

**Study Title**

Identity, Appearance, Spectral Data, Material Balance and  
Mass Spectrometry by GC-MS  
of  
Bis(2-ethylhexyl) tetrabromophthalate

**Data requirements**

REACH requirement EC/1907/2006

**Author**

Rainer Jungheim

**Study completion date**

2017-07-10

**Sponsor**

LANXESS Deutschland GmbH  
50569 Köln  
Kennedyplatz 1  
Germany

**Testing facility**

CURRENTA GmbH & Co. OHG  
Analytik  
51368 Leverkusen  
Germany

**Laboratory Project Identification**

Study No.: 2016/0149/01

---

*This page is intentionally left blank for the purpose of submitting administrative information that is required by regulations promulgated by various countries.*

---

## CONTENTS

	Page
1. GLP DECLARATION _____	4
2. ARCHIVING _____	4
3. QUALITY ASSURANCE STATEMENT _____	6
4. STUDY TIME TABLE _____	6
5. GLP CERTIFICATE _____	7
6. SUMMARY _____	9
7. EXPERIMENTAL PROCEDURE _____	11
7.1. Methods, guidelines and documents _____	11
7.2. Principle of the test _____	11
8. TEST MATERIAL _____	13
8.1. Sample description _____	13
9. METHODS AND RESULTS _____	14
9.1. Identity, Appearance, Spectral Data, Material Balance and Mass Spectrometry by GC-MS of Bis(2-ethylhexyl) tetrabromophthalate. _____	14
9.1.1. Test: Appearance, physical state of the test item Bis(2-ethylhexyl) tetrabromophthalate. _____	14
9.1.2. Test: FTIR spectrum _____	14
9.1.3. Test: <sup>1</sup> H-NMR spectrum and <sup>13</sup> C-NMR spectrum of the test item Bis(2-ethylhexyl) tetrabromophthalate _____	16
9.1.4. Test: Content and mass spectra of Bis(2-ethylhexyl) tetrabromophthalate by Gas Chromatography (GC-FID and GC-MS). _____	19
9.1.5. Test: Residue of evaporation _____	32
9.1.6. Test: Water content by Karl Fischer technique _____	32

## 1. GLP DECLARATION

This study was conducted in compliance with the OECD principles of Good Laboratory Practice and with the Principles of Good Laboratory Practice according to Annex 1, German Chemical Law.

Date / Signature

Study Director

2017-07-10 R. Jungheim  
Mr. Jungheim

Date / Signature

Head of Test Facility

2017-07-10 Allmendinger  
Dr. Allmendinger / Dr. Konrad

## 2. ARCHIVING

The original report, the study plan, and all raw data pertaining to this study are stored in the "GLP Archive, CURRENTA GmbH & Co. OHG, Analytik, CHEMPARK, Building Q 18, D-51368 Leverkusen". A sample of the test item is stored in "GLP-Sample Store, CURRENTA GmbH & Co. OHG, Analytik, CHEMPARK, Building DA 1, D-41538 Dormagen".

---

*This page is intentionally left blank for the purpose of submitting administrative information that is required by regulations promulgated by various countries.*

### 3. QUALITY ASSURANCE STATEMENT

This report was audited by the Quality Assurance Unit Currenta, Analytik, Quality Management at Currenta GmbH & Co. OHG and this statement confirms that the final report reflects the raw data.

The dates of Quality Assurance inspections and audits are given below.

Audits	Dates of QAU Inspections	Dates of Reports
Study plan review	2017-03-01	2017-03-01
Process based inspection (2016/0041/01)	2017-04-05	2017-04-05
Process based inspection (2016/0120/01)	2017-01-10	2017-01-10
Process based inspection (2016/0030/02)	2017-02-08	2017-02-08
Final report review (draft)	2017-07-07	2017-07-07
Final report review	2017 -07- 10	2017 -07- 10

Date / Signature

2017 -07- 10

*S. Roehrig*

Ms. Roehrig / ~~Dr. Dörzbach-Lange / Dr. Neupert~~

### 4. STUDY TIME TABLE

Study initiation date:	2017-03-01
Study completion date:	2017-07-10
Start of experimental tests:	2017-03-02
End of experimental tests:	2017-06-22

## 5. GLP CERTIFICATE



Ministerium für Arbeit, Integration und Soziales  
des Landes Nordrhein-Westfalen

Fürstenwall 25, 40219 Düsseldorf

Aktenzeichen III 5 – 8673.58

**Gute Laborpraxis/Good Laboratory Practice**  
**GLP-Bescheinigung/Statement of GLP Compliance**  
**(gemäß/according to § 19b Abs. 1 Chemikaliengesetz)**

Eine GLP-Inspektion zur Überwachung der Einhaltung der GLP-Grundsätze gemäß Chemikaliengesetz bzw. Richtlinie 2004/9/EG wurde durchgeführt in: Assessment of conformity with GLP according to Chemikaliengesetz and Directive 2004/9/EEC at:

☒ Prüfeinrichtung/Test facility

☐ Prüfstandort/Test site

**CURRENTA GmbH & Co. OHG**  
**CHEMPARK, Geb. K 46**  
**51368 Leverkusen**

**Prüfungen nach Kategorien**  
(gemäß ChemVwV-GLP Nr. 5.3/OECD guidance)

**Areas of Expertise**  
(according ChemVwV GLP Nr. 5.3/OECD guidance)

Kategorie 1 Prüfungen zur Bestimmung der physikalisch-chemischen Eigenschaften und Gehaltsbestimmungen	category 1 physical-chemical testing
Kategorie 4 Ökotoxikologische Prüfungen zur Bestimmung der Auswirkungen auf aquatische und terrestrische Organismen	category 4 environmental toxicity studies on aquatic and terrestrial organisms
Kategorie 5 Prüfungen zum Verhalten im Boden, im Wasser und in der Luft; Prüfungen zur Bioakkumulation und zur Metabolisierung	category 5 studies on behaviour in water, soil and air; bioaccumulation

Kategorie 6  Prüfungen zur Bestimmung von Rückständen	category 6  residue studies
Kategorie 8  Analytische Prüfungen an biologischen Materialien	category 8  analytical and clinical chemistry testing

Datum der Inspektion

18. November 2015

Die/Der genannte Prüfeinrichtung/Prüfstandort befindet sich im nationalen GLP-Überwachungsverfahren und wird regelmäßig auf Einhaltung der GLP-Grundsätze überwacht.

Auf der Grundlage des Inspektionsberichtes wird hiermit bestätigt, dass in dieser Prüfeinrichtung/diesem Prüfstandort die oben genannten Prüfungen unter Einhaltung der GLP-Grundsätze durchgeführt werden können.

Date of Inspection

18<sup>th</sup> November 2015

The above mentioned test facility/ test site is included in the national GLP Compliance Programme and is inspected on a regular basis.

Based on the inspection report it can be confirmed, that this test facility/test site is able to conduct the aforementioned studies in compliance with the Principles of GLP.

Düsseldorf, 26. August 2016

Im Auftrag



(Steffen Röddecke)



Dienstsiegel/official-seal



---

## 6. SUMMARY

For all tests no official (OECD) guidelines are available. The tests were performed according to internal standard operation procedures and methods, describing the operation for the employed instruments and analytical techniques (see point 7.1)

With the test item Bis(2-ethylhexyl) tetrabromophthalate, Batch no.: GS16337E71 the following analytical determinations were performed:

Results:

### Appearance

Physical state of the test item Bis(2-ethylhexyl) tetrabromophthalate:

Liquid, slight viscous

Colour of the test item Bis(2-ethylhexyl) tetrabromophthalate:

Colourless

### FT-IR Spectroscopy

The founded FTIR bands of structure elements correlate with the structure of the test item Bis(2-ethylhexyl) tetrabromophthalate, see point 9.1.2.

### Identity of Bis(2-ethylhexyl) tetrabromophthalate by NMR-Spectroscopy

The spectroscopical data of the <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were in agreement with the test item Bis(2-ethylhexyl) tetrabromophthalate. The spectra and the correspondence of the recorded chemical shifts to the molecular structure are presented under point 9.1.3.

### Material balance of Bis(2-ethylhexyl) tetrabromophthalate

The content of the test item Bis(2-ethylhexyl) tetrabromophthalate was determined by GC-analysis. The quantification was done by area normalization with consideration of water content and non-volatile components.

	Bis(2-ethylhexyl) tetrabromophthalate Batch no.: GS16337E71
2-Ethylhexyl 2,3,4,5-tetrabromobenzoate (Component 1)	2.5 %
Bis(2-ethylhexyl) 3,4,?-tribromophthalate (Components 2 and 3)*	0.5 %
Bis(2-ethylhexyl) 2,3,4,5-tetrabromophthalate (Component 4)	95.5 %
Sum of unknown components (18), each component $\leq 0.3$ %	0.9 %
Residue of evaporation	0.63 %
Water content by K. F.	< 0.1 %
Sum of all	100.0 %

\* For the two components at RT = 10.9 minutes and RT = 11.4 minutes the two structural isomers bis(2-ethylhexyl) 3,4,5-tribromophthalate and bis(2-ethylhexyl) 3,4,6-tribromophthalate could be proposed.

#### Gas Chromatography - Mass Spectrometry (GC-MS)

For structure elucidation GC-MS chromatogram (TIC) and GC-MS spectra of the components of the test item Bis(2-ethylhexyl) tetrabromophthalate were recorded. The proposed structures and the corresponding MS spectra of the components of the test item Bis(2-ethylhexyl) tetrabromophthalate are described in Figures 8 – 14 under point 9.1.4.3

The material balance is complete with respect to the state of the art.

The stipulated content for further use of Bis(2-ethylhexyl) tetrabromophthalate was: 95.5 %.

## 7. EXPERIMENTAL PROCEDURE

### 7.1. Methods, guidelines and documents

REACH regulation EC/1907/2006EU Directive 91/414/EEC

Currenta internal method 2011-0527201-96D – Appearance, physical state of the test item, see point 9.1.1.

SOP 00128 Version 4 – FT-IR spectroscopy. This SOP is an internal SOP describing the recording of a Fourier Transform Infrared spectrum employing a Thermo Scientific Nicolet iS5 spectrometer, see point 9.1.2.

Method 2012-0620501-08D and method 2012-0620601-08D. These methods are internal methods describing the recording and interpretation of a  $^1\text{H}$ -NMR and a  $^{13}\text{C}$ -NMR spectrum employing a NMR-Spektrometer Bruker Avance III 400, see point 9.1.3

GC-FID method with quantification by area normalization and GC mass spectrometry is described in point 6.1.1.

Currenta internal method 2011-0520901-96D – Residue of evaporation.

Currenta internal method 2011-0131401-90D and 2011-0131301-90D – Water content by Karl Fischer technique.

### 7.2. Principle of the test

#### Appearance, physical state of the test item

The test item was visual inspected at ambient temperature (23 °C). The colour and the physical state of the test item were described.

#### Fourier Transform Infrared (FTIR) Spectroscopy

An infrared transmission spectrum is generated by comparison of the intensity of the infrared radiation after passing the sample and after passing the empty optical path or a blank solution. Infrared absorption bands are typical for structural elements of the test substance and therefore useful for identity determinations.

#### Nuclear Magnetic Resonance (NMR) Spectroscopy

NMR Spectra are generated by inducing nuclear magnetical resonance of atom nuclei. The resonance frequency of specific atom nuclei ( $^1\text{H}$ ,  $^{13}\text{C}$ ) depends on their chemical environment and is therefore specific for a molecule.

#### Gas Chromatography (GC)

The content of Bis(2-ethylhexyl) tetrabromophthalate is determined by GC-analysis using a M&N Optima 5 HT capillary column and a flame ionization detector (FID). The quantification was done by area normalization with consideration of water content and unvolatilizable components. Due to the similar structures of the main and the minor components, all components show an equal response to the FID. For this reason the received area percents are equal to weight percents.

#### Identity by Mass Spectrometry (MS)

A solution of the test item is led to the mass spectrometric investigation after passing a gas chromatographic column. Inside an ion source the molecules are bombarded with free electrons emitted from a filament with 70 eV (electron impact ionization). Molecular ion and typical fragmentation patterns of the molecular ion can be generated. The fragments are actually charged ions with a certain mass and are recorded after separation in an electromagnetic field. The received mass spectrum is a characteristic fingerprint of the molecule and can be used to identify the structure.

#### Residue of evaporation

The sample is weighed into a tared round bottom flask with standard ground joint. The sample is slowly heated up under vacuum in a Büchi-bulb tube distilling oven until constant weight is reached.

#### Water content by Karl Fischer

The originally weighted sample of the test item is dissolved in the Karl Fischer solvent or in an appropriate solvent mixture and titrated back with the Karl Fischer titrant. The end point detection is detected biamperometrically using a Pt-indicator electrode. Karl Fischer solvent and Karl Fischer titrant are commercial reagents for determination of water content.

## 8. TEST MATERIAL

### 8.1. Sample description

Test item: Bis(2-ethylhexyl) tetrabromophthalate

Chemical name: bis(2-ethylhexyl) 3,4,5,6-tetrabromophthalate

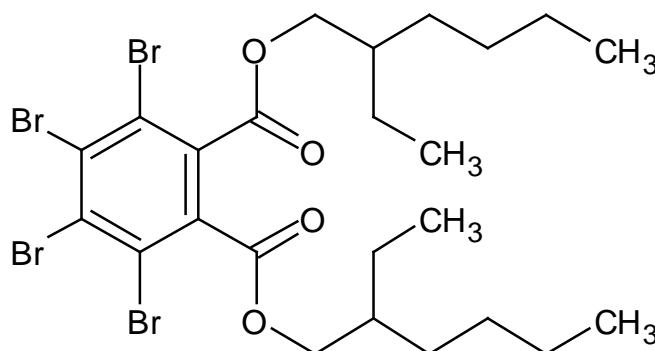
CAS name: 1,2-Benzenedicarboxylic acid, 3,4,5,6-tetrabromo-, 1,2-bis(2-ethylhexyl) ester

CAS number: 26040-51-7

Empirical formula:  $C_{24}H_{34}Br_4O_4$

Molecular mass: 706.2 g/mol

Structural formula:



Batch number: GS16337E71

Sample number: 2970

Date of receipt: 2016-12-22

Expiry date: 2018-05-12

## 9. METHODS AND RESULTS

### 9.1. Identity, Appearance, Spectral Data, Material Balance and Mass Spectrometry by GC-MS of Bis(2-ethylhexyl) tetrabromophthalate.

9.1.1. Test: Appearance, physical state of the test item Bis(2-ethylhexyl) tetrabromophthalate.

Method no.: 2011-0527201-96D

Supervisor: Rainer Jungheim

Result: Physical state: Liquid, slight viscous  
Colour: Colourless

Procedure:

The test item Bis(2-ethylhexyl) tetrabromophthalate was visual inspected at ambient temperature (23 °C). The colour and the physical state of the test item were described.

9.1.2. Test: FTIR spectrum

Method no.: SOP 00128 Version 4

Supervisor: Dr. Tretzel

Result: Found structure elements correlate with structure

Procedure: Fourier Transform - Infrared Spectrometry

The sample was prepared in form of a thin film on a KBr disk. A high resolution FTIR spectrum is scanned and evaluated (see Figure 1).

Identity was confirmed by interpretation of the following structural parts.

Structural parts: O-C=O: 1737 cm<sup>-1</sup>  
CH<sub>2</sub>: 2930, 2860, 1462 (including CH<sub>3</sub>) cm<sup>-1</sup>  
CH<sub>3</sub>: 2959, 2872, 1462 (including CH<sub>2</sub>), 1381 cm<sup>-1</sup>  
Aromatic: 1535, 1515 cm<sup>-1</sup>  
C=C-C-O-R: ca. 1250 bis 1225 cm<sup>-1</sup>  
                  ||  
                  O



9.1.3. Test:  $^1\text{H}$ -NMR spectrum and  $^{13}\text{C}$ -NMR spectrum of the test item  
Bis(2-ethylhexyl) tetrabromophthalate

Method no.: 2012-0620501-08D, NMR-measurement  
2010-0620601-08D, NMR-structure elucidation

Supervisor: Dr. Westfeld

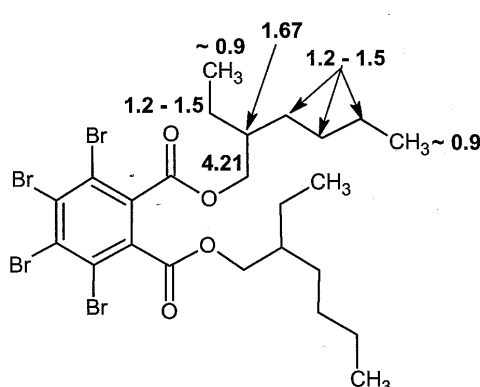
Result: Observed resonances are in agreement with the test item

Procedure:

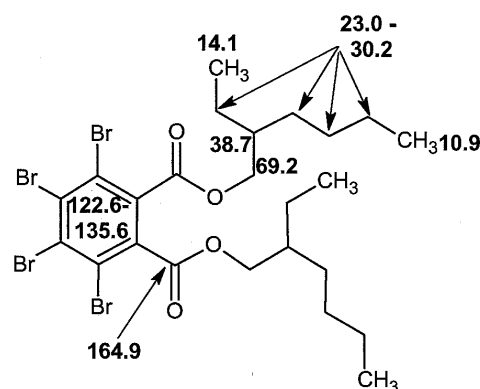
Nuclear Magnetic Resonance (NMR) Spectroscopy

The sample was weighed and dissolved in deuterated chloroform ( $\text{CDCl}_3$ ) for NMR technique. Finally,  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR spectra were recorded (2012-0620501-08D). The structure of the analyte is derived from the spectral characteristics of the signals (2012-0620601-08D).

Details, such as experimental conditions and interpretation, see enclosed spectra (Figure 3 and Figure 4). Figure 2 shows the structure and the results with the chemical shifts of the  $^1\text{H}$ -nuclei and  $^{13}\text{C}$ -nuclei of the test item Bis(2-ethylhexyl) tetrabromophthalate.



Chemical shifts  $^1\text{H}$ -NMR in ppm  
(Solvent:  $\text{CDCl}_3$ , Reference: TMS)



Chemical shifts  $^{13}\text{C}$ -NMR in ppm  
(Solvent:  $\text{CDCl}_3$ , Reference: TMS)

Figure 2: Structure and results of  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR data of the test item Bis(2-ethylhexyl) tetrabromophthalate, chemical shifts in ppm, reference: tetramethylsilane (TMS), solvent: deuterated chloroform ( $\text{CDCl}_3$ ).



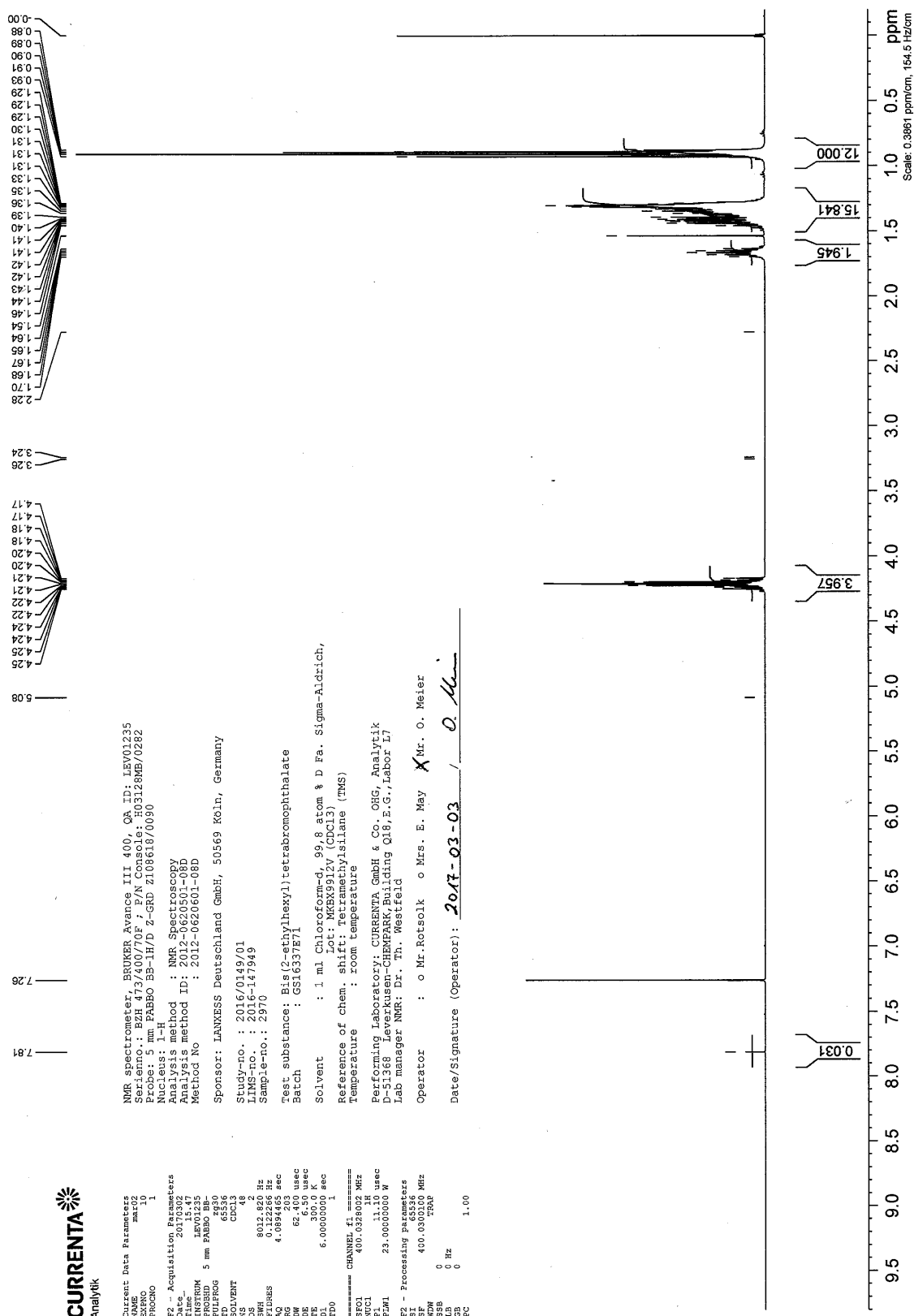
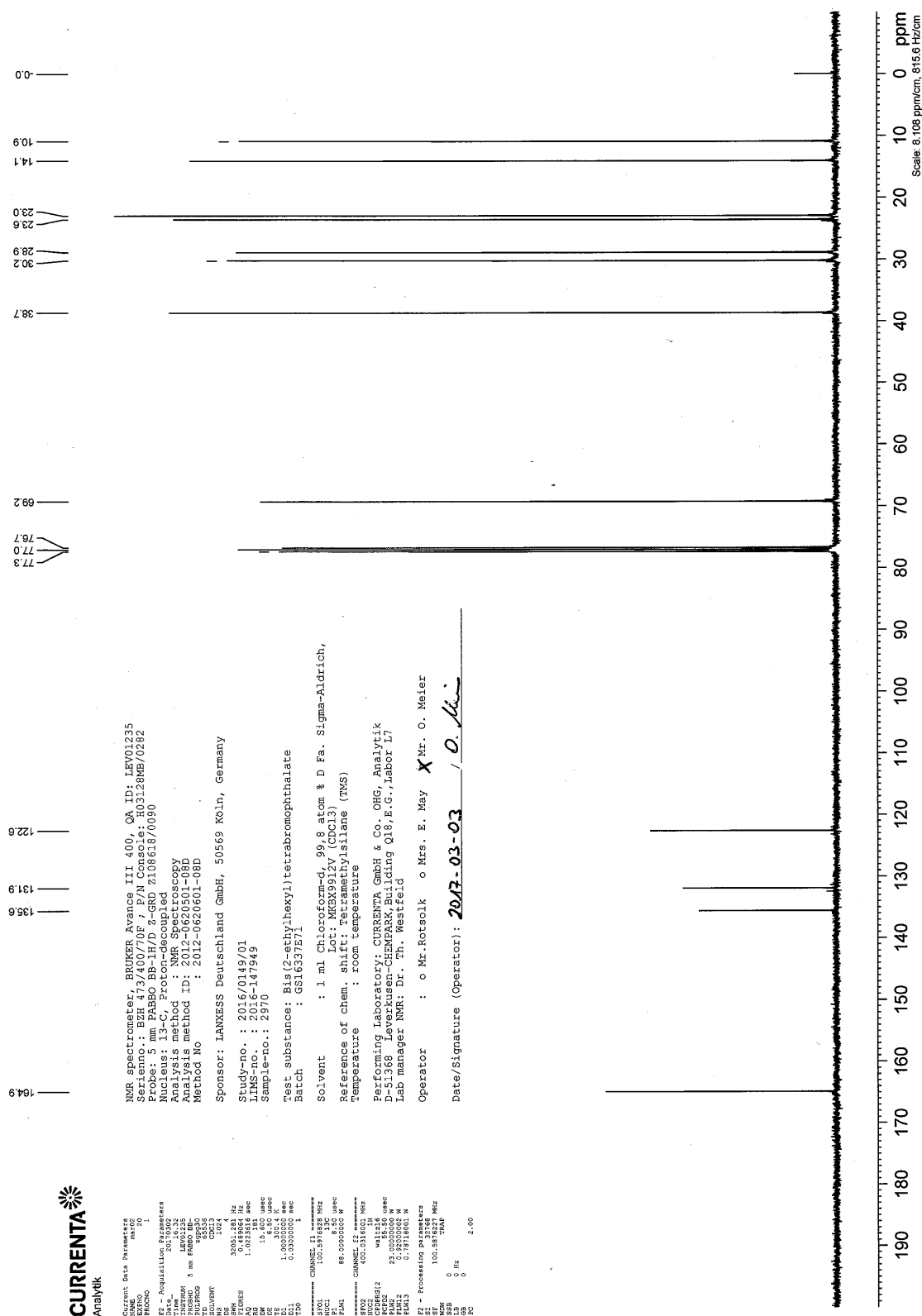


Figure 3: <sup>1</sup>H-NMR spectrum of the test item Bis(2-ethylhexyl)tetrabromophthalate in CDCl<sub>3</sub>.

Figure 4: <sup>13</sup>C-NMR spectrum of the test item Bis(2-ethylhexyl)tetrabromophthalate in CDCl<sub>3</sub>.

9.1.4. Test: Content and mass spectra of Bis(2-ethylhexyl) tetrabromophthalate by Gas Chromatography (GC-FID and GC-MS).

Supervisor: Dr. Schröder

Method parameters:

Procedure: Capillary Gas Chromatography (GC) with FID and MS detection

Gas chromatograph: Agilent 6890

Chromatographic column: Fused silica capillary

Stationary phase: M&N 726104.15 Optima 5 HT

Length: 15 m

Internal diameter: 0.32 mm

Film thickness: 0.10 µm

Carrier gas: Helium

Split flow: 99.9 ml / minute

Flow: 6.0 ml / minute constant flow

Sample injection: Split injection

Injection volume: 1.0 µl

Injector temperature: 320 °C

Temperatur program:

Temp. [ <i>g</i> ] = °C	Time [ <i>t</i> ] = min	Ramp [ <i>g</i> ] = K/min
100	--	15
380	20	15
300	--	--

FID-Detector:

Detector temperature: 350 °C

MS-Detector:

Ionisation method: Electron ionization (EI-positive)

Ion Source: 230 °C

Quadropole: 150 °C

Transfer-line: 400 °C

Electron-Energy: 70 eV

Multiplier: 2047 V

Data acquisition: Scan-Modus

Scanning Mass Range: 12 – 800

Sample preparation: 134.8 mg of the test item was dissolved with 1.5 ml acetonitrile.

#### 9.1.4.1. Results:

Quantification was done by area normalization with consideration of water content and non-volatile components. Due to the similar structures of the main and the minor components, all components show an equal response to the FID-detector. For this reason the received area percents are equal to weight percents.

Table 1: Identified components of Bis(2-ethylhexyl) tetrabromophthalate determined by GC-FID and GC-MS.

Component	Retention time (RT)
2-Ethylhexyl 2,3,4,5-tetrabromobenzoate (Component 1)	9.2 minutes
Bis(2-ethylhexyl) 3,4,?-tribromophthalate (Components 2 and 3)*	10.9 / 11.4 minutes
Bis(2-ethylhexyl) 2,3,4,5-tetrabromophthalate (Component 5)	12.3 minutes

\* For the two components at RT = 10.9 minutes and RT = 11.4 minutes the two structural isomers bis(2-ethylhexyl) 3,4,5-tribromophthalate and bis(2-ethylhexyl) 3,4,6-tribromophthalate could be proposed.

Table 2: Content of the test item Bis(2-ethylhexyl) tetrabromophthalate determined by GC-FID.

Component	Test 1 Content [%]	Test 2 Content [%]	Mean Value [%]
2-Ethylhexyl 2,3,4,5-tetrabromophthalate (Component 1)	2.47 %	2.47 %	2.5 %
Bis(2-ethylhexyl) 3,4,?-tribromophthalate (Components 2 and 3)*	0.50 %	0.54 %	0.5 %
Bis(2-ethylhexyl) 2,3,4,5-tetrabromophthalate (Component 4)	95.57 %	95.44 %	95.5 %
Unknown impurities	0.84 %	0.92 %	0.9 %
Number of unknown impurities, each component ≤ 0.3 %	16	18	18
Sum			99.4 %

\* For the two components at RT = 10.9 minutes and RT = 11.4 minutes the two structural isomers bis(2-ethylhexyl) 3,4,5-tribromophthalate and bis(2-ethylhexyl) 3,4,6-tribromophthalate could be proposed.

9.1.4.2. Example chromatograms of GC-FID

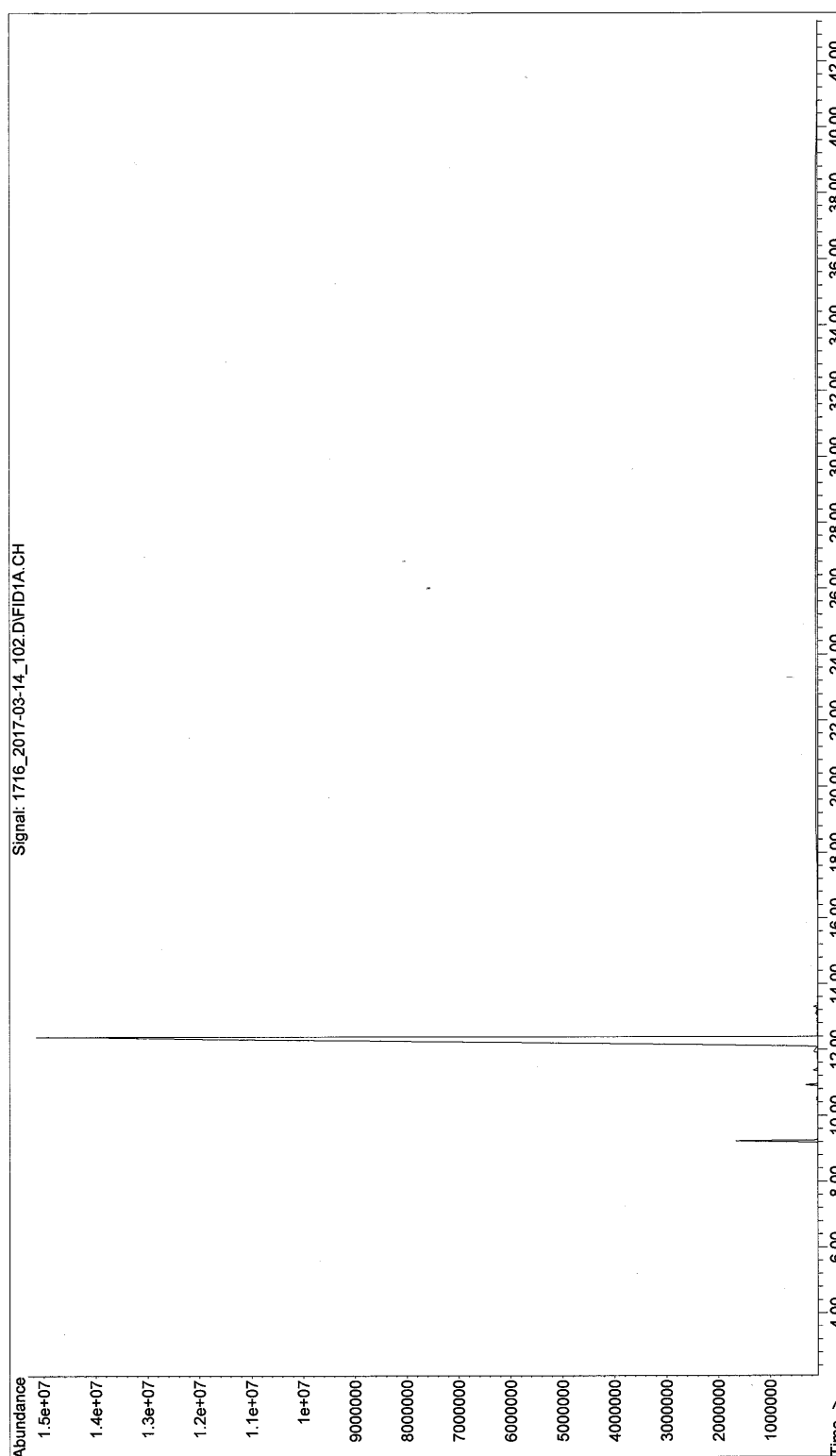


Figure 5: GC-FID chromatogram of the test item Bis(2-ethylhexyl) tetrabromophthalate.

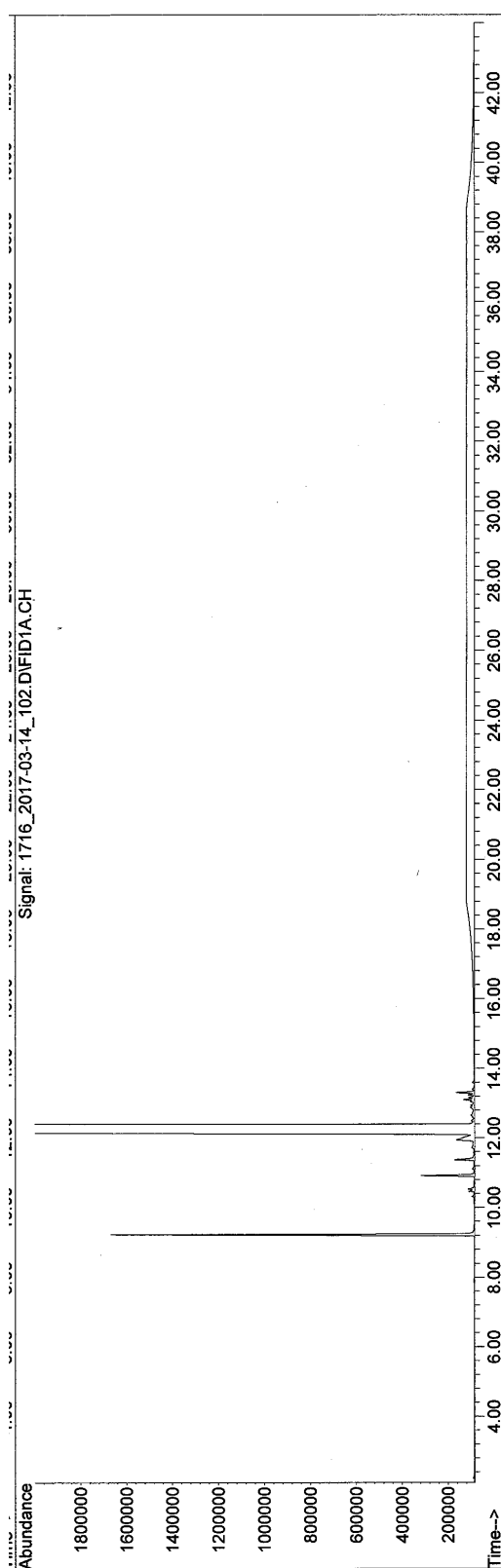


Figure 6: GC-FID chromatogram of the test item Bis(2-ethylhexyl) tetrabromophthalate (zoomed).

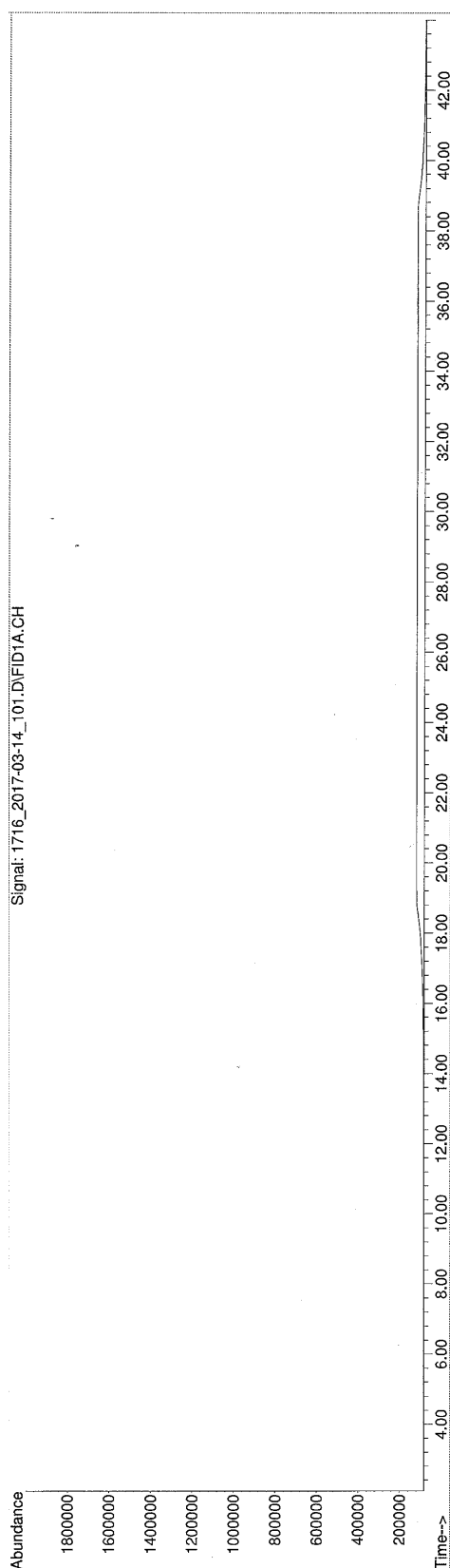


Figure 7: GC-FID chromatogram, blank



9.1.4.3. Chromatograms of GC-MS (TIC) and MS-spectra

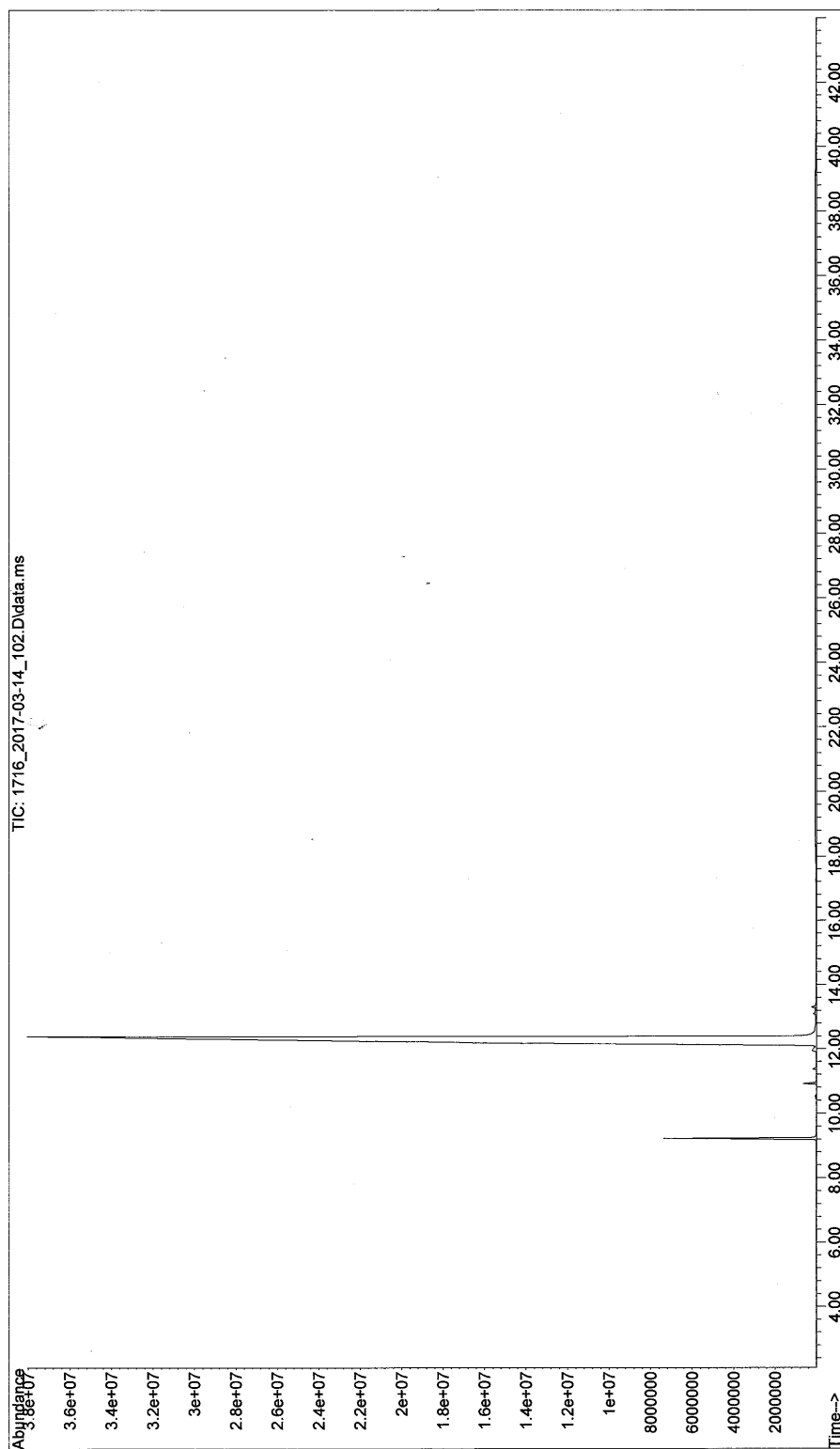


Figure 8: GC-MS chromatogram (TIC) of the test item Bis(2-ethylhexyl) tetrabromophthalate.

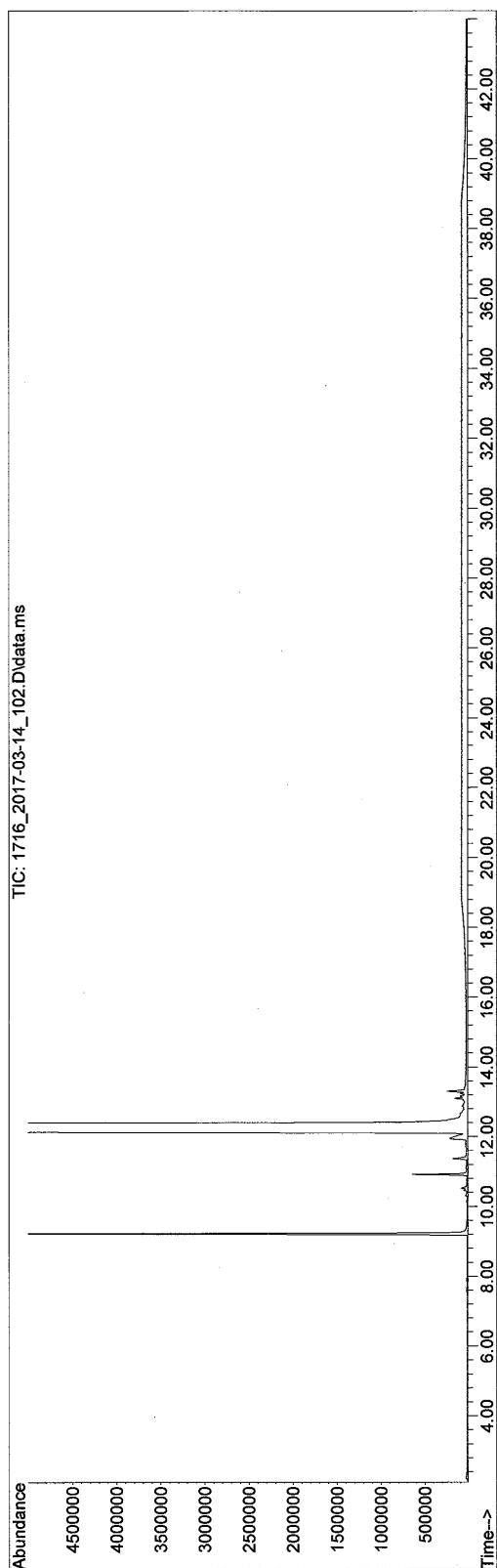


Figure 9: GC-MS chromatogram (TIC) of the test item Bis(2-ethylhexyl) tetrabromophthalate (zoomed).

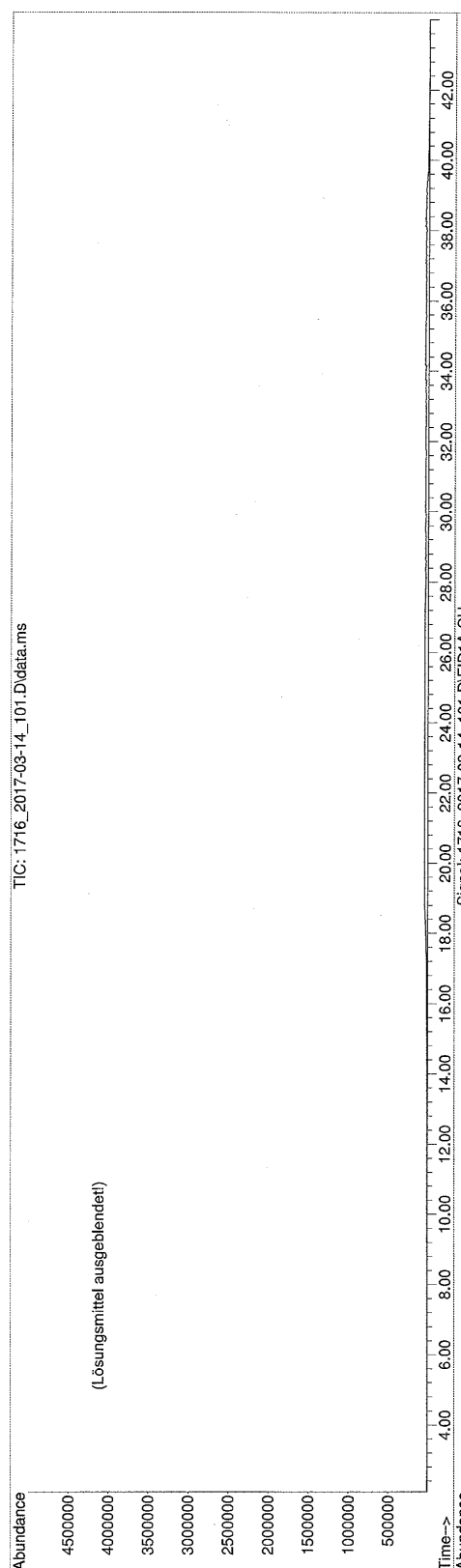


Figure 10: GC- MS chromatogram (TIC), blank

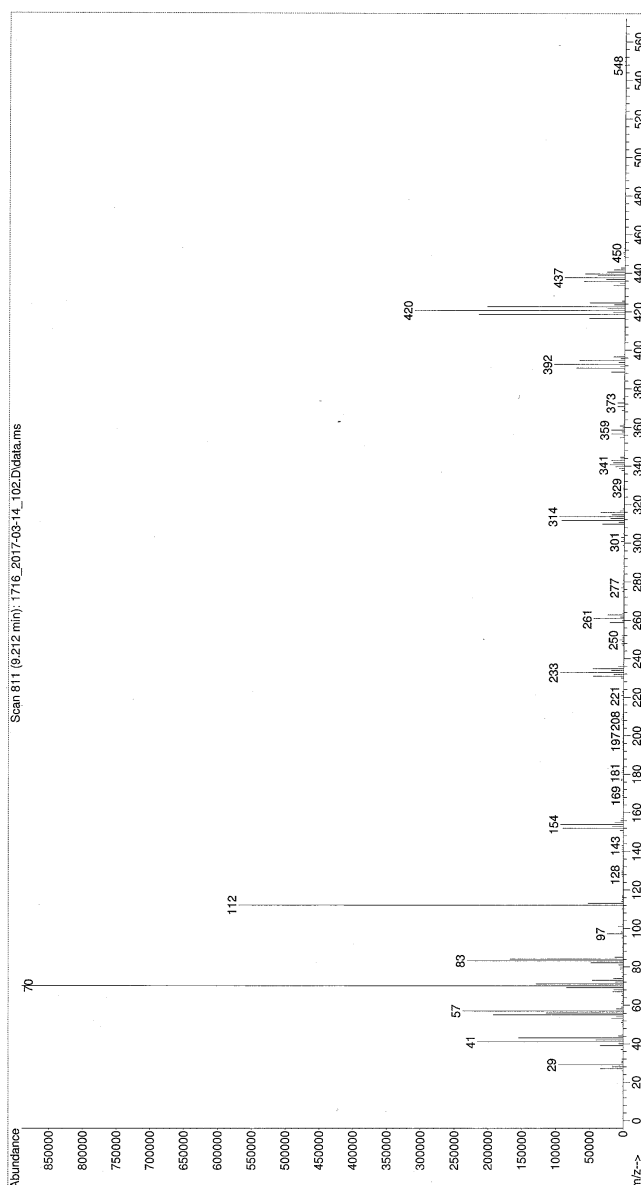


Figure 11: EI-MS spectrum of the component 1 at RT = 9.2 minutes

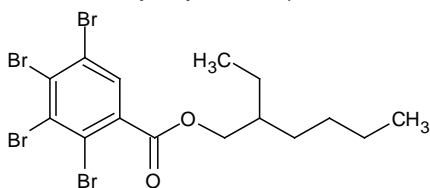
Assignment of major m/z peaks:

m/z 70: Fragment formula:  $C_5H_{10}$

m/z 112: Fragment formula:  $C_8H_{16}$

m/z 420: Fragment formula:  $C_6HBr_4CO$

For the component at RT = 9.2 minutes the following structure could be proposed (isomerism is possible):



2-Ethylhexyl 2,3,4,5-tetrabromobenzoate

Molecular formula:  $C_{15}H_{18}O_2Br_4$

Molecular weight: 550 g/mol

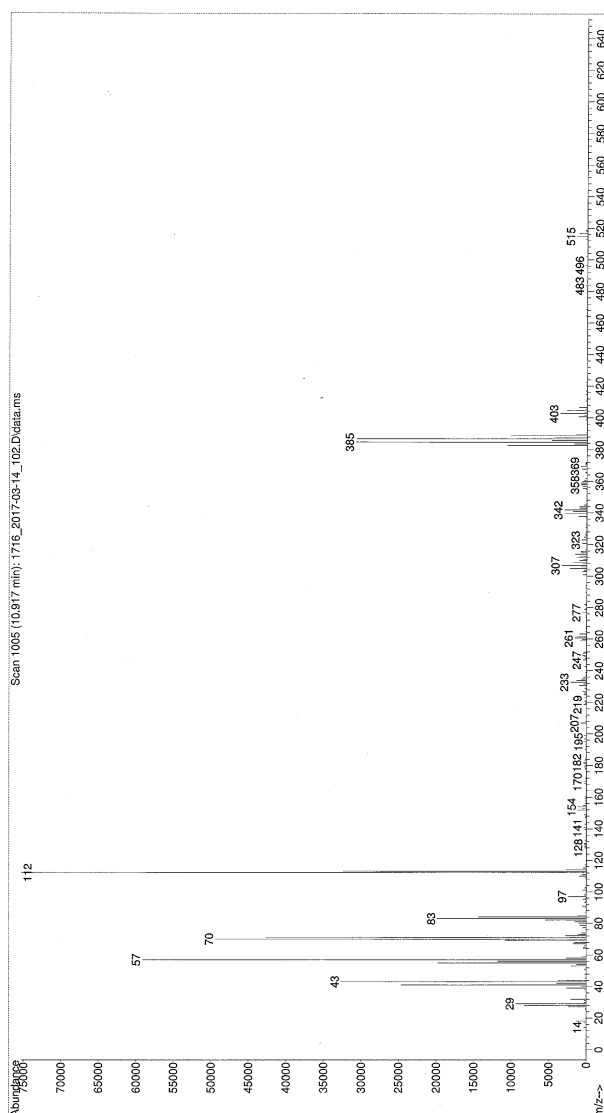


Figure 12: EI-MS spectrum of the component 2 at RT = 10.9 minutes  
For assignment of major m/z peaks and the proposed structure(s)  
see Figure 13.

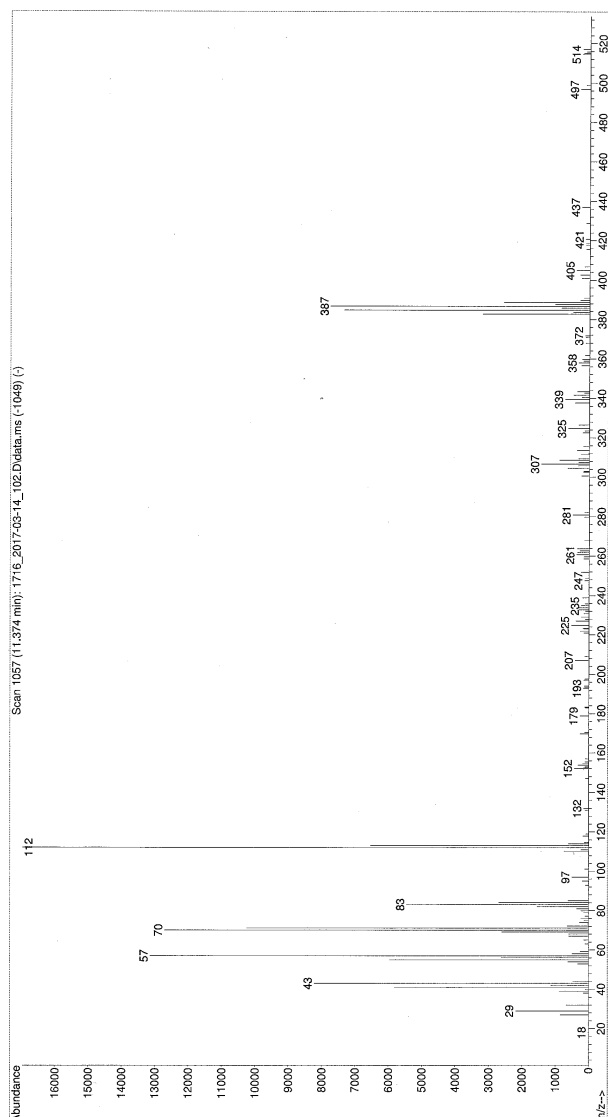


Figure 13: EI-MS spectrum of the component 3 at RT = 11.4 minutes

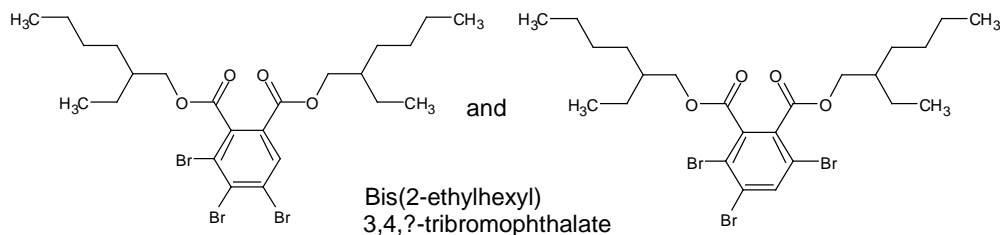
Assignment of major  $m/z$  peaks:

$m/z$  57: Fragment formula:  $C_4H_9$

$m/z$  112: Fragment formula:  $C_8H_{16}$

$m/z$  387: Fragment formula:  $C_6HBr_3C_2O_3H$

For the two components at RT = 10.9 minutes and RT = 11.4 minutes the following two isomeric structures could be proposed:



Molecular formula:  $C_{24}H_{35}O_4Br_3$

Molecular weight: 627 g/mol

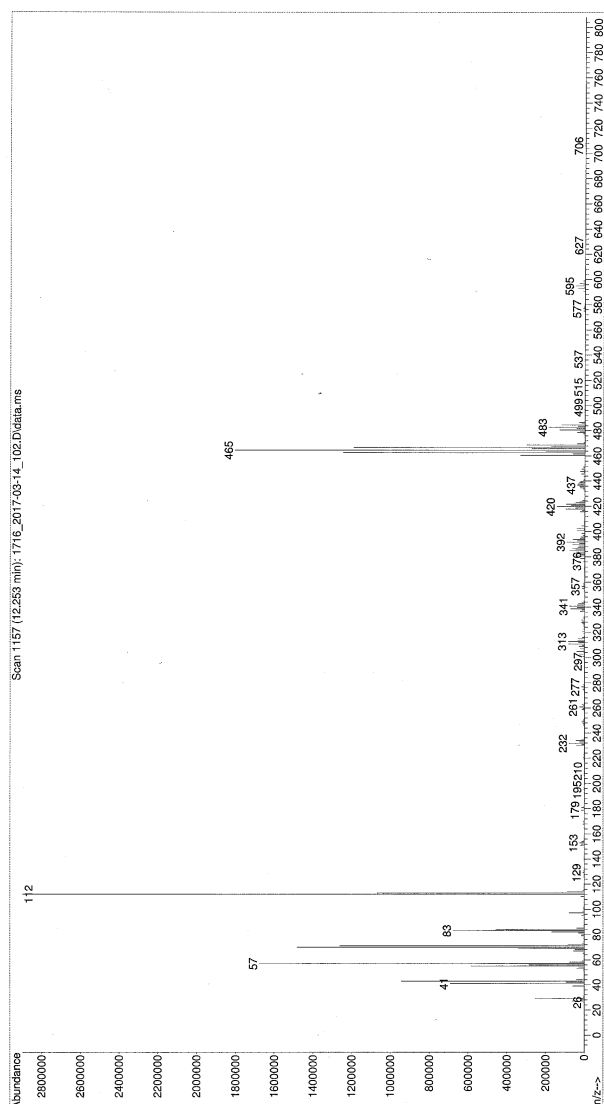


Figure 14: EI-MS spectrum of component 4 at RT = 12.3 minutes

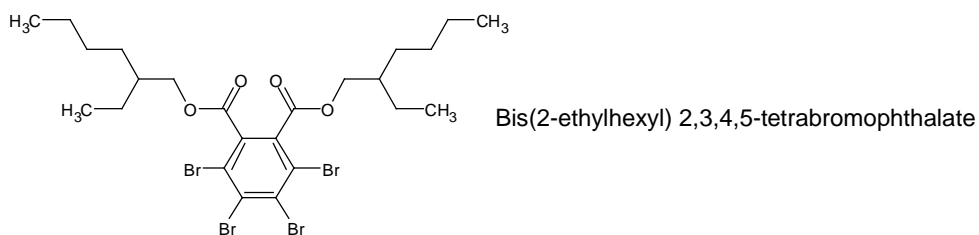
Assignment of major m/z peaks:

m/z 57: Fragment formula:  $C_4H_9$

m/z 112: Fragment formula:  $C_8H_{16}$

m/z 465: Fragment formula:  $C_6Br_4C_2O_3H$

For the component at RT = 12.3 minutes the following structure could be proposed:



Molecular formula:  $C_{24}H_{34}O_4Br_4$

Molecular weight: 706 g/mol

9.1.5. Test: Residue of evaporation

Method no.: 2011-0520901-96D

Supervisor: Dr. Schröder

Conditions: 250 °C, < 0.1hPa

Result: 0.63 %

Procedure:

The sample is weighed into a tared round bottom flask with standard ground joint. Under the above-mentioned conditions the sample is slowly heated up in a Büchi-bulb tube distilling oven until constant weight is reached.

9.1.6. Test: Water content by Karl Fischer technique

Method no.: 2011-0131301-90D and 2011-0131401-90D

Supervisor: Stefan Hendricks

Result: < 0.1 %

Procedure: Karl Fischer technique

The originally weighted sample of the test item was dissolved in the Karl Fischer solvent or in an appropriate solvent mixture and titrated back with the Karl Fischer titrant. The end point detection was detected bipotentiometrically using a Pt-indicator electrode. Karl Fischer solvent and Karl Fischer titrant are commercial reagents for determination of water content.