

WCSR Advice 2017-13 A

SCIENTIFIC COMMITTEE REACH (WCSR)

ADVICE ON MEASURING METHODS FOR CERTAIN RESTRICTED
SUBSTANCES OF THE ANNEX XVII OF REACH – PART A :
PHTALATES IN SOFT PVC, PAHS IN PLASTICS, NONYLPHENOL
AND NONYLPHENOL ETHOXYLATES IN TEXTILE



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WCSR Advice 2017-13 A

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CONFLICT OF INTEREST

No member has declared any conflict of interest.

RAPPORTEUR

The Scientific Committee REACH thanks the rapporteur Guido Vanermen.

PUBLIC CONSULTATION

A comment from Centexbel was received in the Public Consultation ending on 2 February 2018.

ADOPTION OF THE ADVICE

The Scientific Committee REACH advice was adopted by consensus on the meeting of 19/4/2018 and the comment on possible interference of DEHT on the GC-MS signal of DOP (p. 13) was adopted by written procedure on 26/10/2018.

LEGAL FRAMEWORK OF THE ADVICE

Cooperation agreement of 17 October 2011 between the Federal State, the Flemish Region, the Walloon Region and the Brussels Capital Region concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH)

Ministerial decree of 8 July 2014 appointing the members of the Scientific Committee REACH established under Article 3, § 3 of the Cooperation Agreement of 17 October 2011 between the Federal State, the Flemish Region, the Walloon Region and the Brussels Capital Region concerning the Registration, Evaluation, Authorisation and restriction of Chemicals (REACH)

Ministerial decree of 2 June 2016 on dismissal and appointment of members of the Scientific Committee REACH

Ministerial decree of 5 October 2016 on appointment of members of the Scientific Committee REACH

DISCLAIMER

The Scientific Committee REACH reserves, at any time, the right to change this advice when new information and data become available after the publication of this version.

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1 Scope of the advice

The WCSR will select the most scientifically appropriate method for a list of substances restricted under the annex XVII of REACH .

The selection of the most appropriate methods will be carried out on the basis of:

- Availability of international standardized methods (EN, ISO, ASTM, ...)
- Availabilities of European national standards for the substances and matrices in question
- Validated test methods in literature
- The industrial methods

The methods will be evaluated with regard to application area, limit of quantification, limit of detection, expected measurement uncertainty and repeatability.

A description of the analytical method will be given, including specific requirements :

- Method of detection (total content or migration);
- Preparation of the samples and extraction;
- Solvents;
- Purification,
- Particle size reduction;
- Minimum intake;
- Use of isotope labelled internal standards;
- QC samples;
- Type of machine used for the analysis (including settings);
- Etc.

Within this report advice on the analytical methods of the following substances and matrices is given:

- Nonylphenol and nonylphenol ethoxylates in textile
- Phthalates in soft PVC
- PAH in plastics.

Within the REACH regulation the following restrictions have been set:

- Nonylphenol and nonylphenol ethoxylates in textile: Concentration (Anx XVII entry 46a): *0,01 % by weight*

- Phthalates in soft PVC: concentration (Anx XVII entry 51-52): *0,1 % by weight of the plasticised material*
- PAH in plastics: Concentration: (Anx XVII entry 50.5: Article consommateurs): *1 mg/kg (0,0001 % by weight of this component) of any of the listed PAHs.*

2 Phthalates in soft PVC

Phthalates can be found in plastics, textiles, coatings or paints, etc., in toys and children's products. Being a plasticizer, phthalates often exist in PVC as well as other plastics including polyvinyl acetate (PVA), polyvinylidene chloride (PVDC), and polyurethane (PU). PVC is used in toys, children's products and many other consumer products in the form of wire and cable insulation, etc. Phthalates might also be used as solvents and/or plasticizers in paints, inks, adhesives, sealants, air fresheners, and scented products, but are more likely to be used when the finished product shall be flexible, such as a printed design on apparel, or in paints, adhesives, or sealants on flexible substrates. Certain plastics, such as polyethylene and polypropylene, usually do not contain plasticizers, but surface coatings and adhesives on them can contain phthalates. Even though some plastics do not need plasticizers, phthalates are still added, which means that phthalates can be found in some elastomers or synthetic rubbers. Most natural and synthetic fibres and textiles are not expected to contain phthalates but printed designs, coatings, surface treatments and elastic components can contain phthalates.

Examples of materials that can contain phthalates are

- PVC and related polymers, such as polyvinylidene chloride (PVDC) and polyvinyl acetate (PVA),
- soft or flexible plastics, except polyolefins,
- soft or flexible rubber, except silicone rubber and natural latex,
- foam rubber or foam plastic, such as PU,
- surface coatings, non-slip coatings, finishes, decals, and printed designs,
- elastic materials in apparel, such as sleepwear,
- adhesives and sealants, and
- electrical insulation.

(Source: ISO 8124-6)

Phthalate plasticizers comprise approximately 92% of plasticizer production in the world, with di(2-ethylhexyl) phthalate (DEHP) alone accounting for approximately 50% of this amount (Becker et al., *Int. J. Hyg. Environ. Health* 212, 685, 2009). The industrial applications of phthalates are related to the length of their ester chain. Higher molecular-weight phthalates, such as DEHP, di-isononyl phthalate (DiNP) and di-isodecyl phthalate (DiDP), are primarily used as plasticizers to soften PVC products, while the lower-molecular-weight phthalates, such as diethyl phthalate (DEP), di-n-butyl phthalate (DnBP), di-iso-butyl phthalate (DiBP) and butyl benzyl phthalate (BBzP), are widely used as solvents to hold color and scent in various consumer and personal care products. DINP is a mixture of esters of phthalic acid with C8-C10 alkyl alcohols (C9 rich). DIDP consists of C9-C11 (C10-rich) branched alkyl esters.

The following phthalic acid esters are included in REACH, annex 17 entries 51 en 52:

- dibutyl phthalate (DBP)
- benzyl butyl phthalate (BBP)
- bis(2-ethylhexyl) phthalate (DEHP)
- di-n-octyl phthalate (DNOP)
- di-iso-nonylphthalate (DINP)
- di-iso-decyl phthalate (DIDP)

They shall not be used as substances or in mixtures, in concentrations greater than 0,1 % by weight of the plasticised material, in toys and childcare articles.

Remark that other phthalates are considered to be substances of very high concern and appear on the candidate list for authorisation (according to REACH, art. 59 – 10)

- Diisobutyl phthalate (DIBP)
- Bis(2-methoxyethyl) phthalate
- 1,2-Benzenedicarboxylic acid, dihexyl ester, branched and linear
- 1,2-Benzenedicarboxylic acid, dipentyl ester, branched and linear
- 1,2-Benzenedicarboxylic acid, di-C6-10-alkyl esters
- 1,2-benzenedicarboxylic acid, di-C6-10-alkyl esters or mixed decyl and hexyl and octyl diesters
- 1,2-Benzenedicarboxylic acid, di-C6-8-branched alkyl esters, C7-rich
- 1,2-Benzenedicarboxylic acid, di-C7-11-branched and linear alkyl esters
- 1,2-Benzenedicarboxylic acid, mixed decyl and hexyl and octyl diesters

For the determination of phthalates in consumer goods the following international standards have been published:

- **ISO 8124-6:2014** - Safety of toys - Part 6: Certain phthalate esters in toys and children's products
- **EN ISO 14389:2014** -Textiles -- Determination of the phthalate content -- Tetrahydrofuran method

Remarks:

- The **ECHA Compendium of analytical methods recommended by the Forum to check compliance with REACH annex XVII restrictions** makes reference to US EPA 8061A which is a general method for the determination of phthalate esters in various solid and liquid matrices. The method makes use of GC-ECD as detection technique; this technique is subject to interferences and nowadays only rarely available in the laboratories.
- Method **CPSC-CH-C1001-0.9.3 (2010)** and method **CPSC-CH-C1001-0.9.4 (2018)**, published by the US Consumer Product Safety Commission, are comparable to EN ISO 14389. The extraction method and detection technique (GC-MS) are identical, however smaller intakes are used as well as other quantitation ions. CPSC-CH-C1001-0.9.3 (2010) determines all REACH annex XVII phthalates, CPSC-CH-C1001-0.9.4 (2018) determines additionally DIBP, DnPP, DnHxP and DCHP, but does not determine DIDP.

Summaries of both standards are given in Table 1. Comments are given on some aspects of the method and method performance characteristics are included.

On the basis of this comparative table the following conclusions can be made with regard to the appropriateness of the methods:

- **ISO 8124** is the recommended method for the analysis of toys and other children products. It shows excellent method performance characteristics and when comparing results from different laboratories only the results obtained with this method will be accepted. Nevertheless the method has some drawbacks, which should be considered at the next revision of the standard:
 - The parameter list is limited to 6 phthalates and should be extended to all phthalates of concern
 - Soxhlet extraction is used as extraction technique; this is a laborious technique with high solvent consumption; sonication or shaking will give equivalent results
 - Improvement of the results (trueness) is possible by addition of isotope labelled internal standards to the extraction solvent
 - To safeguard the chromatographic quality precipitation of co-extracted polymers using a non-solvent should be carried out prior to GC-injection

- **EN ISO 14389** shows good within-laboratory repeatabilities but strongly deviating between-laboratory results which might result from the small intakes and the differences in sample pretreatment of the coated/printed textile products. Nevertheless it is the recommended method for textiles. The method is comparable to ISO 8124 but:
 - It is applicable to a broader list of phthalates
 - Extraction is easily carried out by sonication
 - Co-extracted polymers are removed by precipitation
 - The internal standard is added to the extraction solvent; also here we recommend the use of isotope-labelled phthalates

TABLE 1: SUMMARY OF STANDARDS FOR THE ANALYSIS OF PHTHALATES IN PLASTICS

	ISO 8124-6	ISO 14389
Scope	<p>Toys and children's products made of plastics, textiles and coatings</p> <p>Parameter list:</p> <ul style="list-style-type: none"> - di-n-butyl phthalate (DBP) - benzyl butyl phthalate (BBP) - bis-(2-ethylhexyl) phthalate (DEHP) - di-n-octyl phthalate (DNOP) - di-iso-nonylphthalate (DINP) - di-iso-decyl phthalate (DIDP) <p>Remark: standard may be applicable to other phthalates but needs validation</p>	<p>Textiles (with polymer finish, coating or print)</p> <p>Parameter list:</p> <ul style="list-style-type: none"> - di-n-butyl phthalate (DBP) - benzyl butyl phthalate (BBP) - bis-(2-ethylhexyl) phthalate (DEHP) - di-n-octyl phthalate (DNOP) - di-iso-nonylphthalate (DINP) - di-iso-decyl phthalate (DIDP) - di-iso-butyl phthalate (DIBP) - di-n-pentyl phthalate (DPP) - di-iso-heptyl phthalate (DIHP) - di-methoxyethyl phthalate (DMEP)
Sample pretreatment	<p>Cutting of representative part into small pieces (<5 mm)</p> <p>Comment: particle size reduction to <1 mm recommended to improve extraction efficiency</p>	<p>Cutting of coated/printed textile part into small pieces (<5 mm)</p> <p>Remark: all samples are analysed in duplicate</p> <p>Comment: particle size reduction to <1 mm recommended</p>

Extraction	<p>Recommended intake: 1g (minimum 100 mg)</p> <p>Soxhlet extraction with 120 ml dichloromethane during 6 h <i>or</i></p> <p>Immersion in 80 ml dichloromethane during 1.5h at 80°C, followed by reflux for 1.5h</p> <p>Concentration of the extract to a final volume of 10 ml, addition of internal standards (optional)</p> <p>Comment: internal standards are added to the final extract and will therefore not correct for extraction recoveries or evaporation losses</p>	<p>Intake: 300 mg</p> <p>Ultrasonic extraction with 10 ml THF at 60°C for 1 h, with addition of internal standard</p> <p>Precipitation of co-extracted polymer with 20 ml hexane or acetonitrile</p> <p>Centrifugation and transfer of supernatant to injection vial</p>
Measurement	<p>GC-MS (non-polar column, split injection, electron ionisation)</p> <p>Identification: based on retention times, diagnostic ions and relative intensities (see Table 2 for diagnostic ions)</p> <p>Quantification ions: m/z 149, except DNOP (279), DINP (293), DIDP (307)</p> <p>Comment: coextracted polymer will lead to rapid deterioration of the chromatographic performance; polymers can be precipitated in hexane</p>	<p>GC-MS (non-polar column, splitless injection, electron ionisation)</p> <p>Identification: based on retention times, diagnostic ions and relative intensities</p> <p>Quantification ions: m/z 149, except DNOP (279), DINP (293), DIDP (307), DIHP (265)</p>

Quantification	<p>External or internal standard method</p> <p>Recommended internal standard: benzyl benzoate or di-n-pentyl phthalate</p> <p>Comment: these internal standards are not appropriate as these compounds may be present in the samples; the use of aromatic ring d₄-labelled phthalates should be recommended as internal standards</p>	<p>Internal standard method: dicyclohexyl phthalate (DCHP)</p> <p>Comment: this internal standard is not appropriate as this compound may be present in the samples; the use of aromatic ring d₄-labelled phthalates should be recommended as internal standards</p>
Method performance characteristics	<p>Limit of quantification (LOQ):</p> <ul style="list-style-type: none"> - DBP, BBP, DEHP, DNOP: 0.001% - DINP, DIDP: 0.005% (isomeric mixtures) <p>Intralab coefficient of variation (CV_r): <2-9%</p> <p>Interlab coefficient of variation (CV_R): <4-25%</p> <p>(validated for PVC, PUR, polyacrylic acid and nitrocellulose plastics and coatings)</p>	<p>Limit of detection (LOD)</p> <ul style="list-style-type: none"> - DBP, BBP, DEHP, DNOP, DIBP, DPP: 0.004% - DINP, DIDP, DIHP, DMEP: 0.02% <p>Intralab coefficient of variation (CV_r): <3-19%,</p> <p>Interlab coefficient of variation (CV_R): high</p>

TABLE 2: GC-MS DIAGNOSTIC IONS FOR PHTHALATE ESTERS (ISO 8124-6)

Chemicals	Retention time min	Diagnostic ions <i>m/z</i>	Relative intensity
BB (IS)	7,4	<u>105</u> , 91, 212, 194	100:46:17:09
DBP	8,1	<u>149</u> , 150, 223, 205	100:09:05:04
DAP (IS)	8,9	<u>149</u> , 150, 237, 219	100:10:06:03
BBP	9,6	<u>149</u> , 091, 206, 238	100:72:23:03
DEHP	10,3	<u>149</u> , 167, 279, 150	100:50:32:10
DNOP	11,3	149, <u>279</u> , 150, 261	100:18:10:03
DINP	10,7-13,0	149, 127, <u>293</u> , 167	100:14:09:06
DIDP	11,0-14,5	149, 141, <u>307</u> , 150	100:21:16:10

Comment on possible interference of di-2-ethylhexyl terephthalate (DEHT) on the GC-MS signal of di-n-octyl phthalate (DNOP)

Terephthalates are esters of terephthalic acid such as the 1,4-benzenedicarboxylic acid ester known as DEHT, DEHTP or DOTP (CAS n° 6422-86--2) which offers low temperature performance, better resistance to soapy water extraction and low volatility. In plastisols, these plasticisers provide lower initial viscosity and better stability but requires higher fusion and processing temperature. Terephthalates exhibit lower levels of compatibility with PVC than ortho-phthalates limiting their use for the production of durable goods (*source*: Plasticisers Information Centre).

Concerns about the potential risk of di-2-ethylhexyl phthalate (DEHP) have led most companies to replace DEHP with DEHT. It is widely available and tested and has a comprehensive toxicological portfolio (see e.g. PubChem), with the conclusion that it can be used in toys, beverage packaging and medical devices

DEHT is co-extracted with the phthalates of concern and is injected into the GC-MS system as well. On nonpolar GC-columns (e.g. 5% polydiphenylsiloxane 95% polydimethylsiloxane) DEHT and DNOP show quasi similar retention behaviour which may lead, depending on column supplier, column dimensions and DEHT concentration to positive or negative interference on the DNOP signal. The use of DNOP is restricted (limit value of 0.1% for children's toys and child care articles which can be placed in the mouth), the use of DEHT is not. For a correct quantification of DNOP it is indispensable that analytical differentiation of both phthalates is achieved.

Mass spectrometric characteristics

Mass spectra for DNOP and DEHT are shown in Figure 1. For the sake of completeness also MS spectra of DEHP and di-2-ethylhexyl isophthalate (the 1,3-isomer) are given. In the MS spectrum of DNOP the ions 149 and 279 are predominant. Depending on instrument settings other ions may be present as well (see e.g. the MS-spectrum from the Tokyo University). Another specific ion is ion 167. The MS spectrum of DEHP is comparable to that of DNOP, with the same characteristic ions 149, 167 and 279. In case of di-ethylhexyl isophthalate the same ions can be found but the predominant ion is 112. In the spectrum of the terephthalate isomer the ions 112, 149, 167 and 279 are present as well but additionally a high abundance is observed for ion 261. This ion shows a low abundance in the MS spectra of the other phthalates and can be considered to be characteristic for DEHT. Also ion 279 is more abundant in the DEHT spectrum compared to the spectra of the other phthalates. In addition to the retention time match, high relative abundancies of the ions 261 and 279 compared to that of 149 will be a criterion for the identification of DEHT. Nevertheless as quantification of most phthalates including DNOP is carried out on the basis of ion 149 and as ion 149 is one of the more abundant ions of DEHT it is clear that in case of insufficient chromatographic resolution DEHT will interfere on the signal of a coeluting phthalate.

Chromatographic separation

In Figure 2 GC-MS chromatograms of DNOP, DEHT and also DEHP are shown. The chromatograms were recorded using a nonpolar DB-XLB column (30 m x 0.25 mm id *0.25 µm film thickness). The retention times for DNOP, DEHT and DEHP are 23.32, 23.45 and 21.73 min resp.. DEHP is well separated on a nonpolar column from DEHT and there is no risk of interference. The retention times of DNOP and DEHT only differ little, but the peaks are quasi baseline separated. However it is clear that in case of reduced chromatographic resolution or retention time shift, e.g. caused by matrix effects, DEHT will interfere on the signal of DNOP. Positive interference occurs when the DEHT peak shifts to lower retention time, negative interference when the DNOP disappears in the foot of a much larger DEHT peak (see as an example Figure 3).

In Figure 4 GC-MS ion chromatograms are shown for an extract of PVC containing different phthalates (Frontier Lab application note PYA1-074E). The chromatograms were recorded on a nonpolar Ultra ALLOY-5 (30 m x 0.25 mm id *0.25 µm film thickness) column. For ion 149 two peaks are observed at the retention time of 10.2 min. These peaks are baseline separated and belong to DNOP and DEHT (= DOTP). Selection of the ions 261 and 279 allows to attribute the later eluting peak to DEHT and if desired to quantify this compound on the basis of the m/z 261 and 279 peak areas.

Conclusion

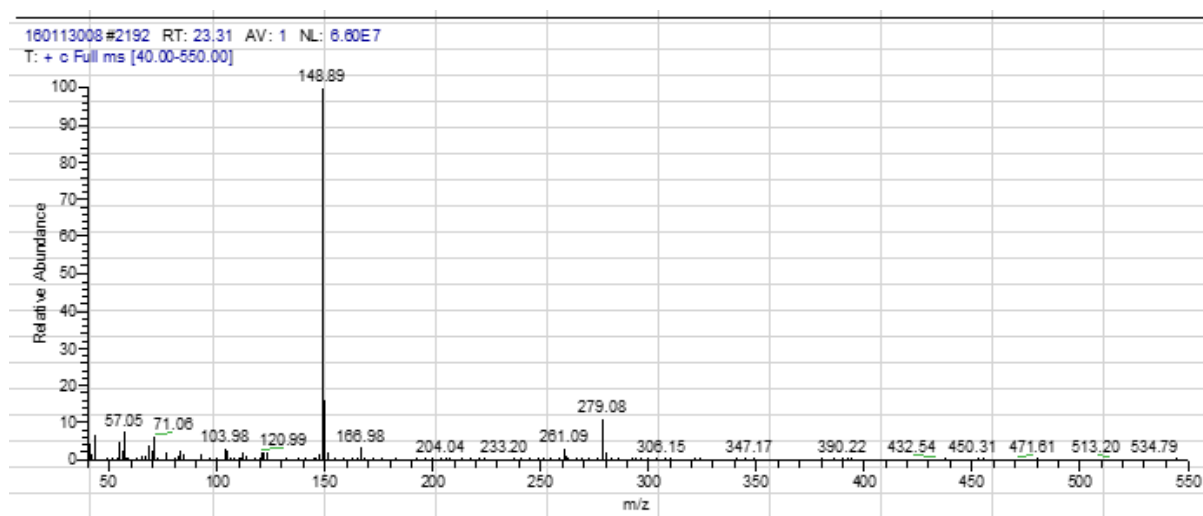
All phthalate standard methods make use of nonpolar columns for the separation of the phthalate compounds of concern. These standards should include a clause with regard to the possible interference by DEHT (we recommend to contact the respective CEN Technical Committees in this regard). Chromatographic separation should be conducted on a column which allows baseline separation of DNOP and DEHT. Nevertheless due to retention time drift (e.g. due to matrix constituents) false positive results for DNOP are still possible in case DEHT is present. On the other hand high concentrations of DEHT relative to DNOP may, in case of reduced chromatographic resolution, lead to false negative results because of disappearance of the DNOP peak in the foot of the DEHT peak. Therefore the presence of DEHT should always be checked by inclusion of the DEHT ions 261 and 279 in the GC-MS data acquisition method. The presence of DEHT is confirmed on the basis of the registered peak heights in the chromatograms of the ions 261 and 279 relative to that of ion 149. If the ions show comparable heights DEHT is considered to be present. An additional GC-MS analysis should then be performed on an appropriate second column of different polarity in order to separate DNOP and DEHT and to quantify DNOP interference-free.

Remark:

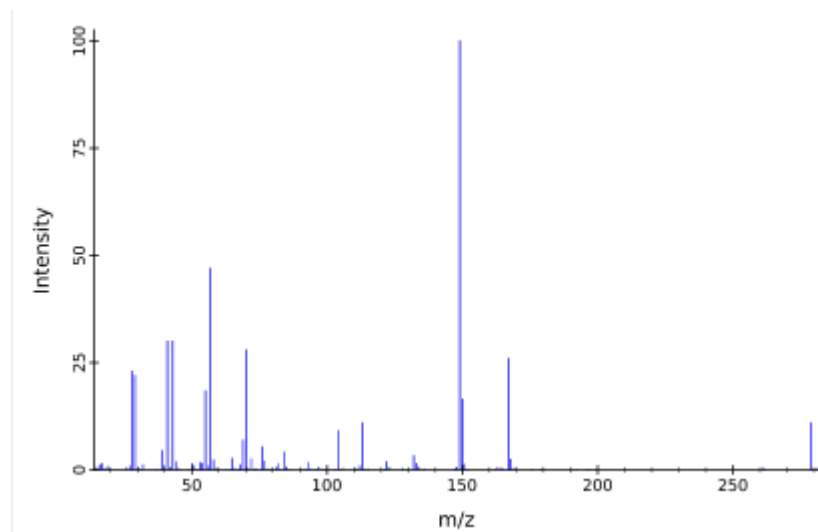
Possible interference by DEHT is not limited to DNOP but will also occur on the signal of DINP. Figure 5 shows a chromatogram of DINP recorded on the same column. From the chromatogram it can be seen that the peak of the DINP isomer cluster starts at 22 min and that DEHT (retention time 23.32 min) will coelute with the DINP peak resulting in false positive results. For a correct quantification of DINP, the DINP peak should be separated from the DEHT peak by reanalysis on a column of different polarity or the DEHT contribution should be quantified on the basis of the m/z 261 signal and subtracted from the DINP+DEHT concentration determined on the basis of m/z 149.

Figure 1: MS spectra for different dioctyl phthalate isomers

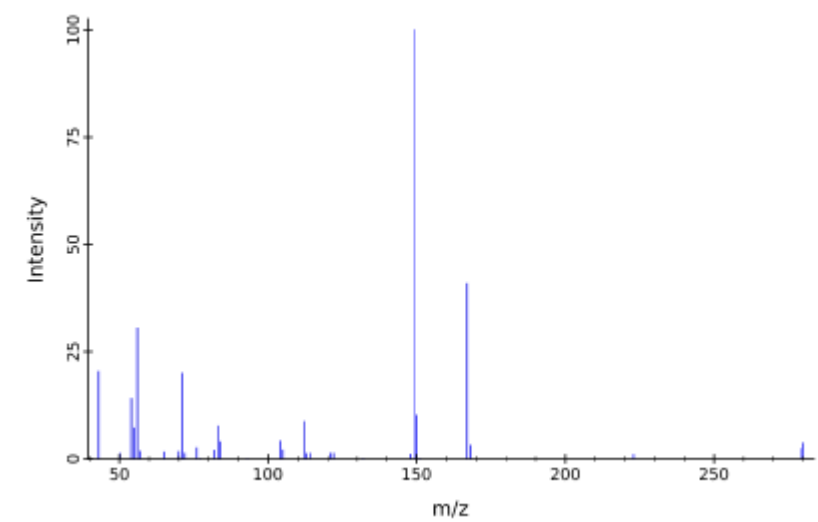
di-n-octyl phthalate (MS data from VITO)



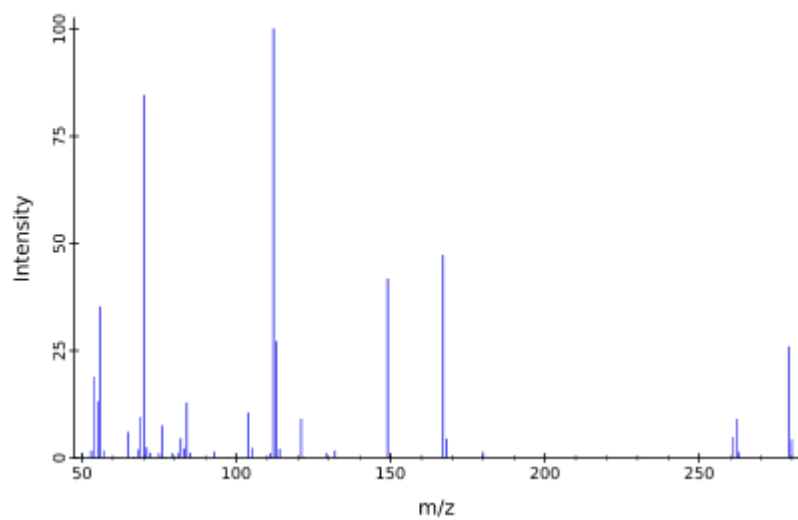
di-n-octyl phthalate (MS data from Kimito Funatsu, Graduate School of Engineering, The University of Tokyo, see PubChem)



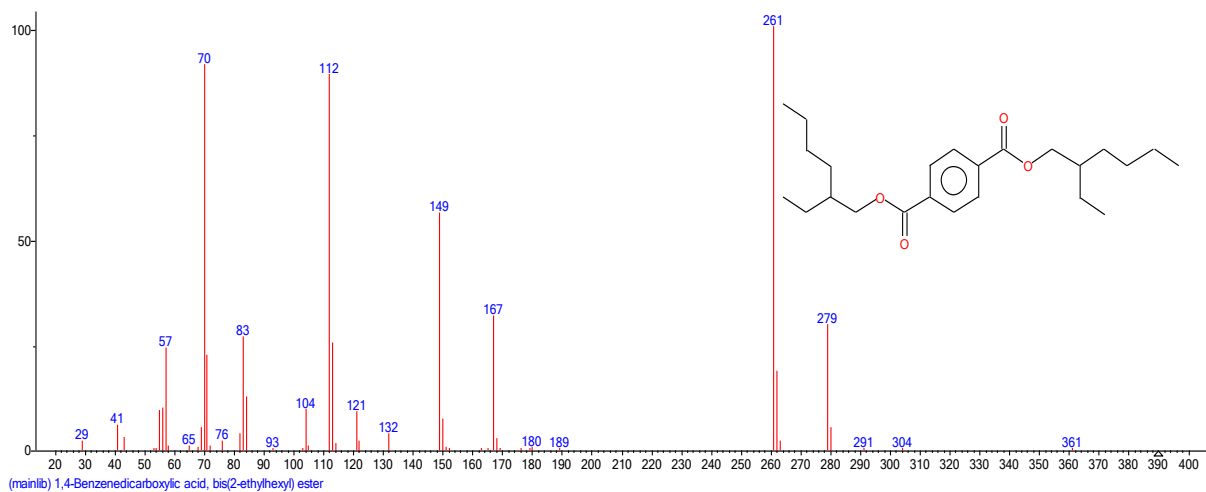
di-2-ethylhexyl phthalate (idem)



di-2-ethylhexyl isophthalate (idem)



d-2-ethylhexyl terephthalate (MS data from NIST)



di-2-ethylhexyl terephthalate (MS data from VITO)

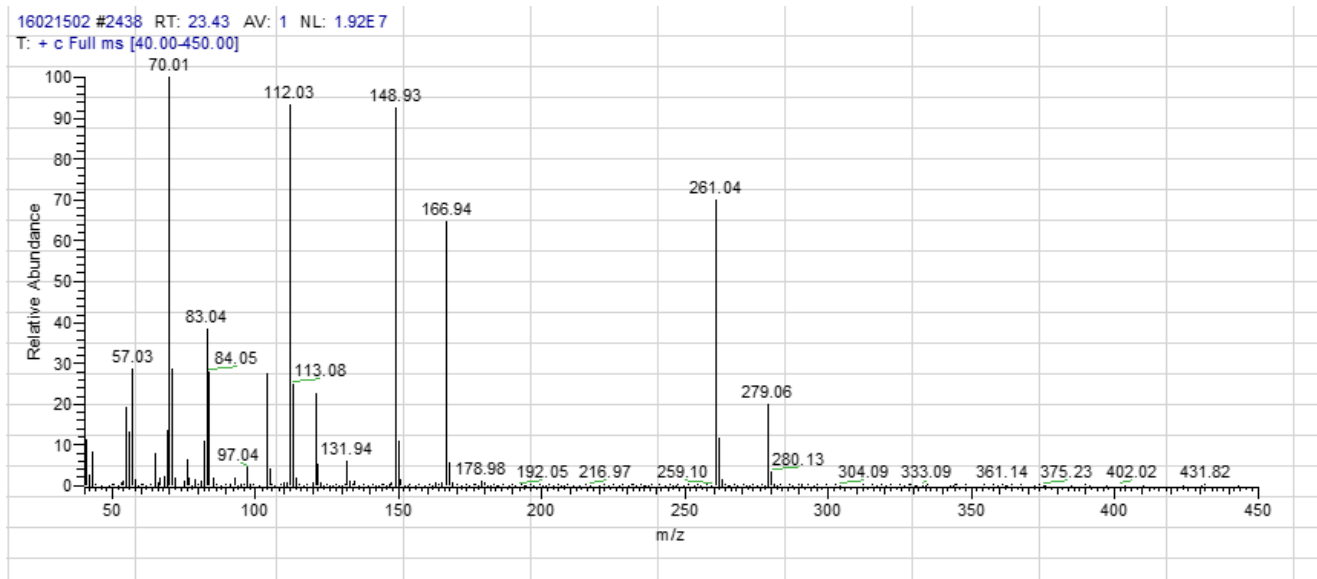
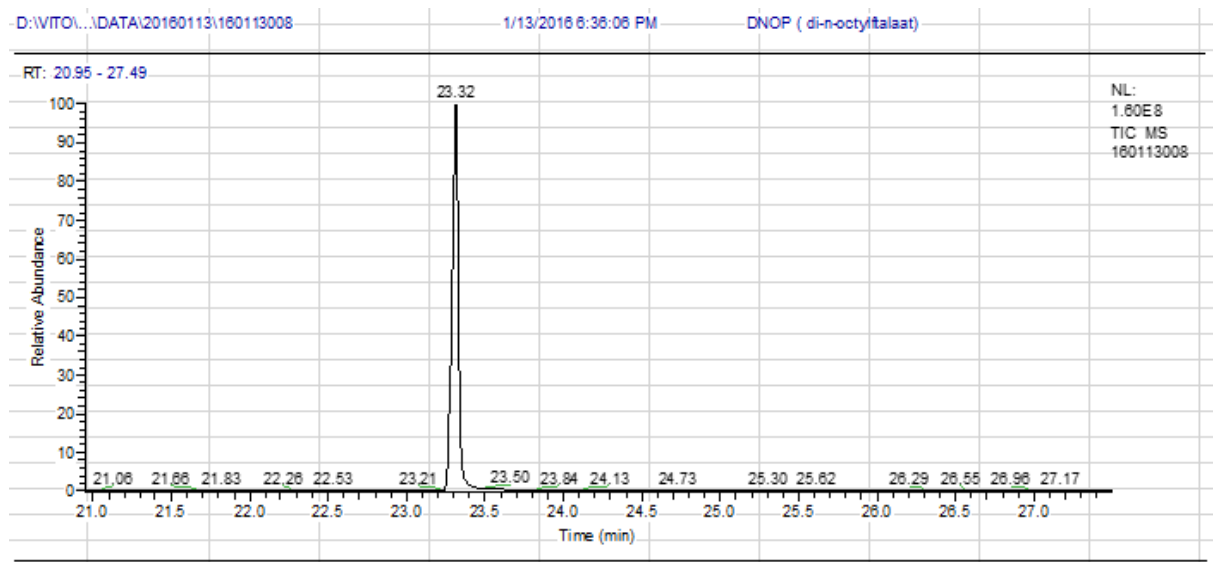
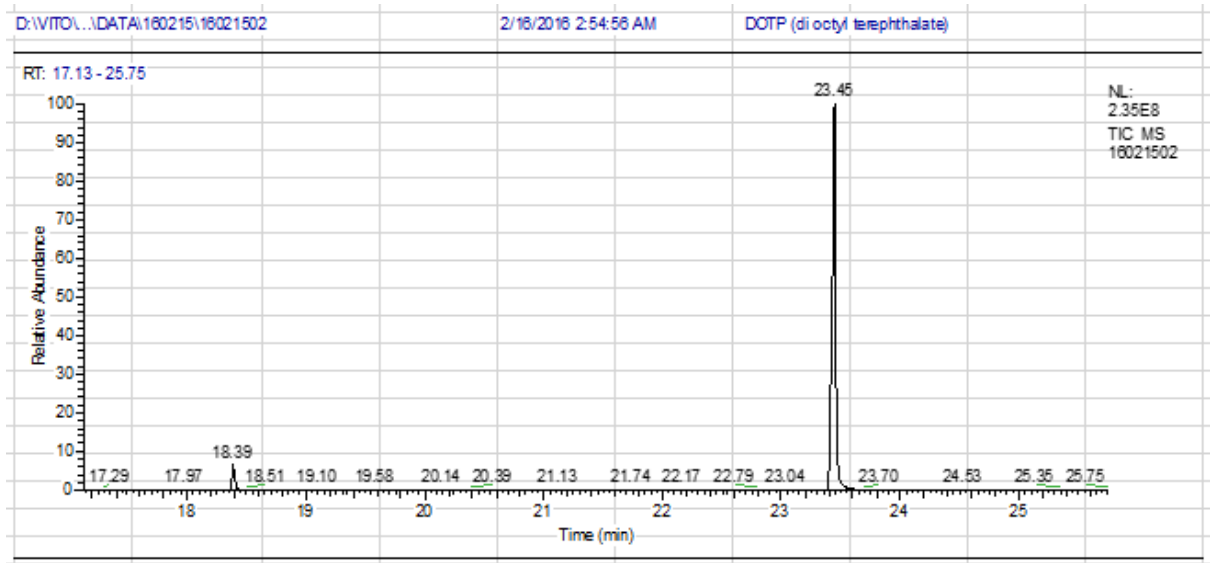


Figure 2: GC-MS chromatograms for dioctyl phthalate isomers (from VITO)

di-n-octyl phthalate



di-2-ethylhexyl terephthalate



di-2-ethylhexyl phthalate

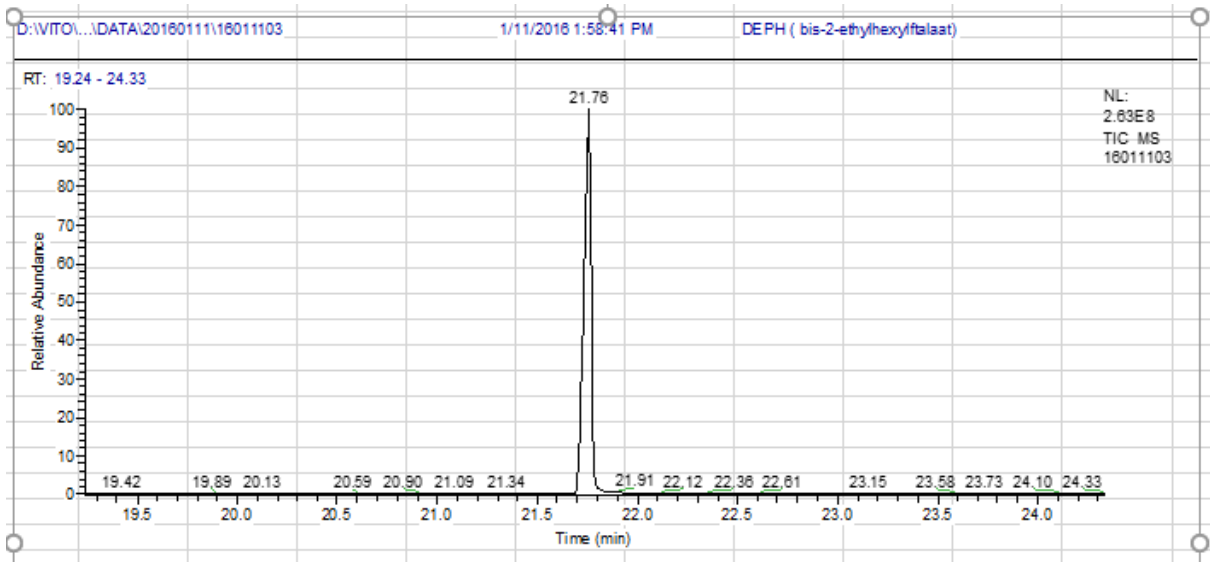


Figure 3: Chromatogram illustrating the disappearance of DNOP in the DEHT peak in case of high DEHT concentration and insufficient chromatographic resolution

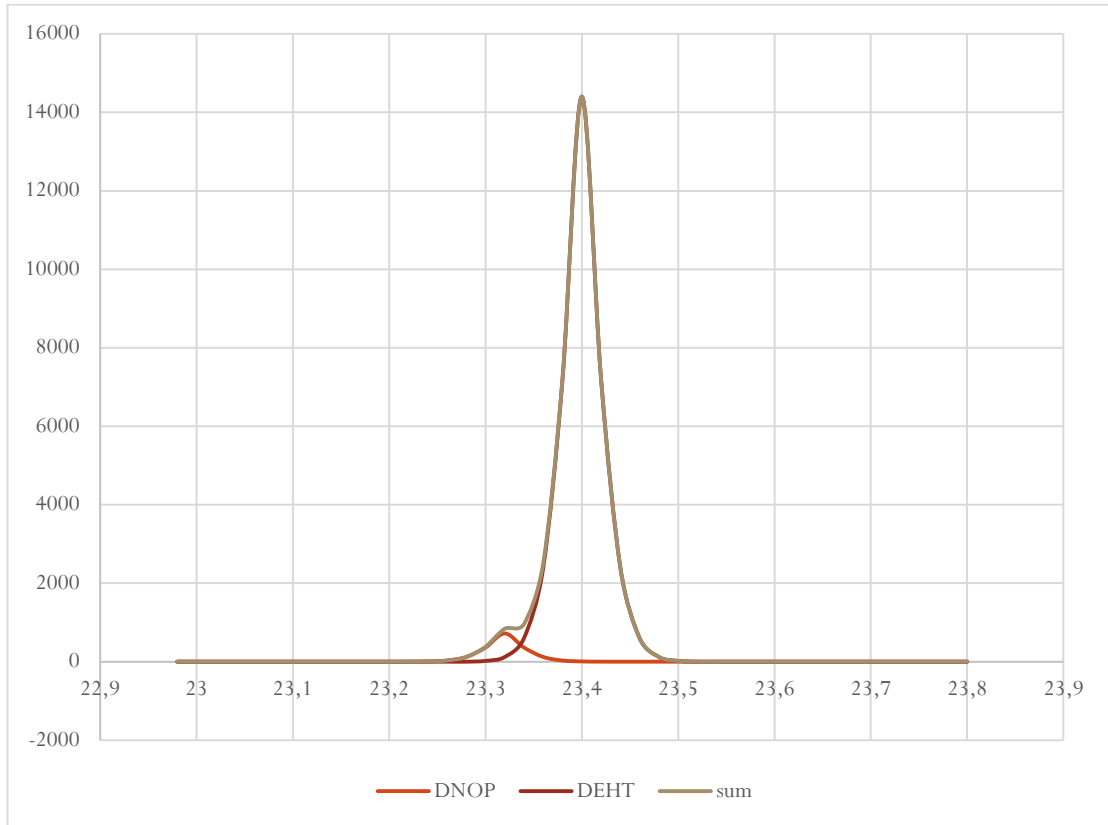


Figure 4: Ion chromatograms for DNOP and DETP in PVC (from technical note Frontier Lab PYA1-074E)

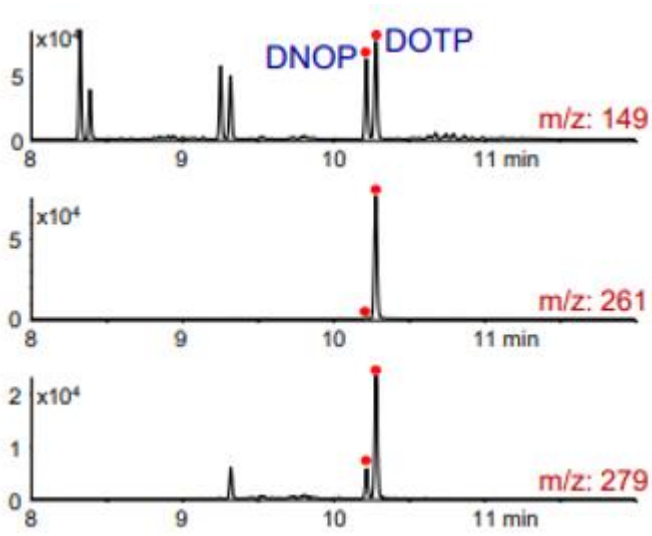
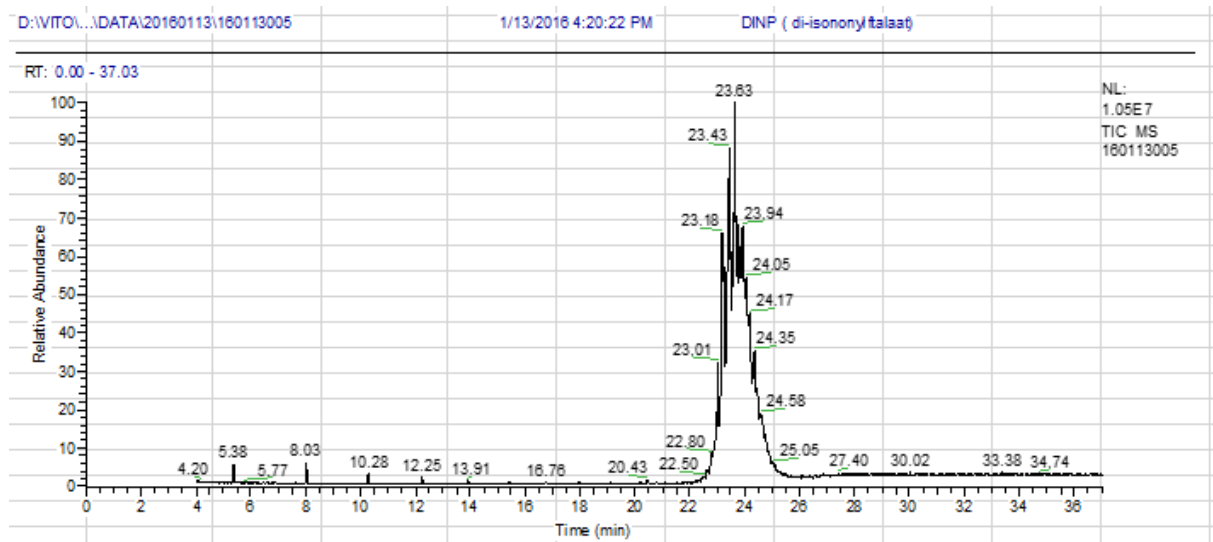


Figure 5: GC-MS chromatogram of di-isononyl phthalate (DINP)



3 Polycyclic aromatic hydrocarbons in plastic

PAHs are natural constituents of mineral oil (petrogenic PAHs) or are generated during combustion (pyrogenic PAHs). More or less the same PAHs will be present whether the source is pyrogenic or petrogenic, but the relative composition of the mixture of PAHs are different depending on the source. Two types of additives, i.e. extender oils and carbon black, which are found in rubber and plastic products are known to contain PAHs. Extender oils are mineral oil products which are derived from crude oil (petrogenic PAHs) whereas carbon black is a material produced by the incomplete combustion or thermal decomposition of heavy petroleum such as e.g. coal tar (mainly pyrogenic PAHs). Carbon black is used as a pigment and reinforcement in rubber and plastic products.

Extender oils in the rubber and plastic industry are mainly used by:

- manufacturers of soft polymers.
- manufacturers of finished rubber products in order to aid processing; that is mixing operation, reducing compounding time and improving processability and modify the physical properties of the finished product

The main functions of extender oils are causing swelling of the polymer and to function as lubricants between the stiff rubbery polymers and softeners. By adding extender oils the molecular weight, viscosity and solvency of the base polymers can be varied. Further, because of oil content more additional ingredients can be blended. A major use of extender oils is therefore as additives in rubber tyres where the additives add important rubber characteristics and properties to, e.g. winter and summer, tyres. The content of PAH in extender oils may vary between mineral oil fractions.

Carbon black (CAS no.: 1333-86-4) is also an additive which is used in tyres, rubber and plastic products, printing inks and coatings (ICBA, 2010). Carbon black is virtually pure elemental carbon in the form of colloidal particles that are produced by incomplete combustion or thermal decomposition of gaseous or liquid hydrocarbons under controlled conditions. Its use in tyres, rubber and plastic products, printing inks and coatings is related to properties of specific surface area, reinforcement of the material, particle size, structure, conductivity and colour. Due to the source and production method carbon black may contain residues of PAHs. In the process a significant amount of the PAHs is removed. For most of the PAHs only 0-5% of the incoming PAHs are present in the carbon black products compared to the crude oil, but still high amounts of certain PAHs can be present.

(Source: *PAHs in toys and childcare products* – Survey of Chemical Substances in Consumer products N° 114 2011 – Danish EPA)

The following PAH are included in REACH, annex 17 entry 50:

- Benzo[a]pyrene (BaP)
- Benzo[e]pyrene (BeP)

- Benzo[a]anthracene (BaA)
- Chrysen (CHR)
- Benzo[b]fluoranthene (BbFA)
- Benzo[j]fluoranthene (BjFA)
- Benzo[k]fluoranthene (BkFA)
- Dibenzo[a,h]anthracene (DBAhA)

No international standard for the determination of PAH in plastic products has been published so far. However the suitability of the following environmental standards for the determination of PAH in construction products has been tested within CEN/TC 351/WG 5:

- **CEN/TS 16181** - *Sludge, treated biowaste and soil - Determination of polycyclic aromatic hydrocarbons (PAH) by gas chromatography (GC) and high performance liquid chromatography (HPLC)*
Remark: CEN/TS 16181 will be merged with EN 15527 - Characterization of waste - Determination of polycyclic aromatic hydrocarbons (PAH) in waste using gas chromatography mass spectrometry (GC/MS) (work item of CEN/TC 444/WG 2)
- **NEN 7331** - *Bitumen and bitumen containing materials - Determination of the content of polycyclic aromatic hydrocarbons (PAH) and of benzene, toluene, ethylbenzene and xylene (BTEX) - Gas-chromatographic method with mass spectrometric detection (Dutch standard)*

A German standard for analysis of PAH in consumer products is:

- **AfPS GS 2014:01 PAK** – *Testing and assessment of polycyclic aromatic hydrocarbons (PAHs) in the course of awarding the GS mark.*

The standard is issued by the Product Safety Commission of the Federal Institut for Occupational Safety and Health and is applied in the scope of the awarding of “Gebrauchssicherheit” certificates. This method was originally published as ZEK 01-2-08 by “Central Experience Exchange Committee” in cooperation with the German Accreditation Body.

Remarks:

- The **ECHA Compendium** of analytical methods recommended by the Forum to check compliance with REACH annex XVII restrictions makes reference to US EPA 8270 which is not a PAH method but a general method for the determination of semi-volatile compounds in extracts of soil, waste, air sampling media and water.
- **EN 16143** - *Petroleum products - Determination of content of Benzo(a)pyrene (BaP) and selected polycyclic aromatic hydrocarbons (PAH) in extender oils - Procedure using double LC cleaning and GC/MS analysis* specifies a procedure for the determination of the content of benzo(a)pyrene in extender oils which are commonly used in the rubber industry for the production of tyres or parts of tyres. The method also yields the sum of the eight PAH listed above. Analysis of other PAHs is possible in principle, but needs validation to secure the analysis. The application range for this method is from approximately 4 mg/kg to 15 mg/kg for the eight individual PAHs and from approximately 0,5 mg/kg to 2 mg/kg for BaP. The method uses the same detection method as CEN/TS 16171 and NEN 7331, but no extraction step is included and clean up, by column chromatography on silica gel and the less common Sephadex LH20, is different .

Summaries of CEN/TS 16181, NEN 7331 and AfPS GS 2014:01 PAK are given in Table 3. Comments are given on some aspects of the method and method performance characteristics are included.

All standards measure all 16 EPA PAHs:

- Acenaphthene
- Acenaphthylene
- Anthracene
- Benzo[a]anthracene
- Benzo[a]pyrene
- Benzo[b]fluoranthene
- Benzo[ghi]perylene
- Benzo[k]fluoranthene
- Chrysene
- Dibenzo[ah]anthracene
- Fluoranthene
- Fluorene
- Indeno[1,2,3-cd]pyrene
- Naphthalene
- Phenanthrene
- Pyrene

In AfPS GS 2014:01 PAK 2 additional PAH are included:

- Benzo[e]pyrene
- Benzo[j]fluoranthene

All standards use GC-MS as detection technique with the same diagnostic ions. Also calibration and quantification are similar (internal standard method with isotope labelled PAH as internal standards). The only differences are the extraction and clean up methods. CEN/TS 16181 is a more general procedure which allows the use of different extraction and clean up techniques, with acetone/petroleum ether or toluene as extraction solvent. NEN 7331 recommends soxhlet extraction with petroleum ether. CEN/TS 16181 and NEN 7331 have been shown to be equivalent with regard to the analysis of construction materials (CEN/TC 351/WG 5). In AfPS GS 2014:01 PAK the extraction is easily carried out by ultrasonication with toluene. Compared to the other standards the extraction time is short. Although toluene is a very good solvent for PAH it might be questionable if an extraction time of 1 h is sufficient to extract PAH quantitatively from a polymer matrix (no information on recovery experiments using plastics with known PAH concentration was found). However recovery experiments carried out with soil, sludge, compost and building debris showed that there is no difference in results obtained with different extraction methods: 1 h shaking or ultrasonication gave the same results as 16 h soxhlet extraction (CEN/TC 444/WG2). Therefore we propose to accept all 3 standards for the determination of PAH in plastics and rubbers. For plastic materials we recommend a particle size reduction to <1 mm in order guarantee sufficient extraction yields.

TABLE 3: SUMMARIES OF NEN 7331, CEN/TS 16182 AND AfPS GS 2014:01 PAK

	NEN 7331 - PAH part	CEN/TS 16181	AfPS GS 2014:01 PAK
Scope	<p>Bitumen and bitumen containing material</p> <p>Parameter list:</p> <ul style="list-style-type: none"> - All EPA PAH <p>Comment: Benzo[e]pyrene and benzo[j]fluoranthene are not included</p>	<p>Sludge, treated biowaste and soil</p> <p>Parameter list:</p> <ul style="list-style-type: none"> - All EPA PAH <p>Comment: Benzo[e]pyrene and benzo[j]fluoranthene are not included</p>	<p>Rubbers, plastics, paints</p> <p>Parameter list:</p> <ul style="list-style-type: none"> - All EPA PAH - Benzo[e]pyrene - Benzo[j]fluoranthene
Sample pretreatment	<p>Cutting of representative part followed by cryogenically grinding to particle size <1 mm</p>	<p>Optional : freeze drying or chemical drying with Na₂SO₄</p>	<p>Cutting of representative part to particle size <3 mm</p> <p>Comment: particle size reduction to <1 mm recommended for improvement of extraction efficiency</p>

Extraction	<p>Recommended intake: 10 g</p> <p>Addition of d-labelled internal standards</p> <p>Soxhlet extraction with 200 ml petroleum ether (PE) for 16 h</p> <p>Clean up by liquid-liquid partitioning with DMSO, followed by addition of water to DMSO extract and back extraction into hexane</p> <p>Washing of hexane layer with water and drying with Na₂SO₄</p> <p><i>Or:</i></p> <p>Addition of acetonitrile (ACN) to aliquot of PE extract, followed by evaporation of PE, filtration of ACN solution and solvent exchange to toluene</p>	<p>Recommended intake: 2-20 g</p> <p>Addition of d-labelled internal standards</p> <p>Shaking with 50 ml acetone for 30 min , followed by addition of 50 ml PE and shaking for 12 h, then removal of acetone by shaking with 400 ml water</p> <p><i>Or</i></p> <p>Soxhlet or PLE extraction with toluene</p> <p><i>Or</i></p> <p>Shaking with 50 ml water, 40 g NaCl, 100 ml acetone, 50 ml PE for 12 h, then separation of organic layer and removal of acetone by washing with 150 ml water</p> <p>Concentration of extract to smaller volumes (if needed)</p> <p>Clean up (optional) on silica or alumina</p> <p><i>or</i> by GPC</p> <p><i>or</i> by dimethylformamide/cyclohexane partitioning</p>	<p>Recommended intake: 500 mg</p> <p>Ultrasonic extraction for 1 h at 60°C with 20 ml toluene containing d-labelled internal standards</p> <p>Clean up (optional) on deactivated silica, elution with PE</p>
Measurement	<p>GC-MS:</p> <ul style="list-style-type: none"> - slightly polar column (CP-SIL 8 type) - splitless or on-column injection 	<p>GC-MS:</p> <ul style="list-style-type: none"> - 5% phenylmethylsiloxane - splitless - electron ionization 	<p>GC-MS:</p> <ul style="list-style-type: none"> - slightly polar column (HT8 type) - splitless - electron ionization

	<ul style="list-style-type: none"> - electron ionization - acquisition SIR mode <p>Identification: based on retention times, diagnostic ions and ion ratios; see Table 4 for diagnostic ions</p>	<ul style="list-style-type: none"> - acquisition SIR mode <p>Identification: based on retention times, diagnostic ions and ion ratios; see Table 4 for diagnostic ions</p> <p>or HPLC-FLD/DAD</p> <p><i>Comment: The HPLC method is less selective and may be not suited for the analysis of plastics and rubbers; the HPLC method was not included in the waste standard EN 15527</i></p>	<ul style="list-style-type: none"> - acquisition SIR mode <p>Identification: based on retention times and diagnostic ions; see Table 4 for diagnostic ions</p>
Quantification	<p>Internal standard method</p> <p>Internal standards: d-labelled, at least 3:</p> <ul style="list-style-type: none"> - d₈-naphthalene - d₁₀-anthracene - d₁₂-chrysene 	<p>Internal standard method</p> <p>Internal standards: d-labelled, at least 5</p>	<p>Internal standard method</p> <p>Internal standards: d-labelled, at least 3</p>
Method performance characteristics	<p>Limit of detection (LOD): 0.1-1.5 mg/kg depending on PAH and material</p> <p>Intralab repeatability (CV_r): <11%</p> <p>Intralab reproducibility (CV_R): <20% (validated for clay pigeons containing 0.3-6 mg/kg PAH)</p>	<p>Limit of detection (LOD): 0.01 mg/kg (without concentration step)</p> <p>Intralab coefficient of variation (CV_r): <15%</p> <p>Interlab coefficient of variation (CV_R): 17-45% (higher values for some volatile PAH) (validated for sludge and compost containing 5-2400 µg/kg)</p>	<p>Limit of quantification (LOQ): 0.2 mg/kg (without concentration step)</p> <p><i>Repeatability and reproducibility data not included in the standard</i></p>

- TABLE 4: GC-MS DIAGNOSTIC IONS FOR PAH AND RELATIVE INTENSITIES

Compound	CAS-RN	Diagnostic ion 1 <i>m/z</i>	Diagnostic ion 2 <i>m/z</i>	Diagnostic ion 3 <i>m/z</i>
Naphthalene	91-20-3	128 (100)	102 (11)	-
Acenaphthene	83-32-9	154 (70)	153 (100)	76 (10)
Acenaphthylene	208-96-8	152 (100)	150 (3)	[76] (0)
Fluorene	86-73-7	166 (81)	165 (100)	[139] (4)
Anthracene	120-12-7	178 (100)	152 (12)	[76] (0)
Phenanthrene	85-01-8	178 (100)	152 (9)	[76] (3)
Fluoranthene	206-44-0	202 (100)	200 (31)	[100] (3)
Pyrene	129-00-0	202 (100)	200 (2)	[101] (4)
Benzo(a)anthracene	56-55-3	228 (100)	226 (3)	[114] (2)
Chrysene	218-01-9	228 (100)	226 (6)	[113] (4)
Benzo(b)fluoranthene	205-99-2	252 (100)	250 (22)	126 (5)
Benzo(k)fluoranthene	207-08-9	252 (100)	250 (22)	126 (5)
Benzo(a)pyrene	50-32-8	252 (100)	250 (18)	[113] (11)
Indeno(1,2,3-cd)pyrene	193-39-5	276 (100)	138 (12)	[274] (4)
Dibenz(a,h)anthracene	53-70-3	278 (100)	139 (9)	[276] (5)
Benzo(ghi)perylene	191-24-2	276 (100)	138 (12)	[274] (4)

4 Nonylphenol and nonylphenol ethoxylates in textile

Nonylphenol is a family of closely related organic compounds (position isomers) composed of phenols bearing a saturated C9 alkyl chain. It is used as precursor in the manufacture of antioxidants, lubricating oil additives, laundry and dish detergents, emulsifiers, and solubilizers. It is also an intermediate for the production of tris(4-nonylphenyl) phosphite (TNPP), which is an antioxidant used to protect polymers, such as rubber, vinyl polymers, polyolefins and polystyrenics in addition to being a stabilizer in plastic food packaging. Barium and calcium salts of nonylphenol are used as heat stabilizers for polyvinyl chloride (PVC). Nonylphenol is the precursor for the manufacture of the non-ionic surfactants nonylphenol ethoxylates. These non-ionic surfactants are in wide use as wetting agents, emulsifiers and dispersants in paints and coating, residential and commercial cleaning products, in pesticide formulations, and in textile and paper processing. Nonylphenol and nonylphenol ethoxylates are only used as components of household detergents outside of Europe. Nonylphenol is also an intermediate in the manufacturing of nonylphenol ether sulfates and phosphates (anionic surfactants used as emulsifier).

Nonylphenol has attracted attention due to its prevalence in the environment and its potential role as an endocrine disruptor and xenoestrogen, due to its ability to act with estrogen-like activity. The estrogenicity and biodegradation heavily depends on the branching of the nonyl sidechain. The major source for the appearance of nonylphenol in the environment is degradation of nonylphenol ethoxylates.

(Sources: Wikipedia, Toxipedia, Ashford's Dictionary of Industrial Chemicals).

4.1 Nonylphenol ethoxylates

For the determination of nonylphenol ethoxylates in textiles the following international standard has been published:

ISO 18254-1:2016 - *Textiles - Method for the detection and determination of alkylphenol ethoxylates (APEO) - Part 1: Method using HPLC-MS*

Remark that ISO/DIS 18254-2- *Textiles - Method for the detection and determination of alkylphenol ethoxylates (APEO) -- Part 2: Method using NPLC* is still under development. The use of NPLC is however much less common in the laboratories.

A summary of ISO 18254-1 is given in Table 5. Comments are given on some aspects of the method and method performance characteristics are included.

4.2 Nonylphenol

For the determination of nonylphenol in textiles no validated standard is available today. However a standard for the determination alkylphenols in textiles is under development and will be most probably published by the end of 2018:

ISO/DIS 21084- *Textiles – Method for the determination of alkylphenols*

In expectation of the publication of ISO 21084 the following environmental standard can be applied:

CEN/TS 16182 – *Sludge, treated biowaste and soil - Determination of nonylphenols (NP) and nonylphenol-mono- and diethoxylates using gas chromatography with mass selective detection (GC-MS)*

CEN/TS 16182 is applicable to solid environmental matrices but the robustness of the method has also been validated for construction products within CEN/TC 351/WG 5.

Remark: Nonylphenol and ethoxylates are not included in the ECHA *Compendium of analytical methods recommended by the Forum to check compliance with REACH annex XVII restrictions*.

Summaries of both standards are given in Table 6. Comments are given on some aspects of the method and method performance characteristics are included.

GC-MS/MS and LC-MS/MS chromatograms of alkylphenols are shown in Figure 1, Figure 2, Figure 3 and Figure 4. From the chromatograms it can be seen that nonylphenol isomers are separated in the GC-MS chromatogram but coelute as one single peak in the LC-MS/MS chromatogram.

With regard to **ISO/DIS 21084** the following conclusions can be made:

- LC-MS/MS is the preferred detection technique. The validation exercise shows better within-lab repeatabilities and between-lab reproducibilities as well as somewhat lower average values compared to GC-MS/MS, indicating that LC-MS/MS is less prone to interferences
- The LC-MS/MS determination can be combined with the determination of APEO.
- GC-MS/MS gives more complicated chromatograms than LC-MS/MS and expert judgement is needed for evaluation of the nonylphenol isomer pattern and the presence of interferences. Moreover methanol is a less suitable GC-MS solvent and derivatisation of alkylphenols is recommended for better peak shapes and to avoid adsorption on active sites in injector and column.

With regard to **CEN/TS 16182** the following conclusions can be made:

- The method is sensitive
- The chromatographic performance is better than the GC-MS method of ISO/DIS 21084 as a result of derivatisation
- The use of ¹³C-labelled internal standards improves the reliability of the method
- The method is more laborious than ISO/DIS 21084
- The validation of the method has been limited to nonylphenol and ethoxylates but it should be possible to extend the scope of the method to octylphenol and ethoxylates
- The method allows the determination of nonylphenol mono-ethoxylates which are not included in ISO 18254-1

4.3 Conclusion

For the determination of the nonionic surfactants octyl- and nonylphenol ethoxylates in textiles **ISO 18254-1** is considered to be appropriate. Methanol extracts are analysed with LC-MS/MS in positive mode. With regard to the standard we recommend however to better describe, at the next revision or when adopting ISO 18254-1 as EN standard, the calibration and quantification procedure, as well as to include alkylphenol mono-ethoxylates in the scope of the method.

For the determination of octyl- and nonylphenols we recommend method **ISO/DIS 21084**, using LC-MS/MS as detection technique, measuring methanol extracts in negative method. However for more reliable quantification the internal method should be used, using ¹³C-labelled analogues as internal standards. In expectation of the final publication of ISO/DIS 21084 and for the determination of nonylphenol and the mono- and diethoxylate derivatives **CEN/TS 16182** can be used. For other alkylphenols an additional validation is needed.

TABLE 5: SUMMARY OF ISO 18254-1

	ISO 18254-1
Scope	Textile products Parameter list: <ul style="list-style-type: none"> - Octylphenol ethoxylates (OPEO_n, with n = 2-16) - Nonylphenol ethoxylates (NPEO_n, with n = 2-16) <p>Comment: it is not clear why mono-ethoxylates are not included in the method</p>
Sample pretreatment	Cutting of representative part into small pieces (<5 mm)
Extraction	Recommended intake: 1 g Ultrasonic extraction with 20 ml methanol at 70°C for 60 min Filtration
Measurement	Instrument: LC-MS or LC-MS/MS LC-column: Reversed phase (C18), 40°C Mobile phase gradient: water/acetonitrile/ammonium acetate (pH 3.6, adjusted with formic acid) MS ionisation mode: positive electrospray Identification: based on retention times and diagnostic ions (see Table 7 for target ions in case of single MS-detection and Table 8 in case of MS/MS (MRM) detection)
Quantification	External standard method The calibration standards are Triton X-100 and IGEPAL CO-630 for resp. OPEO and NPEO Comment: how calibration and quantification should be carried out is insufficiently explained in this standard and may therefore be a source of errors Comment: coeluting matrix constituents may be responsible for ionisation suppression or enhancement effects; for correct quantification standard addition or matrix matched calibration should be applied

Method performance characteristics	Limit of quantification (LOQ): 50 mg/kg (0.005%) Interlab coefficient of variation (CV_R): 10% (validated for blue denim fabric containing ca 1000 mg/kg APEO using LC-MS as detection technique)

TABLE 6: SUMMARY OF ISO 21084 AND CEN/TS 16182 FOR THE DETERMINATION OF ALKYLPHENOLS

	ISO/DIS 21084	CEN/TS 16182
Scope	<p>Textile and textile related products</p> <p>Parameter list:</p> <ul style="list-style-type: none"> - 4-n-octylphenol - 4-t-octylphenol (4-(1,1,3,3-tetramethylbutyl)phenol) - 4-n-nonylphenol - 4-nonylphenol (isomeric mixture) 	<p>Sludge, treated biowast and soil</p> <p>Parameter list:</p> <ul style="list-style-type: none"> - 4-nonylphenol - 4-nonylphenol monoethoxylate - 4-nonylphenol diethoxylate (isomeric mixtures)
Sample pretreatment	Cutting of representative part into small pieces (<5 mm)	Optional : freeze drying
Extraction	<p>Recommended intake: 1 g</p> <p>Ultrasonic extraction with 10 ml methanol at 70°C for 60 min</p> <p>Filtration</p> <p>Concentration of the extract depending on the instrument sensitivity</p>	<p>Recommended intake: 10 g</p> <p>Addition of internal standards</p> <p>Shaking with 10 ml water</p> <p>Shaking with 20 ml acetone</p> <p>Shaking with 20 ml hexane for 2 h</p> <p>Addition of 100 ml water (removal of acetone)</p> <p>Drying of hexane layer with Na₂SO₄</p> <p>Clean up (optional) on silica, alumina or florisil</p>

		Evaporation of 1 ml hexane extract to dryness Derivatisation (silylation) by addition of 1 ml of 5% MSTFA in isooctane
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<p>Measurement</p>	<p>GC-MS/MS:</p> <ul style="list-style-type: none"> - non-polar column (5% phenylmethylsiloxane) - splitless injection - electron ionization - acquisition MRM mode <p>Comment: methanol is not an ideal GC-solvent and for better peak shapes and to avoid adsorption on active sites in the GC-system the derivatization (acetylation or silylation) of the alkylphenols is recommended</p> <p>LC-MS/MS:</p> <ul style="list-style-type: none"> - Column: reversed phase (C18) - Mobile phase gradient: water/acetonitrile - Ionisation mode: electrospray, negative - Acquisition: MRM mode <p>LC-FLD (fluorescence detection):</p> <ul style="list-style-type: none"> - Column: reversed phase (C18), 40°C - Mobile phase gradient: water/acetonitrile - selecting 230 nm for excitation and 296 nm for emission) <p>Comment: as a single phenyl group is only weakly fluorescent and not selective LC-FLD is considered to be a less appropriate detection technique</p> <p>Identification: based on retention times, diagnostic ions and isomer pattern recognition (GC-MS); see Table 9 and Table 10 for resp. GC-MS/MS and LC-MS/MS diagnostic ions; see Figure 1 and Figure 2 for GC-MS/MS chromatograms and Figure 3 for LC-MS/MS chromatograms</p>	<p>GC-MS:</p> <ul style="list-style-type: none"> - non-polar column (5% phenylmethylsiloxane) - splitless injection - electron ionization - SIR acquisition <p>Identification: based on retention times, diagnostic ions and ion ratios and isomer pattern recognition; see Table 11 for diagnostic ions and Figure 4 for GC-MS chromatograms.</p>
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Quantification	<p>External standard method</p> <p>Comment: the standard is insufficiently clear with respect to the calibration and quantitation of nonylphenol based on GC-MS/MS MRM transitions, which might be a cause of errors</p> <p>Comment: appropriate ¹³C-isotope labelled standards are available for these compounds and the use of the internal standard method is highly recommended to correct for extraction recoveries, losses during evaporation and injection volumes, as well as ionisation suppression/enhancement effects caused by coeluting matrix constituents (LC-MS)</p>	<p>Internal standard method</p> <p>Internal standards: ¹³C-4-n-nonylphenol and ¹³C-4-n-nonylphenoldiethoxylate</p>
Method performance characteristics	<p>Limit of quantification (LOQ): not specified</p> <p>Intralab coefficient of variation (CV_r): <4-25%</p> <p>Interlab coefficient of variation (CV_R): <14-69%</p> <p>(validated for textile sample with 100 mg/kg n-nonylphenol and test solutions)</p>	<p>Limit of detection (LOD): 0.02-0.1 mg/kg (without concentration step)</p> <p>Intralab coefficient of variation (CV_r): 3-13%,</p> <p>Interlab coefficient of variation (CV_R): 58-84%</p> <p>(validated for sludge sample containing 2-30 µg/kg)</p>

TABLE 7: CHARACTERISTIC MASSES FOR QUANTITATION USING LC-MS ACCORDING TO ISO 18254-1

NPEO congeners	Target mass, m/z [M + NH ₄]	OPEO congeners	Target mass, m/z [M + NH ₄]
NPEO 16	942	OPEO 16	928
NPEO 15	898	OPEO 15	884
NPEO 14	854	OPEO 14	840
NPEO 13	810	OPEO 13	796
NPEO 12	766	OPEO 12	752
NPEO 11	722	OPEO 11	708
NPEO 10	678	OPEO 10	664
NPEO 9	634	OPEO 9	620
NPEO 8	590	OPEO 8	576
NPEO 7	546	OPEO 7	532
NPEO 6	502	OPEO 6	488
NPEO 5	458	OPEO 5	444
NPEO 4	414	OPEO 4	400
NPEO 3	370	OPEO 3	356
NPEO 2	326	OPEO 2	312

TABLE 8: MRM TRANSITIONS FOR QUANTITATION USING LC-MS/MS ACCORDING TO ISO 18254-1

NPEO congeners	Q1 (m/z)	Q3 (m/z)	Collision energy (eV)	OPEO congeners	Q1 (m/z)	Q3 (m/z)	Collision energy (eV)
NPEO 15	898	133	33	OPEO 15	884	133	33
NPEO 14	854	133	32	OPEO 14	840	133	33
NPEO 13	810	133	31	OPEO 13	796	133	31
NPEO 12	766	133	30	OPEO 12	752	133	30
NPEO 11	722	133	28	OPEO 11	708	133	30
NPEO 10	678	133	29	OPEO 10	664	133	30
NPEO 9	634	133	26	OPEO 9	620	133	25
NPEO 8	590	133	26	OPEO 8	576	560	23
NPEO 7	546	133	22	OPEO 7	532	515	22
NPEO 6	502	485	20	OPEO 6	488	359	19
NPEO 5	458	441	17	OPEO 5	444	315	17
NPEO 4	414	271	13	OPEO 4	400	271	14
NPEO 3	370	227	13	OPEO 3	356	227	12
NPEO 2	326	183	11	OPEO 2	312	183	12

TABLE 9: GC-MS/MS DIAGNOSTIC IONS (MRM TRANSITIONS) FOR ALKYLPHENOLS ACCORDING TO ISO/DIS 21084

Compounds	m/z[Q1]	m/z[Q3]	Collision energy (eV)
4-tert-Octylphenol	135	107	10
	135	77	30
4-n-Octylphenol	107	77	20
	107	51	40
4-n-Nonylphenol	107	77	20
	107	51	40
4-Nonylphenol	107	77	20
	121	77	20
	135	77	30
	149	107	10
	163	107	20
	191	107	20

FIGURE 1: GC-MS/MS TOTAL ION CHROMATOGRAM FOR AN ALKYLPHENOL STANDARD

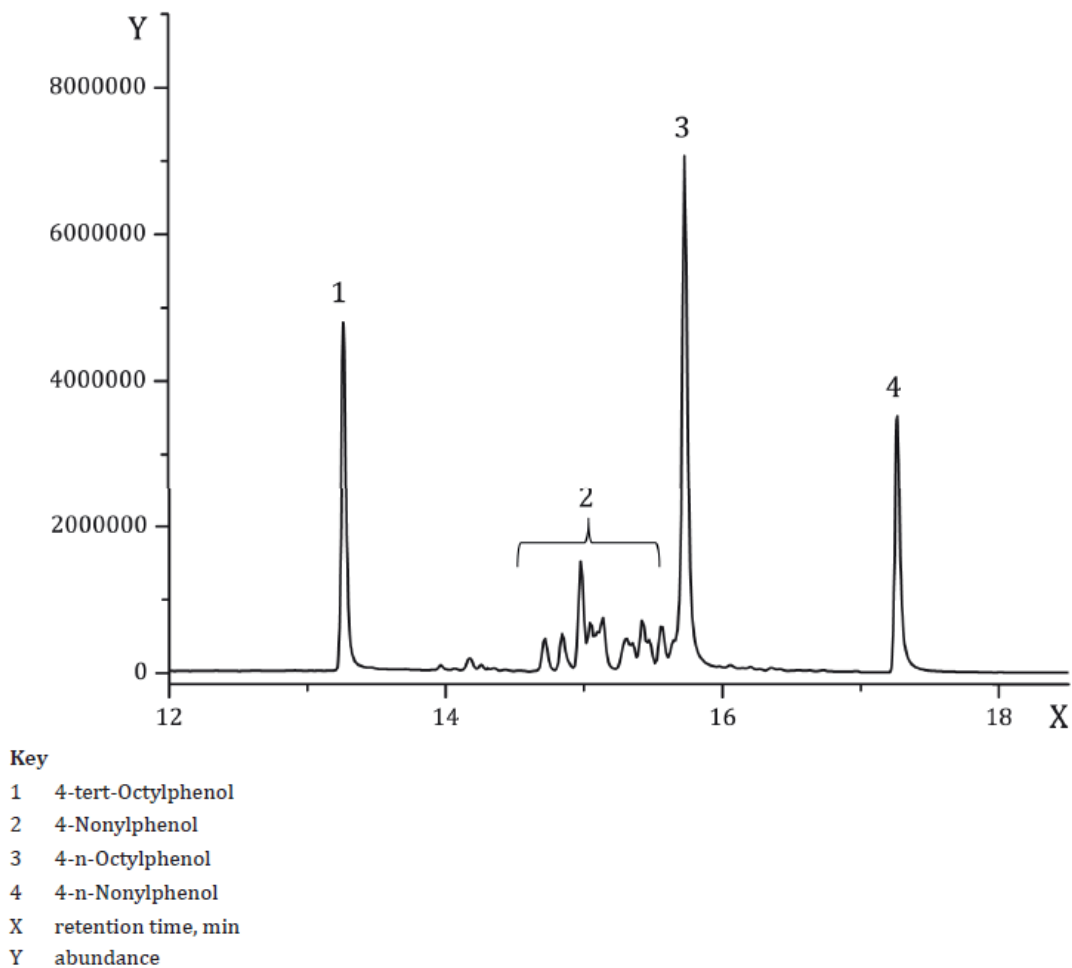


FIGURE 2: NONYLPHENOL ION CHROMATOGRAMS FOR DIFFERENT MRM TRANSITIONS

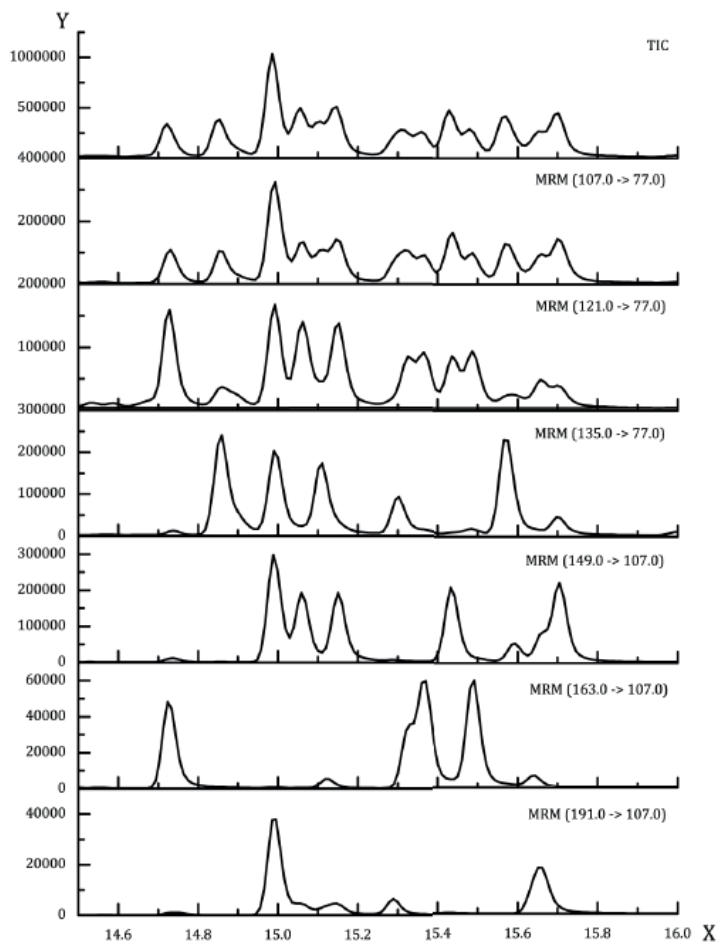
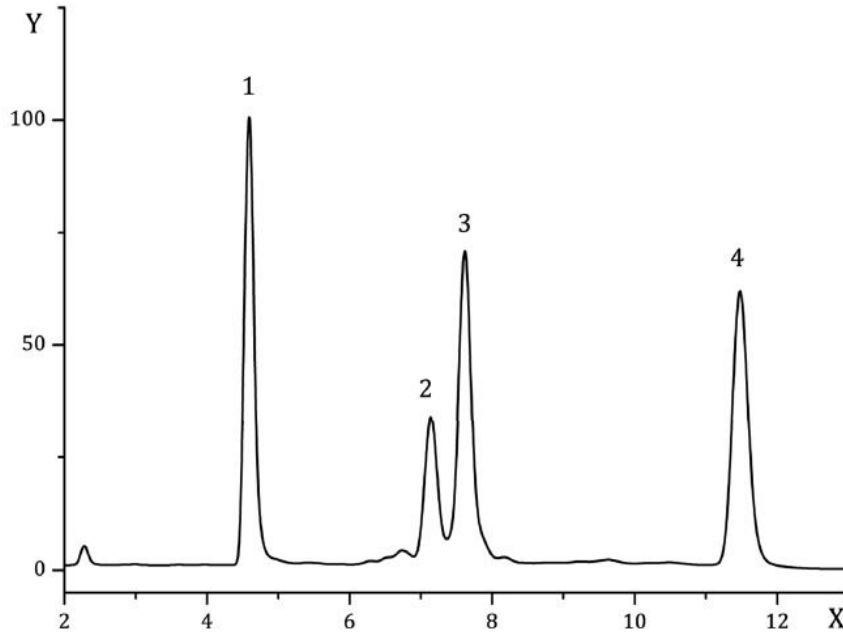


TABLE 10: LC-MS/MS DIAGNOSTIC IONS (MRM TRANSITIONS) FOR ALKYLPHENOLS ACCORDING TO ISO/DIS 21084

Compounds	m/z[Q1]	m/z[Q3]	Collision energy (eV)
4-tert-Octylphenol	205	133	22
4-Nonylphenol	219	133	30
4-n-Octylphenol	205	106	20
4-n-Nonylphenol	219	106	20

FIGURE 3: LC-MS/MS TOTAL ION CHROMATOGRAM FOR ALKYLPHENOLS



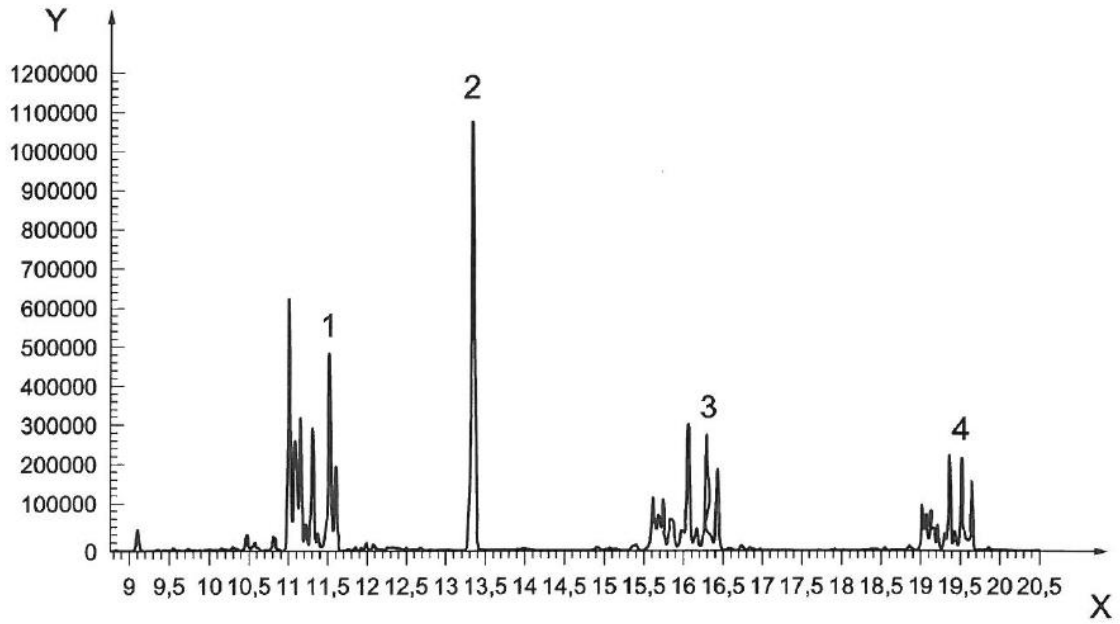
Key

- 1 4-tert-Octylphenol
- 2 4-Nonylphenol
- 3 4-n-Octylphenol
- 4 4-n-Nonylphenol

TABLE 11: GC-MS DIAGNOSTIC IONS FOR NONYLPHENOL AND ETHOXYLATES ACCORDING TO CEN/TS 16182

No	Analyte (MSTFA derivative)	Abbreviation	Selected diagnostic ions			Internal standard for analyte No.
			Target ion M ₁	Qualifier ion M ₂	Qualifier ion M ₃	
1	Nonylphenol	NP	207	221	193	
2	Nonylphenol monoethoxylate	NP1EO	251	265	279	
3	Nonylphenol diethoxylate	NP2EO	295	309	323	
4	¹³ C-labelled 4-n-nonylphenol	¹³ C-4-n-NP	185			1,2
5	¹³ C-labelled 4-n-nonylphenol diethoxylate	¹³ C-4-n-NP2EO	252			3
6	D4-labelled 4-n-nonylphenol	4-n-NP-D4	183			1,2
7	Unlabelled 4-n-nonylphenol	4-n-NP	179			1,2
8	Unlabelled 4-n-nonylphenol diethoxylate	4-n-NP2EO	246			3

FIGURE 4: GC-MS CHROMATOGRAMS FOR SILYLATED NONYLPHENOL AND ETHOXYLATES



Key

- 1 Nonylphenol
- 2 Nonylphenol-d4
- 3 Nonylphenolmonoethoxylate
- 4 Nonylphenoldiethoxylate

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