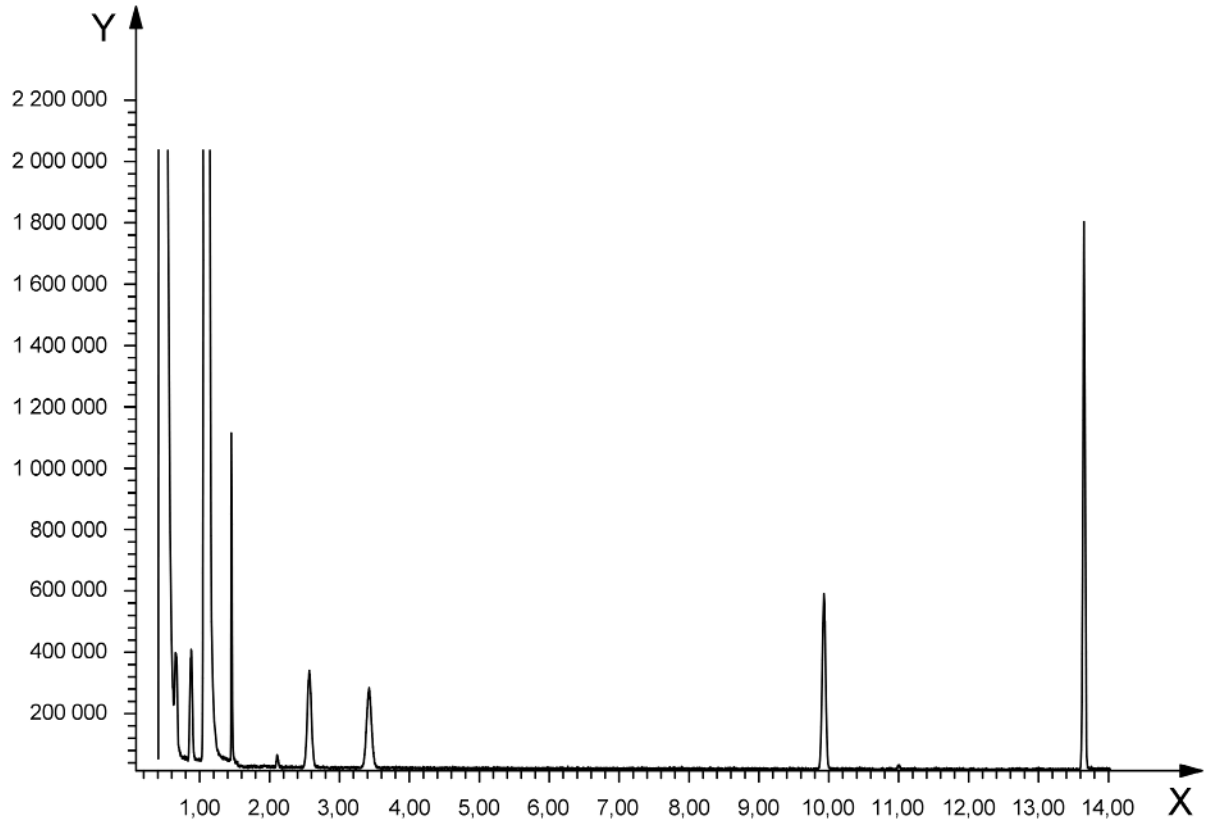
c) level of each specific analyte detected, in µg/g.

# Annex A
(informative)

# Representative chromatograms

## A.1 Total ion chromatogram of all six analytes

The full total ion chromatogram showing all of the analytes is shown in Figure A.1. This chromatogram ranges from an elution time of 0 min to 14 min.



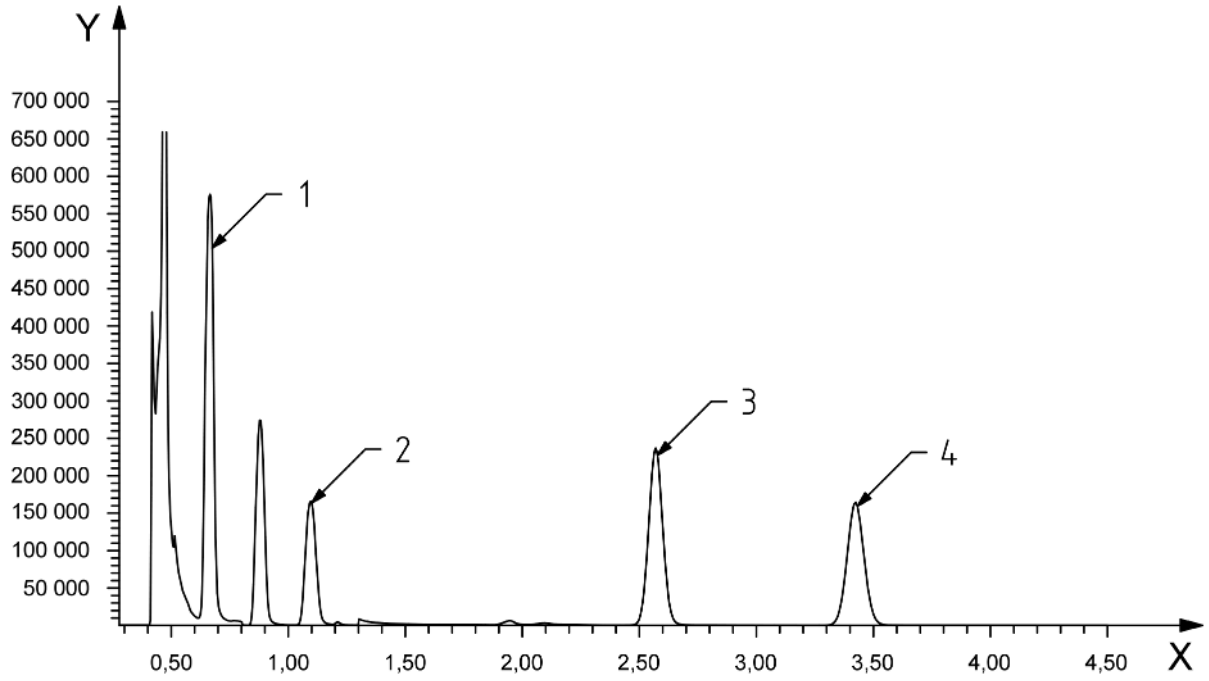

**Key**

| | |
|---|---|
| x-axis | time (min) |
| y-axis | abundance |

**Figure A.1 – Total ion chromatogram of all six analytes**

## A.2 Chromatograms of individual analytes in the selected ion monitoring mode

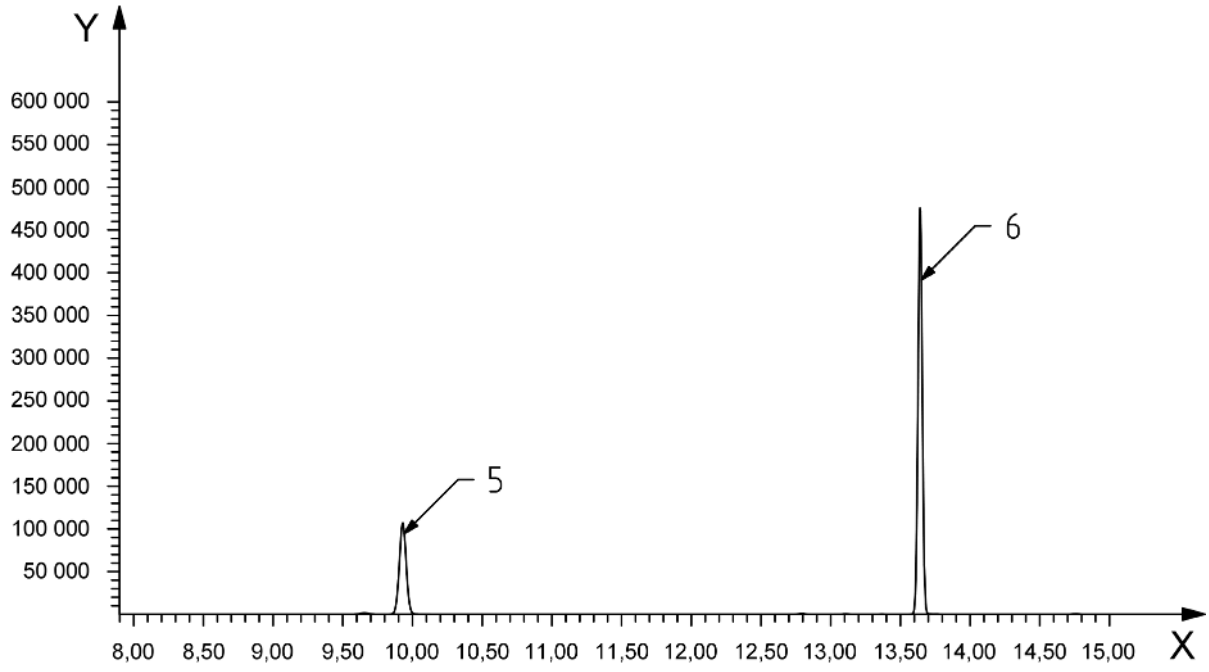
To assist in the interpretation of the analyte peaks, the chromatogram in Figure A.1 is expanded and divided into two sections. Examples of these two sections are shown in Figures A.2 and A.3.




**Key**

| | | | |
|---|---|---|---|
| x-axis | time (min) | 1 | acetaldehyde |
| y-axis | abundance | 2 | ethanol |
| scaled to view from 0 min to 4,7 min | | 3 | ethyl acetate |
| | | 4 | methyl dioxolane |

**Figure A.2 – Section (0 min to 4,7 min) of the selected ion chromatogram**




**Key**

| | | | |
|---|---|---|---|
| x-axis | time (min) | 5 | hexanal |
| y-axis | abundance | 6 | limonene |
| scaled to view from 8 min to 15,2 min | | | |

**Figure A.3 – Section (8 min to 15,2 min) of the selected ion chromatogram**

# Annex B
(informative)

# Example of instrument settings

## B.1 General

The following conditions have been found to be appropriate:

— for the Headspace sampler conditions see Table B.1;

— for the GC-MS conditions see Table B.2;

— for specific ions to monitor see Table B.3.

## B.2 Headspace sampler conditions

**Table B.1 — Headspace sampler conditions**

| Description | Conditions |
|---|---|
| Sample temperature | 150 °C |
| Needle temperature | 160 °C |
| Transfer temperature | 170 °C |
| Thermostat time | 60 min |
| Pressure time | 1,0 min |
| Injection time | 0,1 min |
| Withdrawal time | 1,0 min |
| Head pressure | approximately 100 kPA (15 psi) |

## B.3 Gas chromatography - mass spectrometry (GC-MS) – conditions

**Table B.2 — GC-MS-conditions**

| **Description** | **Condition** |
|---|---|
| Oven temperature programme | • 40 °C for 8 min<br>• 20 °C/min to 300 °C<br>• hold for 5 min |
| Carrier gas | • 35 kPA (5 psi)<br>• constant pressure |
| MS interface temperature | • 280 °C |
| Source temperature | • 230 °C |
| MS conditions | • electron impact<br>• scanning 20 to 450 atomic mass units (amu)<br>to determine SIM group timings<br>• SIM for sample analysis (Table B.3) |

## B.4 Specific ions for selected ion mode (SIM)

To identify the start and end times for recording the specific SIM groups a 1 µl aliquot of the spiking standard (8.4.4) is analysed using the mass spectrometer in scan mode.

**Table B.3 — Diagnostic ions for analytes**

| **Marker compound** | **Specific ions for SIM**<br>m/z |
|---|---|
| Acetaldehyde | 29 and 44 |
| Methyl dioxolane | 73 and 87 |
| Ethanol | 31 and 45 |
| Ethyl acetate | 43 and 70 |
| Hexanal | 56 and 72 |
| Limonene | 68 and 93 |

# Annex C
(informative)

# Performance characteristics

## C.1 General

Validation work has been performed on this method, and the following performance established.

## C.2 Limit of detection

The limit of detection (LOD) has been estimated from the regression analysis of a standard addition curve based on spiked PET samples at five concentrations.

The values are calculated using Formula (C.1):

$$\text{LOD} = \frac{3{,}3 \times se_{\text{m}}}{m} \qquad \text{(C.1)}$$

where

LOD is the limit of detection, in µg/g

$m$ is the slope of the regression line

$se_{\text{m}}$ is the standard error of the slope

The results are given in Table C.2.

## C.3 Limit of quantification

The limit of quantification (LOQ) has been estimated from the regression analysis of a standard addition curve based on spiked PET samples at five concentrations. The values are calculated using Formula (C.2):

$$\text{LOQ} = \frac{10 \times se_{\text{m}}}{m} \qquad \text{(C.2)}$$

where

LOQ is the limit of quantification, in µg/g

$m$ is the slope of the regression line

$se_{\text{m}}$ is the standard error of the slope

The results are given in Table C.2.

## C.4 Precision

The precision of the method has been determined by analysis of triplicate portions of a typical PET test sample. The analysis was conducted using the method described in Clause 8.

The precision, expressed in percent relative standard deviation (%RSD) for the triplicate determinations, is shown in Table C.2.

## C.5 Accuracy

It is not possible to obtain or produce reference samples of PET with known absolute levels of the target analytes with which to demonstrate true accuracy of a test method.

Accuracy has therefore been determined by a comparison of the results obtained on a typical post-consumer PET test sample (using the method described in Clause 8) to the results of a multiple headspace extraction (MHE) analysis of the same sample. See Table C.1.

The results of the MHE analysis may be considered as the reference values.

1. **MHE method.** The samples were analysed using a six-injection MHE analysis on a sample vial containing 1 g of PET test sample. A second vial containing an equivalent 1 g portion of PET test sample and a known amount of each analyte was analysed, also using a six-injection MHE analysis, as an external standard. This was performed in triplicate.

2. **Standard addition method**. Further portions of the same test sample were analysed using a standard addition method at five concentrations. This was performed in triplicate.

3. **Single point calibration standard addition method.** The results from the standard addition method were also calculated by using only two data points − the unspiked sample and the sample spiked with 4 µg. This is to represent the methodology described in Clause 8.

NOTE The single point calibration standard addition method was chosen to ensure the method was efficient and cost effective.

**Table C.1 — Accuracy**

| **Analyte** | **1. MHE method** [a] µg/g | **2. Standard addition method** µg/g | **3. Single point method** µg/g |
|---|---|---|---|
| Acetaldehyde | 6,224 | 6,960 | 6,976 |
| Ethanol | 0,055 | 0,047 | 0,046 |
| Ethyl acetate | 0,056 | 0,043 | 0,030 |
| Methyl dioxolane | 1,228 | 1,163 | 1,164 |
| Hexanal | 0,046 | 0,031 | 0,025 |
| Limonene | 0,117 | 0,069 | 0,087 |
| [a] The results of the MHE experiment are considered as the reference values. | | | |

## C.6 Linearity

The linearity of the method has been assessed using a standard addition method at five concentrations, ranging from 2 to 16 µg/g.

This was performed in triplicate and the average of *n* = 3 data points were used to construct the calibration curves. The results are given in Table C.2.

## C.7 Validation results

**Table C.2 — Limit of detection LOD, Limit of quantification LOQ, Precision, Linearity**

| **Marker compound** | **LOD** µg/g | **LOQ** µg/g | **Precision** [a] %RSD | **Linearity** [b] $R^2$ |
|---|---|---|---|---|
| Acetaldehyde | 0,012 | 0,036 | 9,6 | 1,000 0 |
| Ethanol | 0,026 | 0,078 | 3,3 | 0,999 8 |
| Ethyl acetate | 0,027 | 0,082 | 3,7 | 0,999 9 |
| Methyl dioxolane | 0,023 | 0,068 | 2,9 | 0,999 9 |
| Hexanal | 0,020 | 0,062 | 5,1 | 0,999 9 |
| Limonene | 0,009 | 0,027 | 5,7 | 1,000 0 |

[a] 'Precision' is expressed in percent relative standard deviation i.e. %RSD for the triplicate determinations.
[b] 'Linearity' is reported as $R^2$ i.e. the square of the Pearson product moment correlation coefficient through data points in known y's and known x's

# Bibliography

[1] COMMISSION REGULATION (EC) No 282/2008 of 27 March 2008 on recycled plastic materials and articles intended to come into contact with foods and amending Regulation (EC) No 2023/2006

[2] EUROPEAN PARLIAMENT AND COUNCIL DIRECTIVE 94/62/EC of 20 December 1994 on packaging and packaging waste with L284(2003),L47(2004)L70(2005),L87(2009), L37(2013)

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