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Final report

CEN/TC 351/WG 5 – Construction products Robustness validation of draft methods for eluate and content analysis of organic substances

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SUMMARY

With regard to the assessment of the release of dangerous substances from construction products ‘umbrella’ standards have been defined within CEN/TC 351 for the determination of the content of organic substances in construction products and in eluates of construction products. In these standards reference is made to existing methods of analysis from other fields. To ensure the suitability of the umbrella standards a robustness study has to be conducted to verify if the proposed analytical methods are fit for purpose. The main aspect to be covered is to ensure that methods selected are sufficiently sensitive to allow regulatory limits to be assessed with sufficient precision to draw conclusions on acceptability of the construction products.

In this report the results of the robustness validation are summarised. Repeatability measurements have been carried out for the determination of the content of mineral oil, PAH, BTEX, PCB, PBDE, dioxins and dioxin-like PCB, PCP, phthalates, phenols and biocides in different construction products and in eluates of these construction products according to existing soil, sludge, waste, water and other standards. On the basis of the repeatability data and the achievable limits of detection a decision has been made on the suitability of the standard for construction products. For the determination of the content of most organic substances the proposed analytical standards are adequate. For phthalates and nonylphenols an optimization of the extraction method is advised. For dioxins and dioxin-like PCB no conclusion could be made by lack of suitable material.
For the determination of the content of organic substances in eluates suitable water standards are available for mineral oil, BTEX, dioxins, PCP, phenol index and biocides. No conclusive data are obtained for PAH, PBDE, phthalates and nonylphenol, because of sample differences, to small sample volumes, recovery issues or too low concentrations. Additional experiments will be needed before a decision can be made on suitability.

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CHAPTER 1 INTRODUCTION

1.1. GENERAL

CEN/TC 351 'Construction products: Assessment of release of dangerous substances' was established in 2005 to execute the Mandate 366.

The present robustness validation project aims at establishing the suitability of the following two 'umbrella' standards referring to existing methods of analysis:

- Content of organic substances in construction products (WI 00351024);
- Analysis of organic substances in eluates from construction product (WI 00351026).

The main aspect to be covered is to ensure that methods selected are sufficiently sensitive to allow regulatory limits to be assessed with sufficient precision to draw conclusions on acceptability. The associated analytical methods need to be verified for suitability by carrying out repeatability measurements.

Regarding the content analysis, the robustness validation involves, besides existing established methods, the following newly developed draft standard of CEN/TC 351:

- N 0685 Content of organic substances (work item 00351024) (CEN/TC 351/WG 5 N 0352).

Regarding the analysis of eluates, the robustness validation involves, besides existing established methods, the newly developed draft standard of CEN/TC 351:

- N 0686 Analysis of organic substances in eluates (work item 00351026) (CEN/TC 351/WG 5 N 0353).

1.2. PROJECT DESCRIPTION

The work consists of two parts:

1) Examination of suitability of content analysis methods from other fields for organic substances in construction products and
2) Examination of suitability of analysis methods from other fields for organic substances in eluates from construction products.

The main topic of this study on robustness will be to demonstrate if the **repeatability is good** and the **sensitivity** of the methods proposed is **adequate for the existing regulatory requirements** in Europe.

1.2.1. TASK 1: EXAMINATION OF SUITABILITY OF CONTENT ANALYSIS METHODS FOR ORGANIC SUBSTANCES IN CONSTRUCTION PRODUCTS

For the robustness work sample material and CRM's will be supplied by CEN/TC 351/WG 5. The number and type of samples from construction products and the approximate quantities needed are given below:

Test	Number ofsamples	Number of tests to run	Quantity
Extraction and extract analysis	15	23	1 kg per granular sample or grinded monolithic product

In Table 1 the samples which have to be analysed are grouped per analysis method to be evaluated. All products will be supplied with size-reduced to 95 % < 0,25 mm. The extraction of organic substances is an integral part of the standards referenced. If more than one extraction method is referenced in the method, the choice of the method will be well motivated and evaluated during the implementation phase of the method. All analyses per method and per substance (group) will be done in 5 fold (repeatability conditions). The main goal for this study is to demonstrate the repeatability and the sensitivity of the methods. Some analyses cannot be performed at VITO (organotin , dioxins , furans and dioxin-like PCB) and will be outsourced to a subcontractor (SGS-IAC, Antwerp).

NOTE 1 The construction products in the table are selected as being representative for the various types of products covered by Mandate/366. Products have been selected based on relatively high and expected low concentrations of substances of interest. The sensitivity of the method for the various construction product matrices (mineral products; bituminous products; wood-based products; plastics and rubbers; organic sealants and adhesives) is based on one representative product selected from each category.

1.2.2. TASK 2: EXAMINATION OF SUITABILITY OF ANALYSIS METHODS FOR ORGANIC SUBSTANCES IN ELUATES FROM CONSTRUCTION PRODUCTS.

For the robustness work the eluates and the CRM solution will be supplied. The number and type of eluates from construction products and the approximate quantities needed are given below:

Test	Number of eluates	Number of tests to run	Quantity for producing eluates
Eluate analysis	13	24 for 2 L/S ratios or 2 fractions = 48 tests	1 kg per granular sample or grinded monolithic product

In Table 2 the samples which have to be analysed are grouped per analysis method to be evaluated. For every sample, two eluates will be provided on behalf of CEN/TC 351. The selected materials will be leached according to CEN/TS 16637-2, for monolithic products (analysis of fractions 1 and 3) and to CEN/TS 16637-3, in case of granular material (using fractions obtained at L/S=2 and L/S=10).These ratios are chosen to have two concentration levels for analysis, and these are the most used L/S ratios. All analyses per method, per substance (group) and per eluate will be done in 5 fold (repeatability of the measurements). The main goal for this study is to demonstrate the repeatability and the sensitivity of the methods. The choice of the extraction methods and harmonization of the substances will be well motivated and evaluated during the implementation phase of the project Some analyses cannot be performed at VITO (organotin , dioxins , furans and dioxin-like PCB) and will be outsourced to a subcontractor (SGS-IAC, Antwerp).

1.2.3. DELIVERABLES AND REPORT

The expected results and deliverables of the project are as follows:

- At least one progress report on the details of the action’s implementation and its presentation in WG 5 (deadline for submission: 2 months after receipt of the samples);
- One final technical implementation report for the adaptation of the examined methods (work item 00351024 including precise proposals for adjustment of this draft TS on the basis of the results of the robustness validation, including advice on possible further integration of analysis methods for organics (deadline for submission: 5 months after receipt of the samples). This final technical implementation report shall, in draft form, consist of a statistical evaluation of all data generated (e.g. informative annexes, tables of results, test reports, outlines and flowcharts of the procedures followed), conclusions on suitability of the methods and recommendations for improvement of the harmonised method considered necessary, which can support the standardisation of the examined umbrella document and its publication as TS.
- One comprehensive final report consisting, in their final form, of a series of all necessary data elaborated and analysed (e.g. informative annexes, tables of results, test reports, outlines and flowcharts of the procedures followed, conclusions and definitions to the pass/fail criteria of the methods, final drafts and design of any adjustments on the harmonised method considered necessary), which can support the standardisation of the examined umbrella document and its publication as TS (deadline for submission: 8 months after receipt of the samples).

1.3. SAMPLE DELIVERY AND ANALYTICAL WORK DONE

In Table 3 an overview is given of the receipt of the samples, the origin of the sampes and the analytical work done. From the table it can be seen that the majority of the samples have been delivered, pretreated (particle size reduction or leaching) and analysed.

The following construction product/analytes combinations could not be found and no analytical data on the content of the analytes in the construction products and eluates could be provided:

- PVC flooring containing phthalates
- Asphalt concrete containing PAH
- Insulation foam containing SCCPs
- Render containing organotin compounds

In addition render 1 only contained nonylphenolethoxylates, no biocides were added.

One of the delivered samples has not been analysed, namely the eluate of the polyethylene CRM containing PBDE. The amount of eluate was to small for adequate analysis.

For the determination of the content of phenols in PVC water proofing sheets use was made of another standard, CEN/TS 16182 instead of ISO 14154. ISO 14154 does not allow the determination of nonylphenol and ethoxylates, of which the concentration has to be determined in the eluates of the PVC material. CEN/TS 16182 is also the method which has been used for render 1.

BTEX have been determined in eluates of asphalt aggregates using EN ISO 15680, but no BTEX were detected above LOD. Therefore no effort was made to analyse these eluates with 2 other BTEX methods (EN ISO 17943 and ISO 11423-1).

1.4. EVALUATION OF RESULTS

The following criteria will be applied for the assessment of the suitability of a standard for the determination of organic substances in construction products and eluates:

- Repeatability: for concentrations above 10 times the limit of quantification (LOQ) the repeatability should be ≤15%; in case the concentrations are <10*LOQ repeatabilities up to 25% are acceptable
- Sensitivity: the lowest limit of application of the standard should be achievable; if this is not the case the relevance of the LOQ requirement will be checked with respect to existing regulatory limits
- Trueness: for matrix additions the recovery of the addition should be between 70 and 130%

Table 1: Overview of the samples and the methods to be assessed for the content analysis of construction products

N°	Sample	Specific substances	Method(s) to be used	VITO/Subcontractor	Sample pretreatment/extraction/clean up	Instrument used in method	Instrument used at VITO
1	Wood powder (CRM)	Pentachlorophenol	CEN/TR 14823	VITO	**extraction:** USE with MeOH **derivatisation**: acetylation	GC-ECD	GC-MS
2	Render 1	Nonylphenol (spiked)	CEN/TS 16182	VITO	**drying:** lyofilisation or use of wet material **extraction**: shaking **clean up:** silica/alumina/florisil, derivatization with MSTFA	GC-MS	GC-MS
3	PVC Flooring (old)	Phthalates	CEN/TS 16183	VITO	**drying:** Na$_2$SO$_4$/lyofilisation **extraction:** shaking **clean up**: alumina	GC-MS	GC-MS
	Sealant 1	Phthalates	CEN/TS 16183	VITO	**drying:** Na2SO4/lyofilisation or wet **extraction:** shaking **clean up**: alumina	GC-MS	GC-MS
4	Rubber crumbs	Dioxins, furans and dioxin-like PCBs	CEN/TS 16190	subcontractor	**drying**: lyofilisation/Na$_2$SO$_4$ **extraction**: soxhlet or equivalent **clean up**: GPC, multilayer silica or other adsorbents	GC-HRMS	No longer available at VITO – collaboration foreseen
5	Asphalt concrete	PAH	CENT/TS 16181 (with cryogenic pre-treatment cfr NEN 7331)	VITO	**drying**: Na$_2$SO$_4$/lyofilisation **extraction:** shaking/soxhlet/PLE **clean up**: alumina, silica, GPC, DMF	HPLC-UV-DAD/FLD or GC-MS	GC-MS
	Recycled mixed aggregates	PAH	CEN/TS 16181 (GC-MS part)	VITO	**drying:** Na2SO4/lyofilisation **extraction**: shaking/soxhlet/PLE **clean up**: alumina, silica, GPC, DMF	HPLC-UV-DAD/FLD of GC-MS	GC-MS
6	Asphalt aggregate	Mineral oil	EN 14039	VITO	**extraction**: shaking/USE **clean up**: florisil	GC-FID	GC-FID
	Recycled mixed aggregates	Mineral oil	EN 14039	VITO	**extraction:** shaking/USE **clean up:** florisil	GC-FID	GC-FID
7	Sealant 2	BIT, CIT, MIT	EN 15637	VITO	**extraction**: addition of MeOH, blender **clean up:** SPE	LC-MS/MS	LC-MS/MS

	Render 1	Diuron, OIT, BIT, MIT	EN 15637	VITO	**extraction**: addition of MeOH, blender **clean up:** SPE	LC-MS/MS	LC-MS/MS
	Treated wood (piece)	Propiconazole	EN 15637	VITO	**extraction**: addition of MeOH, blender **clean up:** SPE	LC-MS/MS	LC-MS/MS
	Render 2	Terbutryn, OIT, BIT, MIT	EN 15637	VITO	**extraction**: addition of MeOH, blender **clean up:** SPE	LC-MS/MS	LC-MS/MS
8	Recycled mixed aggregates	PCB	EN 16167	VITO	**drying:** Na2SO4/lyofilisation or wet **extraction**: shaking/soxhlet **clean up**: different types of columns/ GPC/ DMF/desulfurization	GC-MS or GC-ECD	GC-MS
9	Insulation foam (PEF or FEF)	SCCP	EN ISO 18219	VITO	**extraction:** USE with hexane **clean up**: SPE	GC-ECNI-MS	GC-ECNI-MS
10	Plastic product (CRM)	PBDE	EN ISO 22032	VITO	**extraction:** Soxhlet with toluene **clean up**: column with acid and base silica/alumina/GPC	GC-MS or GC-NCI-MS	GC-MS
11	Render 1	Organotin (from biocides, spiked)	EN ISO 23161	subcontractor	method not available at VITO	GC-MS	Not available at VITO – collaboration foreseen
12	Water proofing sheets	Phenols	ISO 14154	VITO	**extraction:** LLE **derivatisation:** acetylation	GC-ECD	GC-MS
13	Asphalt aggregate	BTEX	NEN 7331 - BTEX part	VITO	**extraction**: LLE	GC-MS (purge and trap)	HS-GC-MS
14	Asphalt aggregate	PAH	NEN 7331 - PAH part	VITO	**extraction**: soxhlet **clean up**: silica/alumina	GC-MS	GC-MS
	Asphalt concrete	PAH	NEN 7331 - PAH part	VITO	**extraction**: soxhlet **clean up**: silica/alumina	GC-MS	GC-MS
	Roofing felt (Bitumen shingles)	PAH	NEN 7331 - PAH part	VITO	**extraction**: soxhlet **clean up**: silica/alumina	GC-MS	GC-MS

	Rubber crumbs	PAH	NEN 7331 - PAH part	VITO	**extraction**: soxhlet **clean up**: silica/alumina	GC-MS	GC-MS

Table 2: Overview of the samples and the methods to be assessed for the content analysis of eluates of construction products

N°	Sample	Specific substances	Methods to be used	VITO/subcontractor	Sample pretreatment	Instrument used in method	Instrument used at VITO
1	Wood powder (CRM)	Pentachlorophenol	EN 12673	VITO	**derivatisation**: direct/after extraction **derivatisation**: acetylering	GC-ECD of GC-MS	GC-MS
2	Sealant 2	BIT, CIT, MIT	EN 15637	VITO	**extraction**: addition of MeOH, blender **clean up:** SPE	LC-MS/MS	LC-MS/MS
	Render 1	Diuron, OIT, BIT, MIT	EN 15637	VITO	**extraction**: addition of MeOH, blender **clean up:** SPE	LC-MS/MS	LC-MS/MS
	Treated wood (piece)	Propiconazole, tebuconazole	EN 15637	VITO	**extraction**: addition of MeOH, blender **clean up:** SPE	LC-MS/MS	LC-MS/MS
	Render 2	Terbutryn, OIT, BIT, MIT	EN 15637	VITO	**extraction**: addition of MeOH, blender **clean up:** ChemElut1005	LC-MS/MS	LC-MS/MS
3	Plastic product (CRM)	PBDE	EN 16694	VITO	**extraction:** SPE disk extractie **clean up**: optional with acidified and base silica	GC-HRMS, GC-NCI-MS, GC-MS/MS	GC-MS/MS
4	Water proofing sheets	Phenols	EN ISO 14402	VITO		FIA	FIA
5	Asphalt aggregate	BTEX	EN ISO 15680	VITO	**extraction**: headspace	P&T GC-MS	HS-GC-MS
6	Render 1	Organotin (from biocides)	EN ISO 17353	subcontractor		GC-MS	GC-MS
7	Asphalt aggregate	BTEX	EN ISO 17943	VITO	**extraction**: SPME	Headpace-SPME-GC-MS	HS-GC-MS
8	PVC flooring (old)	Phthalates	EN ISO 18856	VITO	**extraction**: SPE extractie (RP-C18) **clean up:** optional with alumina	GC-MS	GC-MS
	Sealant 1	Phthalates	EN ISO 18856	VITO	**extraction**: SPE extractie (RP-C18) **clean up:** optional with alumina	GC-MS	GC-MS

9	Water proofing sheets	Bisphenol-A	EN ISO 18857-2	VITO	**extraction**: SPE **derivatisation:** MSTFA	GC-MS	GC-MS
	Render 1	Nonylphenol	EN ISO 18857-2	VITO	**extraction**: SPE **derivatisation:** MSTFA	GC-MS	GC-MS
10	Recycled mixed aggregates	Mineral oil	EN ISO 9377-2	VITO	**extraction**: LLE **clean up**: florosil	GC-FID	GC-FID
11	Asphalt aggregate	BTEX	ISO 11423-1	VITO	**extraction**: headspace	Headspace GC-MS	HS-GC-MS
12	Rubber crumbs	Dioxin-like PCBs	ISO 17858	subcontractor		GC-HRMS	No longer available at VITO – collaboration foreseen
	Recycled mixed aggregates	Dioxin-like PCBs	ISO 17858	subcontractor		GC-HRMS	No longer available at VITO – collaboration foreseen
	Recycled mixed aggregates	Dioxins and furans	ISO 17858 or ISO 18073	subcontractor		GC-HRMS	No longer available at VITO – collaboration foreseen
	Rubber crumbs	Dioxins and furans	ISO 17858 or ISO 18073	subcontractor		GC-HRMS	No longer available at VITO – collaboration foreseen
13	Asphalt aggregate	PAH	ISO 28540	VITO	**extraction**: addition of hexane, blender **clean up** : silica	GC-MS	GC-MS
	Asphalt concrete	PAH	ISO 28540	VITO	**extraction**: addition of hexane, blender **clean up** : silica	GC-MS	GC-MS
	Recycled mixed aggregates	PAH	ISO 28540	VITO	**extraction**: addition of hexane, blender **clean up** : silica	GC-MS	GC-MS
	Rubber crumbs	PAH	ISO 28540	VITO	**extraction**: addition of hexane, blender **clean up** : silica	GC-MS	GC-MS

Table 3: Overview of samples delivered and analyses conducted

⬜ Sample not delivered
🟩 Sample delivered and analysed at VITO
🟦 Analysis by subcontractor (SGS)

Content analysis

N°	Sample	Specific substances	Method(s) to be used	Date of delivery	Delivered by	Analysed	Remarks
1	Wood powder (CRM)	Pentachloro-phenol	CEN/TR 14823	7/07/2017	JRC	x	Limited amount of material
2	Render 1	Nonylphenol (spiked)	CEN/TS 16182	21/11/2017	Dr. Robert-Murjahn-Institut GmbH	x	Hardening and particle size reduction by VITO
3	~~PVC Flooring (old)~~	~~Phthalates~~	~~CEN/TS 16183~~	-	-	-	
	Sealant 1	Phthalates	CEN/TS 16183	3/07/2017	Fraunhofer	x	Hardening and particle size reduction by VITO
4	Rubber crumbs	Dioxins, furans and dioxin-like PCBs	CEN/TS 16190	29/09/2017	SGS Intron	x	Particle size reduction by SGS Intron
5	~~Asphalt concrete~~	~~PAH~~	~~CENT/TS 16181 (with cryogenic pre-treatment cfr NEN 7331)~~	-	-	-	Replaced by asphalt aggregate
	Asphalt aggregate	PAH	CENT/TS 16181 (with cryogenic pre-treatment cfr NEN 7331)	6/12/2017	REKO	x	
	Recycled mixed aggregates	PAH	CEN/TS 16181 (GC-MS part)	3/07/2017	Theo Pouw BV	x	Particle size reduction by SGS Intron, delivery 8/11/2017, limited amount of material
6	Asphalt aggregate	Mineral oil	EN 14039	6/12/2017	REKO	x	
	Recycled mixed aggregates	Mineral oil	EN 14039	3/07/2017	Theo Pouw BV	x	Particle size reduction by SGS Intron, delivery 8/11/2017, limited amount of material

~~7~~	Sealant 2	BIT, CIT, MIT	EN 15637	3/07/2017	Fraunhofer	x	Hardening and particle size reduction by VITO
	Render 1	~~Diuron, OIT, BIT, MIT~~	EN 15637	-	-	-	No biocides added, only APEO
	Treated wood (piece)	Propiconazole, tebuconazole	EN 15637	9/08/2017	BAM	x	Particle size reduction by BAM
	Render 2	Terbutryn, OIT, BIT, MIT	EN 15637	31/10/2017	Dr. Robert-Murjahn-Institut GmbH	x	Hardening and particle size reduction by VITO
8	Recycled mixed aggregates	PCB	EN 16167	3/07/2017	Theo Pouw BV	x	Particle size reduction by SGS Intron, delivery 8/11/2017, limited amount of material
~~9~~	~~Insulation foam (PEF or FEF)~~	~~SCCP~~	~~EN ISO 18219~~	-	-	-	
10	Plastic product (CRM)	PBDE	EN ISO 22032	7/07/2017	JRC	x	Limited amount of material, particle size reduction by VITO
11	~~Render 1~~	~~Organotin (from biocides, spiked)~~	~~EN ISO 23161~~	-	-	-	
12	Water proofing sheets (PVC)	Phenols	~~ISO 14154~~ CEN/TS 16182	26/01/2018	Dakgroothandel	x	Particle size reduction by SGS Intron
13	Asphalt aggregate	BTEX	NEN 7331 - BTEX part	6/12/2017	REKO	x	
14	Asphalt aggregate	PAH	NEN 7331 - PAH part	6/12/2017	REKO	x	
	~~Asphalt concrete~~	~~PAH~~	~~NEN 7331 - PAH part~~	-	-	-	
	Roofing felt (Bitumen shingles)	PAH	NEN 7331 - PAH part	5/07/2017	Dakenshop	x	
	Rubber crumbs	PAH	NEN 7331 - PAH part	29/09/2017	SGS Intron	x	Particle size reduction by SGS Intron

Eluate analysis

N°	Sample	Specific substances	Methods to be used	Date of delivery	Delivered by	Analysed	Remarks
1	Wood powder (CRM)	Pentachlorophenol	EN 12673	8/11/2017	SGS Intron	x	Limited amount of eluate (250 ml), only 1 fraction L/S 10
2	Sealant 2	BIT, CIT, MIT	EN 15637	27/11/2017	SGS Intron	x	
	Render 1	~~Diuron, OIT, BIT, MIT~~	EN 15637	-	-	-	No biocides added, only APEO
	Treated wood (piece)	Propiconazole, tebuconazole	EN 15637	9/08/2017	BAM	x	Limited amount of eluate (250 mL)
	Render 2	Terbutryn, OIT, BIT, MIT	EN 15637	22/01/2018	SGS Intron	x	Limited amount of eluate (500 mL)
3	~~Plastic product (CRM)~~	~~PBDE~~	~~EN 16694~~	8/11/2017	SGS Intron		Limited amount of eluate (100 ml), only 1 fraction L/S 10
4	Water proofing sheets (PVC)	Phenols	EN ISO 14402	26/01/2018	SGS Intron	x	
5	Asphalt aggregate	BTEX	EN ISO 15680	6/12/2017	SGS Intron	x	
~~**6**~~	~~Render 1~~	~~Organotin~~	~~EN ISO 17353~~	-	-	-	
7	Asphalt aggregate	BTEX	EN ISO 17943	6/12/2017	SGS Intron	-	
8	~~PVC flooring (old)~~	~~Phthalates~~	~~EN ISO 18856~~	-	-	-	
	Sealant 1	Phthalates	EN ISO 18856	27/11/2017	SGS Intron	x	
9	Water proofing sheets (PVC)	Bisphenol-A	EN ISO 18857-2	26/01/2018	SGS Intron	x	
	Render 1	Nonylphenol	EN ISO 18857-2	26/01/2018	SGS Intron	x	
10	Recycled mixed aggregates	Mineral oil	EN ISO 9377-2	8/11/2017	SGS Intron	x	
11	Asphalt aggregate	BTEX	ISO 11423-1	6/12/2017	SGS Intron	-	
12	Rubber crumbs	Dioxin-like PCBs	ISO 17858	29/09/2017	SGS Intron	x	
	Recycled mixed aggregates	Dioxin-like PCBs	ISO 17858	8/11/2017	SGS Intron	x	

	Recycled mixed aggregates	Dioxins and furans	ISO 17858 or ISO 18073	8/11/2017	SGS Intron	x	
	Rubber crumbs	Dioxins and furans	ISO 17858 or SO 18073	29/09/2017	SGS Intron	x	
13	Asphalt aggregate	PAH	ISO 28540	6/12/2017	SGS Intron	x	
	~~Asphalt concrete~~	~~PAH~~	~~ISO 28540~~	-	-	-	
	Recycled mixed aggregates	PAH	ISO 28540	8/11/2017	SGS Intron	x	
	Rubber crumbs	PAH	ISO 28540	29/09/2017	SGS Intron	x	

CHAPTER 2 DETERMINATION OF THE CONTENT OF MINERAL OIL IN CONSTRUCTION PRODUCTS

2.1. EN 14039 CHARACTERIZATION OF WASTE - DETERMINATION OF HYDROCARBON CONTENT IN THE RANGE OF C10 TO C40 BY GAS CHROMATOGRAPHY

2.1.1. METHOD DESCRIPTION

A summary of EN 14039 and modifications done by VITO is given in Table 4. The method was applied for asphalt aggregate and recycled mixed aggregate.

2.1.2. MEASUREMENT CONDITIONS APPLIED BY VITO

Instrument :	GC/FID Thermo Trace GC Ultra
GC-column :	DB-XLB 15m length x 0.25mm ID x 0.25µm FT
Carrier gas :	Helium, constant colomn flow 1.3ml/min
Injection :	1 µl on-column
GC-oven :	initial temperature 65 °C (1.05 min) 10 °C/min to 100 °C (0 min) 15 °C/min to 320 °C (6 min)
FID temp :	320 °C

2.1.3. CALIBRATION

The calibration curve was constructed using 11 calibration solutions of RIVM-oil in hexane with concentrations of respectively 25, 56, 102, 253, 499, 1119, 2640, 5021, 10760, 20924 and 31312 µg/g. The calibration curve is given in Figure 1 and the curve is linear from 25 to 31312 µg/g.

In case of 10 g intake and a 10 ml final extract volume these concentrations correspond to a sample concentration of 25-31000 mg/kg mineral oil.

The validity of the calibration curve was checked during the measurement of the samples with a control solution containing 10760 µg/g mineral oil. The result was within 10% of the reference value of the control solution.

2.1.4. PERFORMANCE OF THE GC SYSTEM

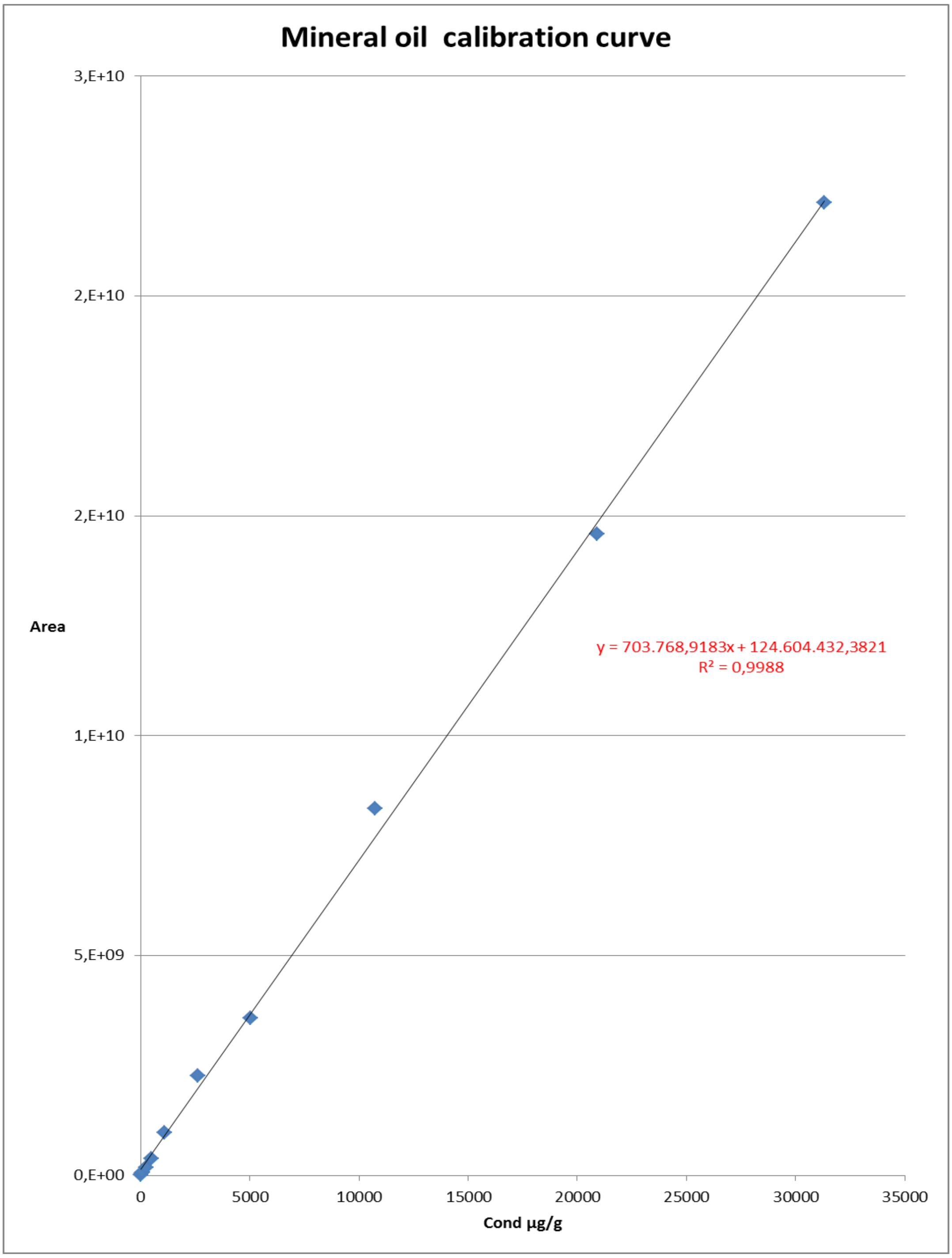
The performance of the GC was checked with a solution of n-alkanes. The n-alkanes C10 – C40 are baseline separated. The performance of the injection system (non-discrimination) was checked with RIVM oil; the ratio of the response of the fraction C20-C40 and the fraction C10-C20 was 1.355 and lies within the range 1.25 - 1.40 for non-discrimination.

For the repeatability check the control solution containing 10760 µg/kg mineral oil was injected three times. The relative standard deviation was <5%.

Table 4: Summary of EN 14039 and method applied by VITO

Sample Parameter list	Short Description of the method to be used	Short description of the VITO Method	Method differences	Comment
Asphalt aggregate Recycled mixed aggregates	- Matrix: solid waste - Intake: 20 g - IS: none - Extraction: agitation or USE or PLE with acetone/hexane (2/1); wash with water to remove acetone - Clean-up: florisil - Measurement: GC-FID - LOQ: 100 mg/kg	- Matrix : asphalt aggregate, recycled mixed aggregates - Intake: 10 g - IS: none - Extraction: PLE with acetone/hexane (1/1); wash with MgSO4 solution in water to remove acetone - Clean-up: florisil - Measurement: GC-FID	- VITO uses hexane as an extraction solvent instead of heptane - VITO adds MgSO4 to the water used for washing the extract	- Allowed by EN 14039 - The addition of MgSO4 enhances the separation of the layers

Figure 1: Calibration diagram of mineral oil



2.2. DETERMINATION OF MINERAL OIL IN ASPHALT AGGREGATE

2.2.1. SAMPLE

Asphalte aggregate was received from REKO. A first particle size reduction was done by SGS Intron. The sample was subsequently ground by VITO to particles <1 mm.

2.2.2. ANALYSIS

- The sample was mixed with drying agent (Celite)
- 10 g of the dried sample was PLE extracted (Dionex ASE) with acetone/hexane (50/50) using the following settings:
    - Heat : 5 min
    - Static: 5 min
    - Flush % : 60% volume
    - Purge: 200 sec
    - Temperature: 100 °C
    - Pressure: 140 bar
- The extract was transferred to a separatory funnel and the aceton was washed out with 250 ml water containing 20 g of magnesium sulphate.
- The hexane layer was dried with anhydrous sodium sulphate and concentrated to 10 g
- The hexane layer was cleaned by shaking with 2 g of activated Florisil
- The extract was filtered on a glass fiber filter and analysed with GC/FID

2.2.3. RESULTS

→ Repeatability

The sample was analysed in five fold. The results are given in Table 5. The average mineral oil content was 2795 mg/kg and the repeatability (expressed as relative standard deviation) was 6.5%.

→ Recovery of the control sample

A soil sample with a mineral oil concentration of 2000 mg/kg was analysed and the recovery was calculated. The recovery was 54%.

→ Sensitivity

The sensitivity, calculated with the lowest calibration standard, is 25 mg/kg sample. This is lower than the detection limit of method EN 14039 (100 mg/kg).

2.2.4. COMMENTS

The repeatability of method EN 14039 for the analysis of mineral oil in asphalt aggregate is good, but the recovery of the control sample was low. Although it can be argumented that the result of a mineral oil determination is method dependent and the repeatability is more important than the trueness, we would advise to consider the addition of an internal standard and calculate the results with internal standard calibration. Method CMA/3/R.1[1] is an example of a method for mineral oil determination with n-C40 as internal standard.

2.2.5. CHROMATOGRAMS

The GC/FID chromatogram of replicate 1 of sample asphalt aggregate is shown in Figure 2.

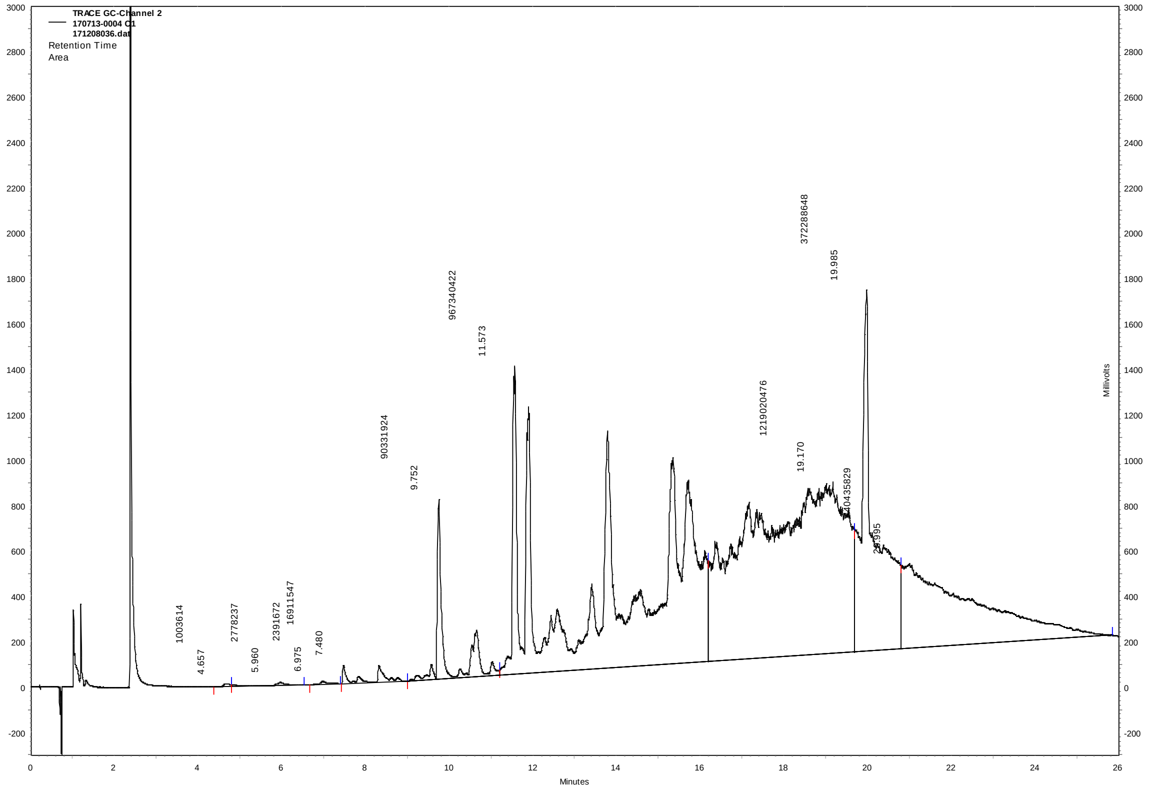
2.2.6. CONCLUSION

Method EN 14039 is suited for the analysis of mineral oil in asphalt aggregate. However the change from external to internal standard calibration should be considered.

Table 5: Measured concentrations of mineral oil in asphalt aggregate using method EN 14039

Replicate n°	**1** mg/kg	**2** mg/kg	**3** mg/kg	**4** mg/kg	**5** mg/kg	**Average** mg/kg	**St.Dev.** mg/kg	**C.V.** %
Mineral oil	2935	2957	2619	2887	2577	2795	182	6,5

Figure 2: GC/FID chromatogram of asphalt aggregate



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[1] Compendium voor Monstername en Analyse, published by the Public Waste Agency of Flanders

2.3. DETERMINATION OF MINERAL OIL IN RECYCLED MIXED AGGREGATES

2.3.1. SAMPLE

A sample of recycled mixed aggregates was received from Theo Pauw BV. A first particle size reduction was done by SGS Intron. The sample was subsequently ground by VITO to particles <1 mm.

2.3.2. ANALYSIS

See 2.2.2.

2.3.3. RESULTS

→ Repeatability

The sample was analysed in five fold. The results are given in Table 6. The average mineral oil content was 709 mg/kg and the repeatability (expressed as relative standard deviation) was 10.7%.

→ Recovery of the control sample

See 2.2.3.

→ Sensitivity

See 2.2.3.

2.3.4. COMMENTS

The repeatability of method EN 14039 for the analysis of mineral oil in recycled mixed aggregates is good, but the recovery of the control sample was low. Although it can be argumented that the result of a mineral oil determination is method dependent and the repeatability is more important than the trueness, we would advise to consider the addition of an internal standard and calculate the results with internal standard calibration. Method CMA/3/R.1[2] is an example of a method for mineral oil determination with n-C40 as internal standard.

2.3.5. CHROMATOGRAMS

The GC/FID chromatogram of replicate 1 recycled mixed aggregate is shown in Figure 3.

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[2] Compendium voor Monsternamen en Analyse, published by the Public Waste Agency of Flanders

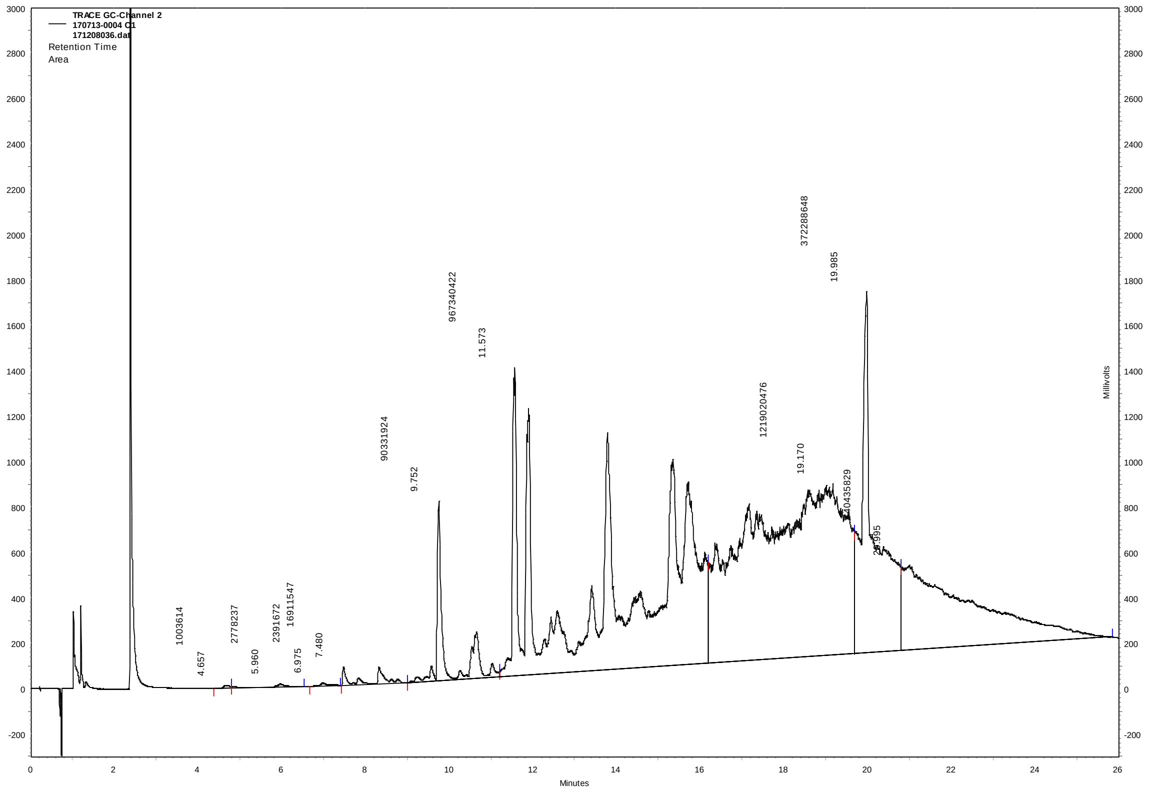
2.3.6. CONCLUSION

Method EN 14039 is suited for the analysis of mineral oil in recycled mixed aggregates. However the change from external to internal standard calibration should be considered.

Table 6: Measured concentrations of mineral oil in recycled mixed aggregates using method EN 14039

Replicate n°	**1** mg/kg	**2** mg/kg	**3** mg/kg	**4** mg/kg	**5** mg/kg	**Average** mg/kg	**St.Dev.** mg/kg	**C.V.** %
Mineral oil	597	782	665	750	749	709	75,8	10,7

Figure 3: GC/FID chromatogram of recycled mixed aggregates



CHAPTER 3 DETERMINATION OF THE CONTENT OF PAH IN CONSTRUCTION PRODUCTS

3.1. CEN/TS 16181 SLUDGE, TREATED BIOWASTE AND SOIL – DETERMINATION OF POLYCYCLIC AROMATIC HYDROCARBONS (PAH) BY GAS CHROMATOGRAPH (GC) AND HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)

3.1.1. METHOD DESCRIPTION

A summary of CEN/TS 16181 and modifications done by VITO is given in Table 7. The method was applied for asphalt aggregate and recycled mixed aggregate. The method was used for the determination of the following PAH:

Naphthalene
Acenaphthylene
Acenaphthene
Fluorene
Phenanthrene
Anthracene
Fluoranthene
Pyrene
Benzo(a)anthracene
Chrysene
Benzo(b)fluoranthene
Benzo(k)fluoranthene
Benzo(a)pyrene
Indeno(1,2,3,c,d)pyrene
Dibenzo(a,h)anthracene
Benzo(g,h,i)perylene

3.1.2. MEASUREMENT CONDITIONS APPLIED BY VITO

Instrument settings:

Hardware	Instrument GC-column	Thermo Quest Trace GC Thermo DSQ MS Agilent VF-17MS 30 m lenght, 0.25 mm ID, 0.25 um FT
Injector parameters	Injection volume Injection modus Injection temperature Pulse pressure Pulse time Purge flow	1 µl Pulsed splitless 300 °C 300 kPa 1.0 min 30 ml/min

	Purge time	1.0 min
GC parameters	Carrier gas	Helium - const flow 1 ml/min
	Initial temperature	75 °C
	Initial time	1.0 min
	Rate #1	15 °C/min
	Final temperature #1	210 °C
	Hold time #1	0 min
	Rate #2	5.0 °C/min
	Final temperature #2	310 °C
	Hold time #2	13 min
MS parameters	Mode	Segmented scan
	Source temperature	250 °C
	Interface temperature	310 °C
	Solvent delay	5.5 min
Segments	m/z	Time
	120 – 180	5.5 – 11.5 min
	170 – 220	11.5 – 20 min
	210 - 250	20 – 25 min
	240 – 300	25 min – run end

Internal standards and ions used for quantitation:

Component	m/z	Internal standard	m/z
Naphthalene	128	D8-naphthalene	136
Acenaphthylene	152	D8-acenaphthylene	160
Acenaphthene	153	D10-acenaphthene	163
Fluorene	166	D10-fluorene	176
Phenanthrene	178	D10-phenanthrene	188
Anthracene	178	D10-anthracene	188
Fluoranthene	202	D10-fluoranthene	212
Pyrene	202	D10-pyrene	212
Benzo(a)anthracene	228	D12-benzo(a)anthracene	240
Chrysene	228	D12-chrysene	240
Benzo(b)fluoranthene	252	D12-benzo(b)fluoranthene	264
Benzo(k)fluoranthene	252	D12-benzo(k)fluoranthene	264
Benzo(a)pyrene	252	D12-benzo(a)pyrene	264
Indeno(1,2,3,c,d)pyrene	276	D12-indeno(1,2,3,c,d)pyrene	288
Dibenzo(a,h)anthracene	278	D14-dibenzo(a,h)anthracene	292
Benzo(g,h,i)perylene	276	D12-benzo(g,h,i)perylene	288
		D10-methylnaphthalene*	152
		D12-perylene*	264

*injection standards

3.1.3. CALIBRATION DIAGRAMS

Six calibration solutions of PAH were prepared in a concentration range of 0.06 to 4.2 µg/ml (except benzo(k)fluoranthene: 0.07 to 5.6 µg/ml). Internal standards (deuterated PAH) and

injection standards (D10-methylnaphthalene and D12-perylene) were added to the calibration solutions in a fixed concentration of 0.8 µg/ml. The calibration curves are given in Figure 4 and are linear over the injected range.
In case of 0.5 g intake and a 1 ml final extract volume these concentrations correspond to a sample concentration of 0.12 to 8.4 mg/kg (except for benzo(k)fluoranthene: 0.14 to 11.2 mg/kg).

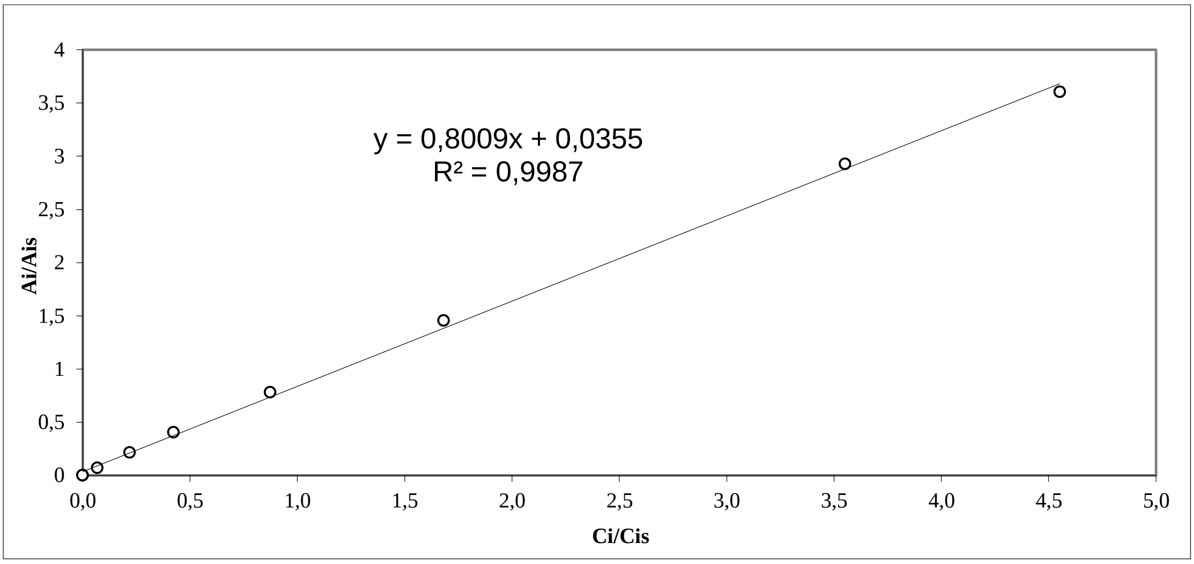
For calibration purposes a calibration verification solution was injected before and after the measurement of the samples. The calibration verification solution contains 0.7 – 2.5 mg/l per PAH and 0.8 µg/l per internal standard. The average relative response factor of the PAH in these solutions was used to calculate the PAH concentration in the sample.

Table 7: Summary of CEN/TS 16181 and method applied by VITO

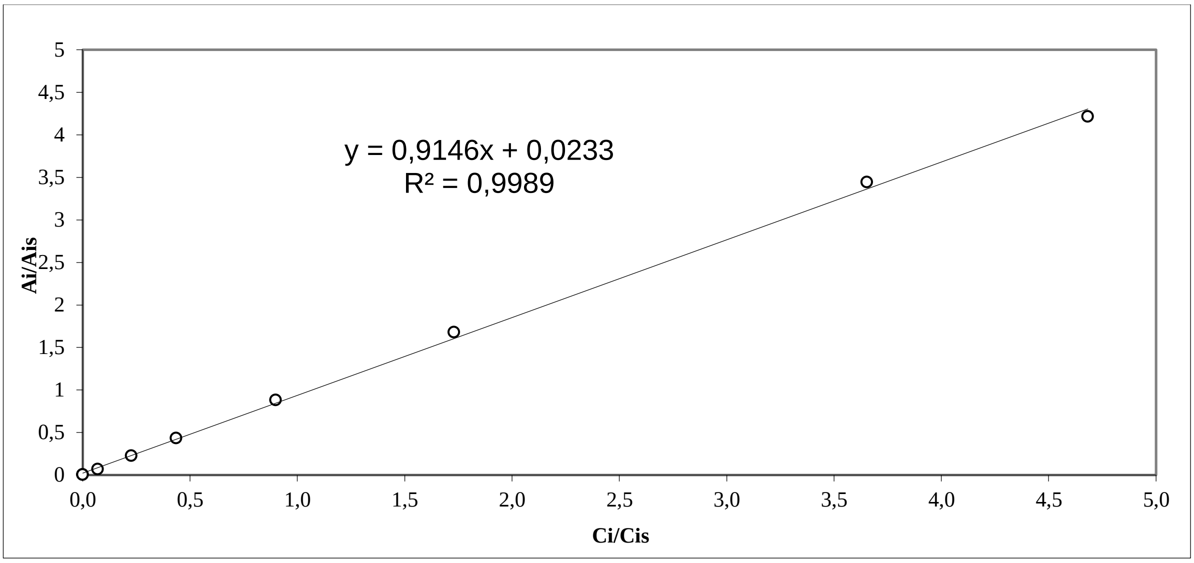
Sample Parameter list	Short Description of the method to be used	Short description of the VITO Method	Method differences	Comment
Asphalt aggregate Recycled mixed aggregates PAH	- Matrix: sludge, biowaste, soil - Intake: 2 – 20 g - IS: deuterated PAH (for MS) - Extraction: agitation with acetone/petroleumether; soxhlet or PLE with toluene - Clean-up : GPC, alumina, silica, partitioning in cyclohexane/DMF - Measurement: GC-MS or HPLC-UV-DAD/FLD - LOQ: 0.01 mg/kg per component	- Matrix : asphalt concrete, recycled mixed aggregates - Intake: 1- 5 g - IS: deuterated PAH - Extraction: agitationwith acetone/petroleumether - Clean-up: alumina/silica - Measurement: GC-MS	- none	

Figure 4: Calibration diagrams of the PAH (method CEN/TS 16181)

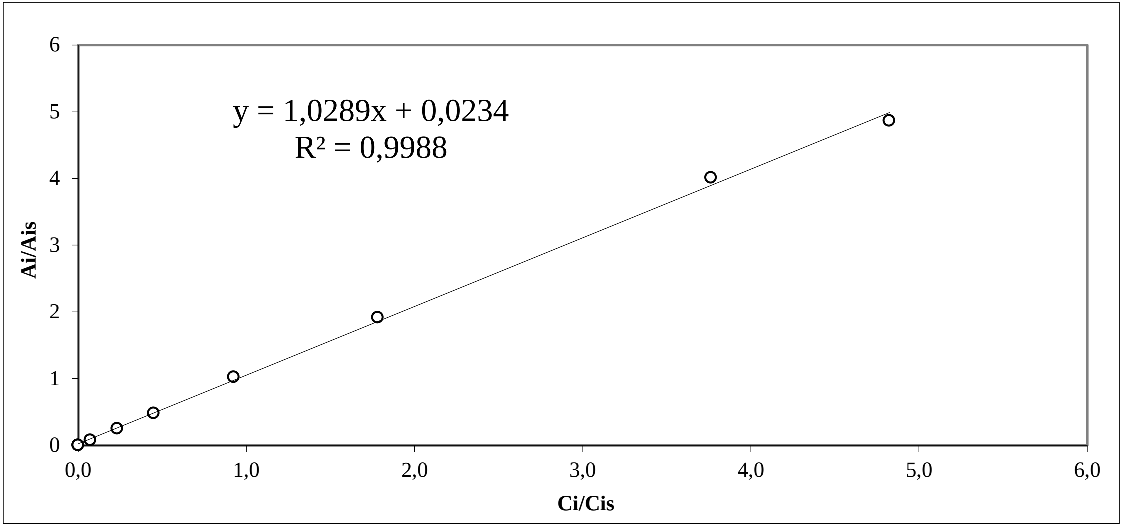
- Naphthalene



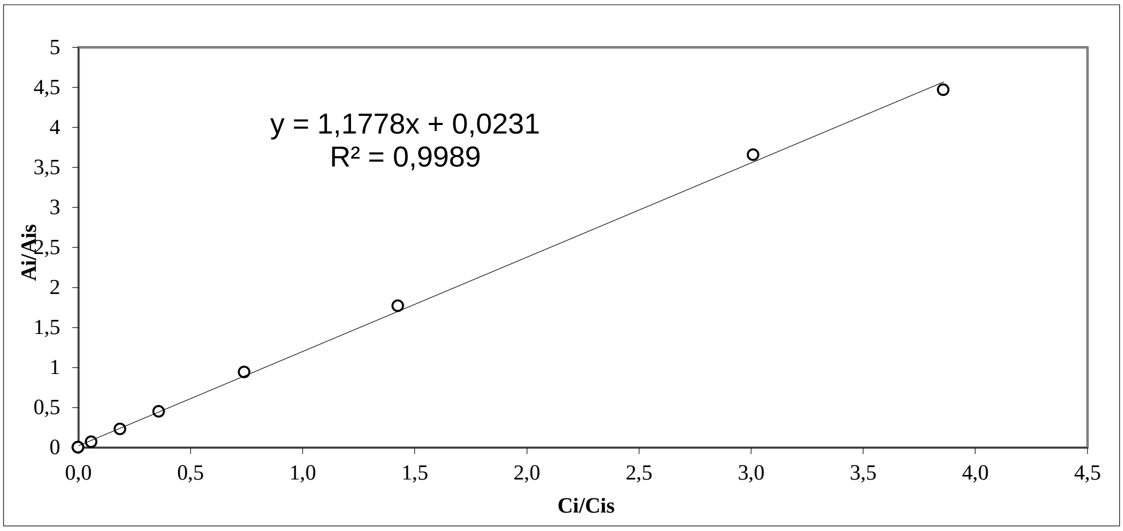
- Acenaphthylene



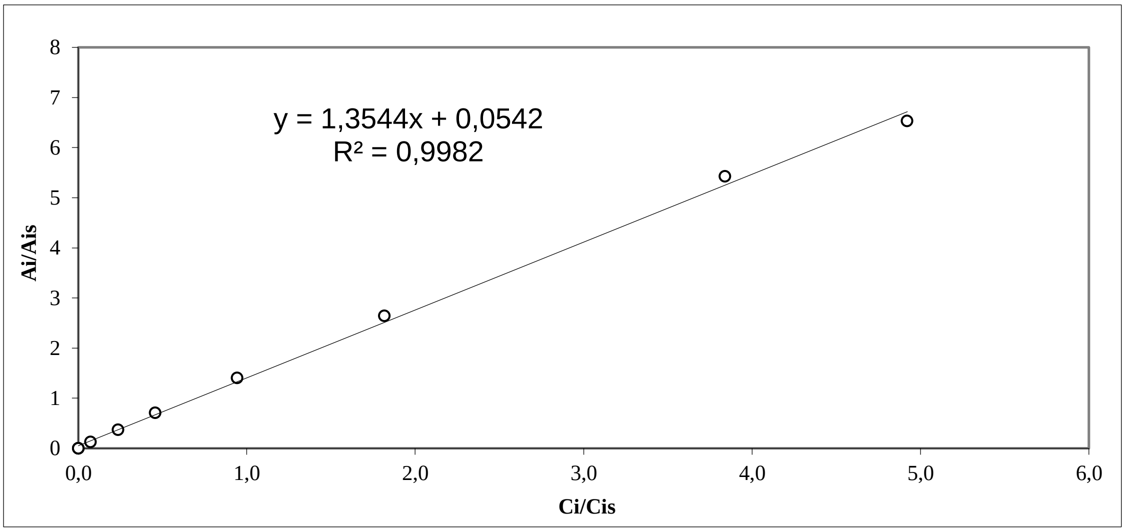
- Acenaphthene



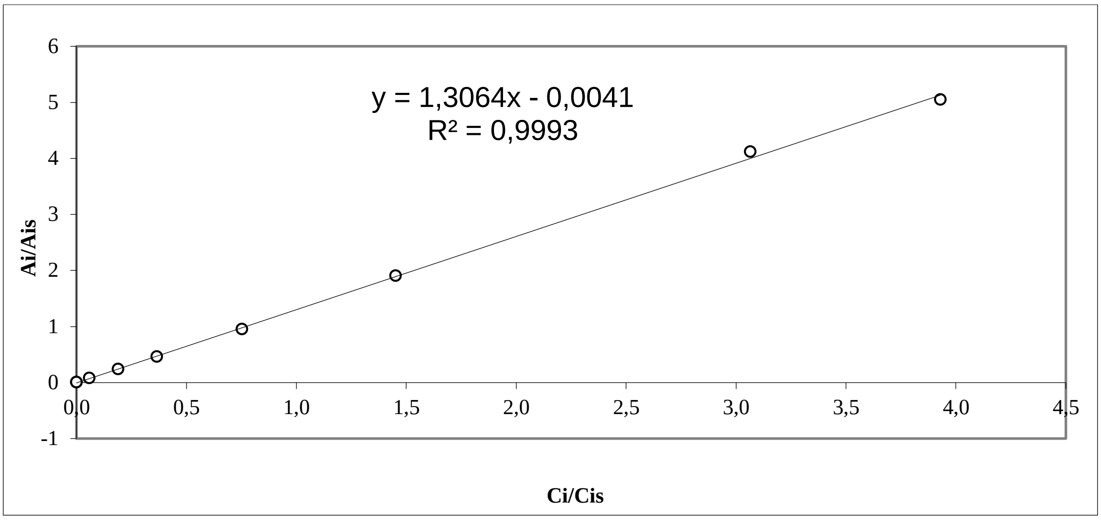
- Fluorene



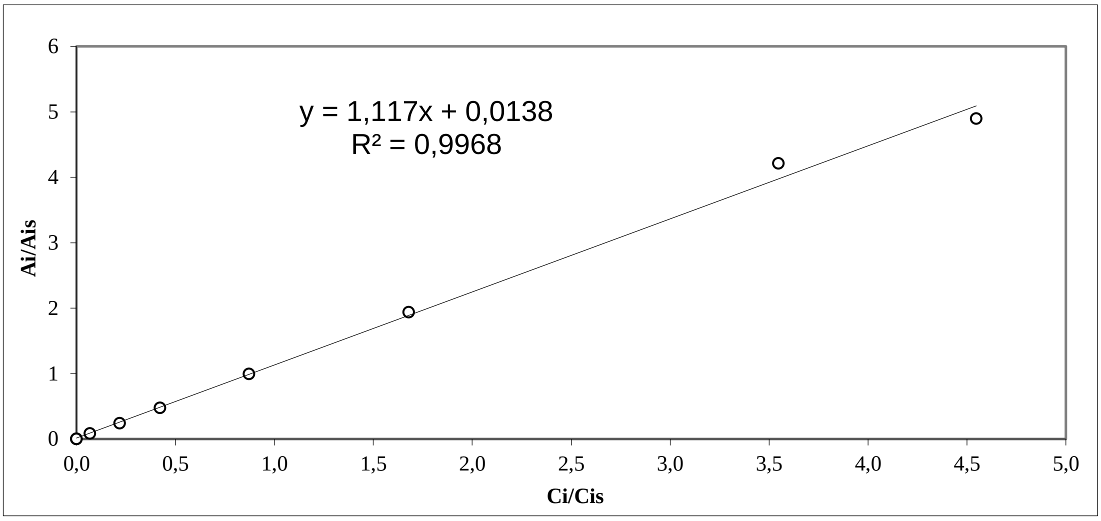
- Phenanthrene



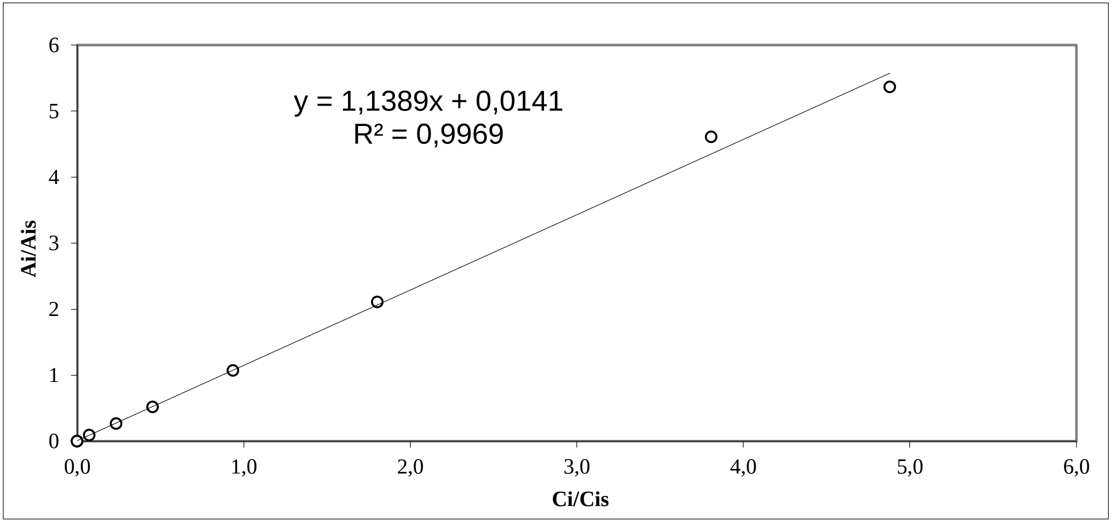
- Anthracene



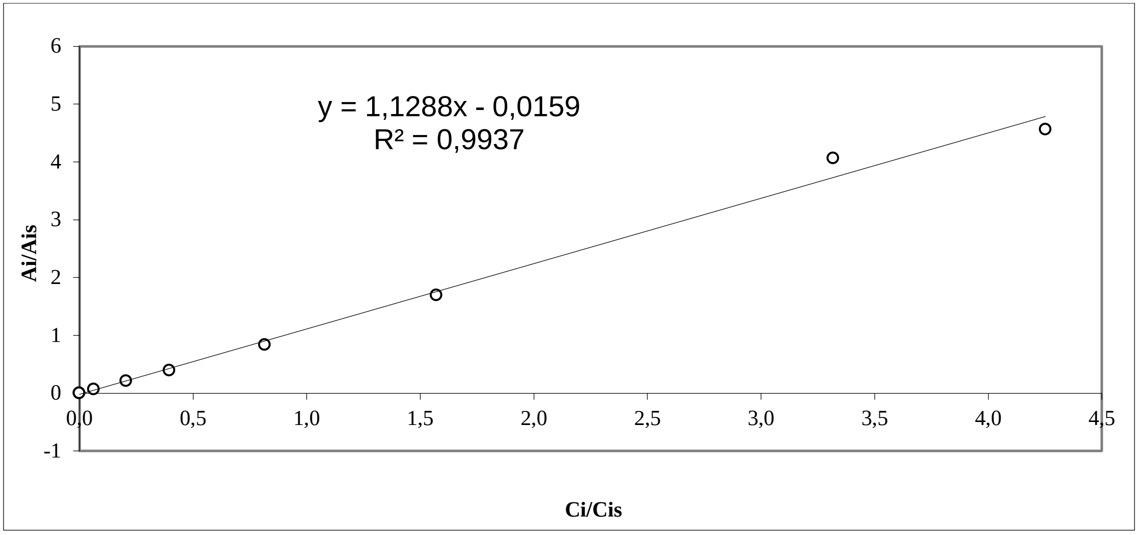
- Fluoranthene



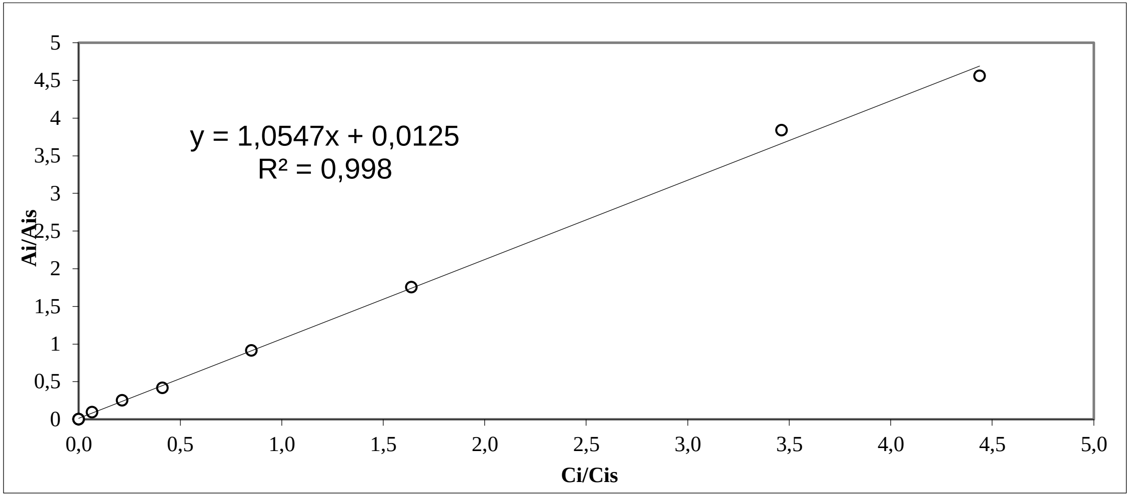
- Pyrene



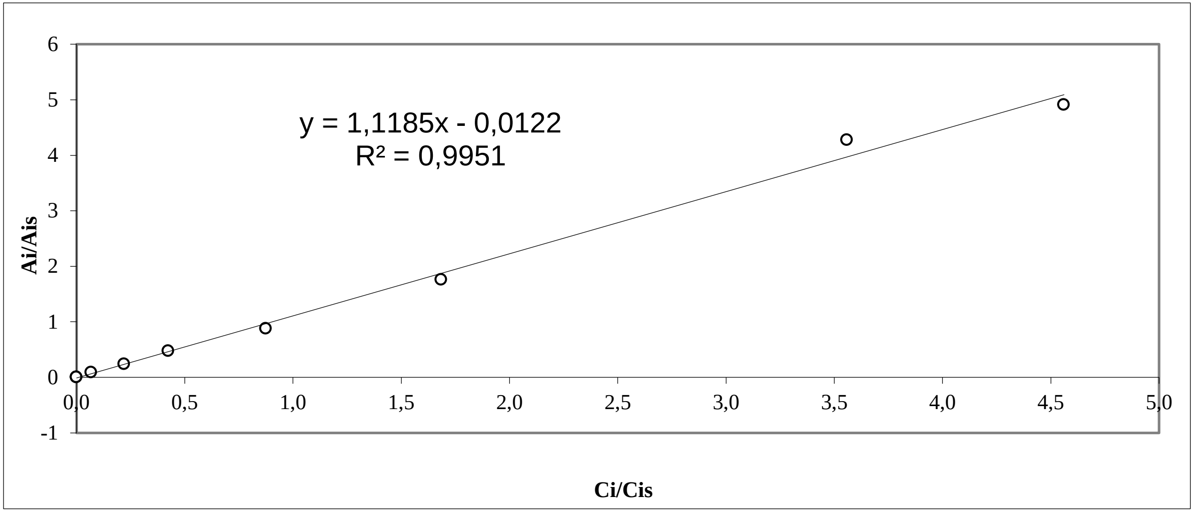
- Benz(a)anthracene



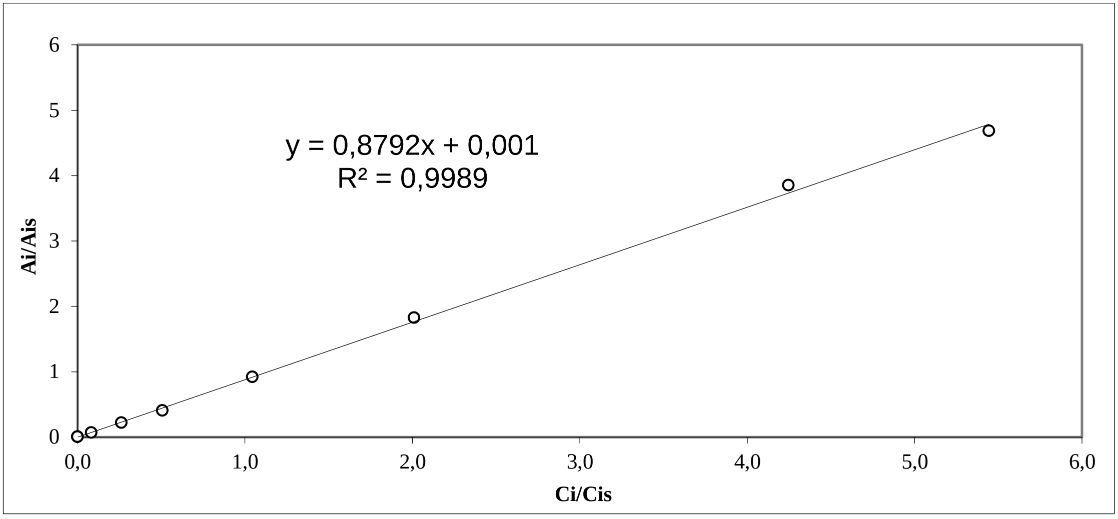
- Chrysene



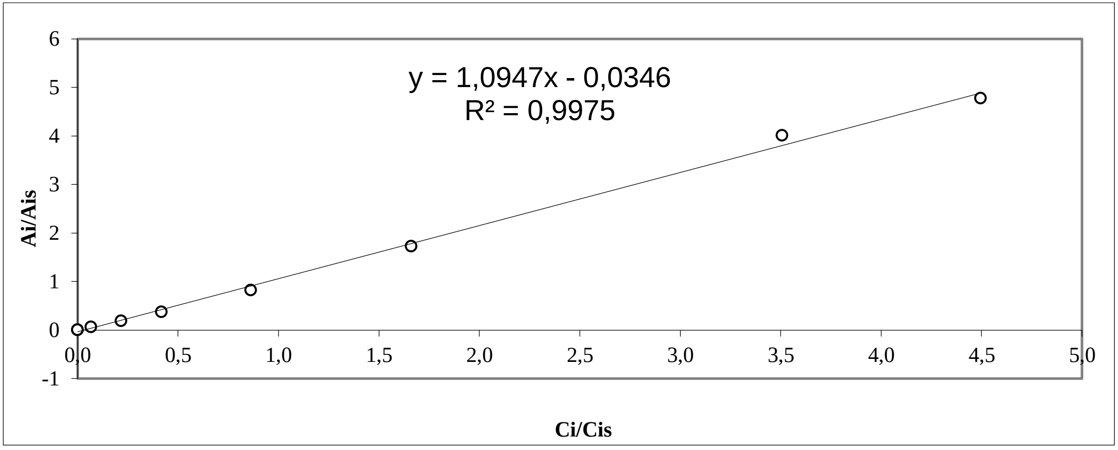
- Benzo(b)fluoranthene



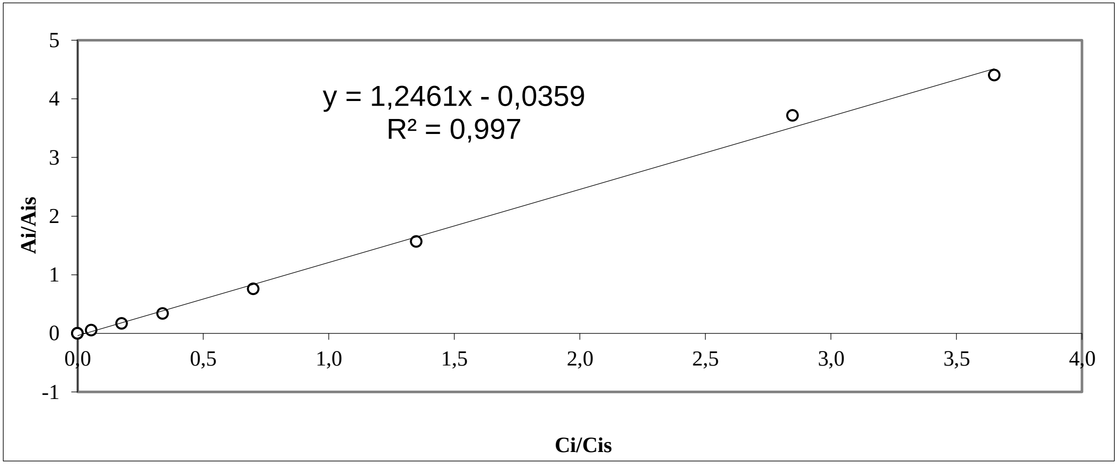
- Benzo(k)fluoranthene



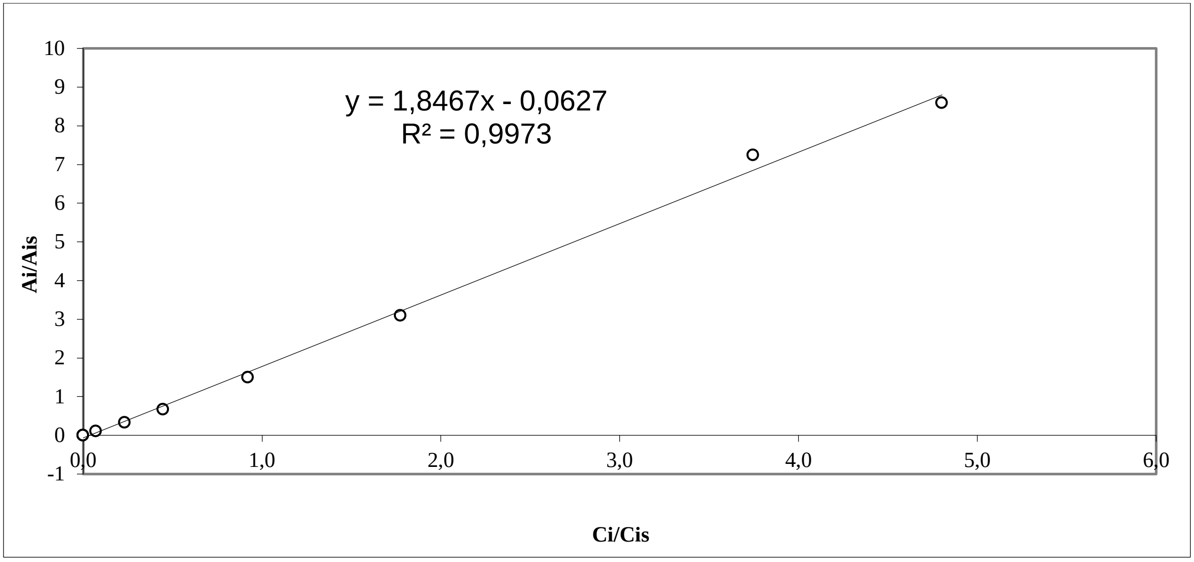
- Benzo(a)pyrene



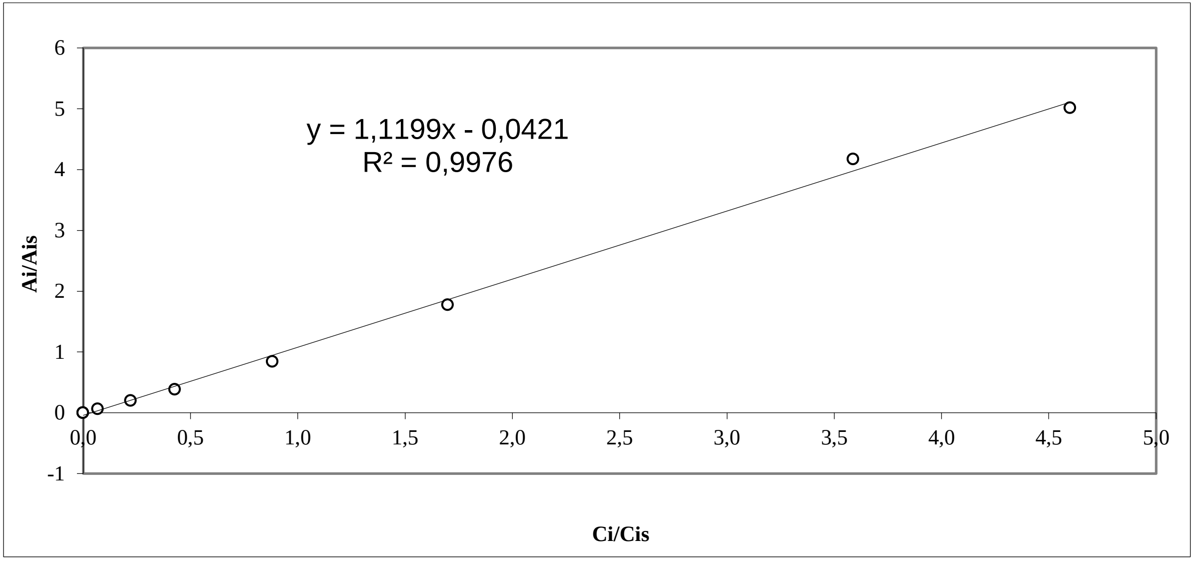
- Indeno(123cd)pyrene



- Dibenzo(ah)anthracene



- Benzo(ghi)perylene



3.2. DETERMINATION OF PAH IN ASPHALT AGGREGATE WITH METHOD CEN/TS 16181

3.2.1. SAMPLE

Asphalt aggregate was received from REKO. A first particle size reduction was done by SGS Intron. The sample was subsequently ground by VITO to particles <1 mm.

3.2.2. ANALYSIS

- 0.5 g of grinded sample was spiked with internal standards
- 50 ml acetone was added and the sample was shaken for 30 min
- 50 ml petroleum ether was added and the sample was shaken for 12 h
- After the solids were settled the supernatant was filtered on a glass fiber filter and transferred to a separatory funnel. The solid phase was washed with 50 ml of petroleum ether and the supernatant was again filtered and added to the funnel.
- The acetone was removed from the extract by washing twice with 200 ml water
- The organic layer was dried with anhydrous sodium sulphate and concentrated to 1 ml with a solvent exchange to toluene
- The injection standards were added to the final extract
- Due to the high PAH concentrations in the sample, the extract was diluted 20 times before it was analysed with GC/MS

3.2.3. RESULTS

→ Repeatability

The sample was analysed in five fold. The results are given in Table 8. The repeatability (expressed as relative standard deviation) is for most PAH lower than 15%. For naphthalene the repeatability is 22%. This is acceptable because of the volatile nature of this compound.

→ Check on method performance

The recoveries of the internal standards in each sample were calculated using the calibration standard as a reference (100%). The results are given in Table 9. The average recovery of the internal standards were for all replicates lower than the requirement of method CEN/TS 16181 (75%). For five individual internal standards the recovery was sometimes lower than the requirement of the method (60%): D8-acenaphthylene, D10-fluoranthene, D10-pyrene, D12-benzo(a)anthracene and D12-chrysene.

→ Sensitivity

The sensitivity of the method was calculated with S/N using the response of naphthalene in the sample. The LOD for naphthalene was 0.18 mg/kg. This is higher than the detection limit of method CEN/TS 16181 (0.01 mg/kg). The reason for the higher detection limit is the low sample intake of 0.5 g and the dilution of the final extract, which was choosen because of the high expected PAH concentrations in the sample. For samples with low PAH concentrations, it is possible to raise the sample intake 20-fold to 10 g. The detection limit will then be around 0.009 mg/kg, which is lower than the detection limit of the method (0.01 mg/kg).

3.2.4. COMMENTS

The repeatability and the LOD of method CEN/TS 16181 using agitation as extraction technique and GC/MS as measurement technique is acceptable for the analysis of PAH in asphalt aggregate. The recovery of the internal standards was sometimes lower than the requirement (60%). However in case of isotope dilution (each PAH has his own deuterated homologue as internal standard) lower recoveries are acceptable as long as the required detection limit can be met.

3.2.5. CHROMATOGRAMS

The GC/MS ion chromatograms of PAH in asphalt aggregate are shown in Figure 5.

3.2.6. CONCLUSION

Method EN 16181, using agitation extraction with acetone/petroleum ether and measurement with GC/MS, is suited for the analysis of PAH in asphalt aggregate. It is advised to lower the requirement for the recoveries of the internal standards (e.g. to 50%).

Table 8: Measured concentrations of PAH in asphalt aggregate using method CEN/TS 16181

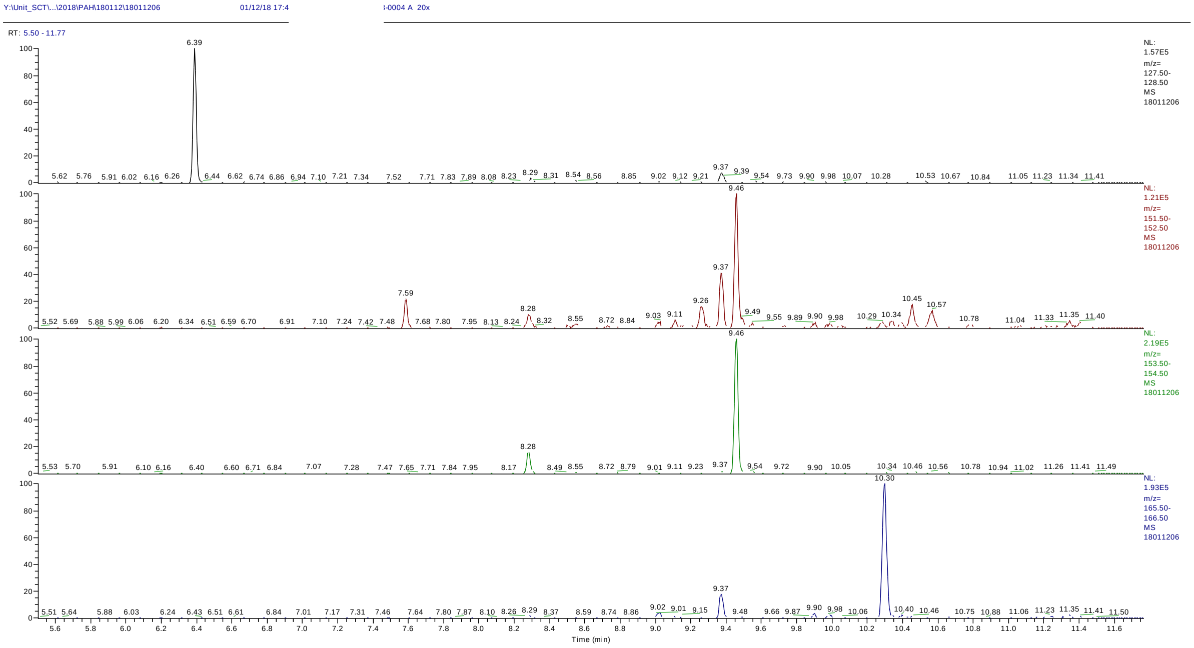
Replicate n°	**1** mg/kg	**2** mg/kg	**3** mg/kg	**4** mg/kg	**5** mg/kg	**Average** mg/kg	**St.Dev.** mg/kg	**C.V.** %
Naphthalene	4,62	3,88	6,51	4,29	4,23	4,71	1,04	22,1
Acenaphthylene	0,61	0,541	0,537	0,487	0,477	0,530	0,05	10,0
Acenaphthene	6,38	6,15	7,44	5,62	5,43	6,20	0,79	12,7
Fluorene	8,85	8,02	8,96	6,73	7,06	7,92	1,01	12,8
Phenanthrene	98,7	95,4	115	84,8	82,6	95,3	13,0	13,6
Anthracene	17,1	16,4	21,8	15,3	15,6	17,24	2,64	15,3
Fluoranthene	268	260	285	223	223	252	27,8	11,0
Pyrene	165	155	166	139	131	151	15,7	10,4
Benzo(a)anthracene	125	114	134	100	98,6	114	15,4	13,5
Chrysene	129	125	140	109	111	123	12,9	10,5
Benzo(b)fluoranthene	95,3	87,9	99,7	80,6	78,8	88,5	9,06	10,2
Benzo(k)fluoranthene	45,5	46	47,4	41,4	40,4	44,1	3,06	6,9
Benzo(a)pyrene	78,3	79,9	84,2	70,2	70	76,5	6,25	8,2
Indeno(1,2,3,c,d)pyrene	42,7	39,5	46,6	38,7	38	41,1	3,56	8,7
Dibenzo(a,h)anthracene	9,69	9,72	10,3	8,13	8,52	9,27	0,91	9,8
Benzo(g,h,i)perylene	44,3	40,9	48,4	36,1	39,1	41,8	4,75	11,4

Table 9: Recoveries of the internal standards in asphalt aggregate using method CEN/TS 16181

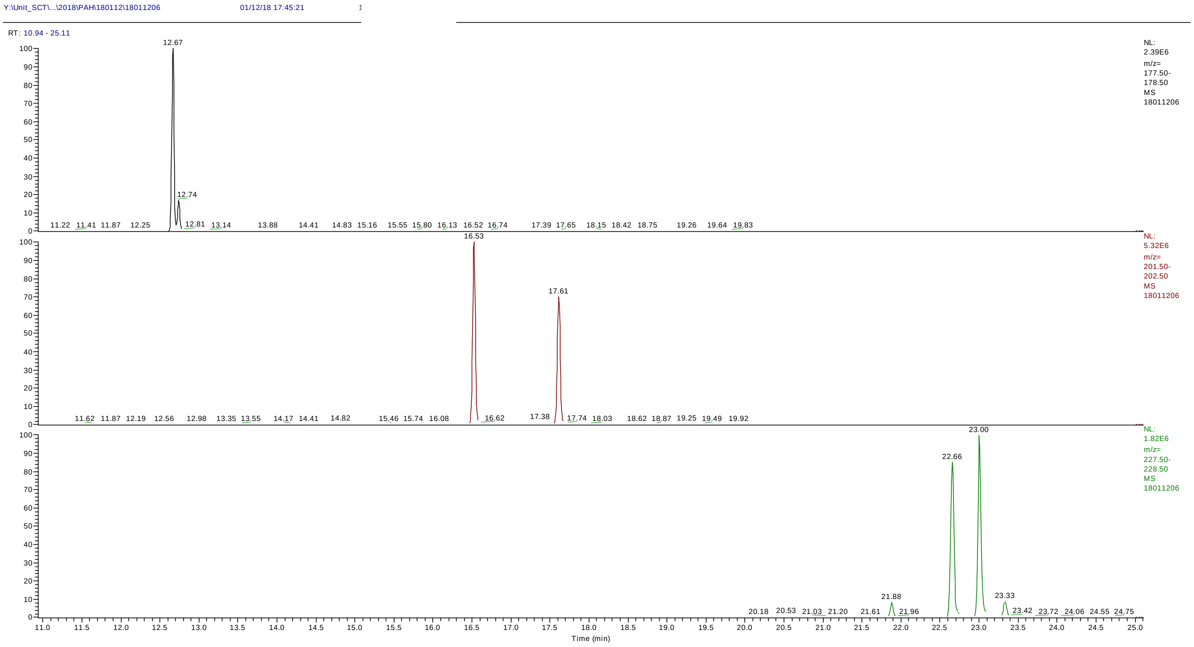
Replicate n°	**1** %	**2** %	**3** %	**4** %	**5** %
D8-naphthalene	72	67	70	66	68
D8-acenaphthylene	56	56	59	56	59
D10-acenaphthene	97	91	94	88	91
D10-fluorene	61	61	66	63	63
D10-phenanthrene	67	62	67	62	66
D10-anthracene	70	66	68	64	69
D10-fluoranthene	53	48	58	50	53
D10-pyrene	62	59	72	58	64
D12-benzo(a)anthracene	53	52	60	54	59
D12-chrysene	57	54	60	56	58
D12-benzo(b)fluoranthene	69	73	61	73	70
D12-benzo(k)fluoranthene	78	77	69	77	73
D12-benzo(a)pyrene	89	84	80	88	82
D12-indeno(1,2,3,c,d)pyrene	72	72	61	75	66
D14-dibenzo(a,h)anthracene	75	70	65	79	65
D12-benzo(g,h,i)perylene	72	77	62	81	69
Average recovery	69	67	67	68	67

Figure 5: GC/MS ion chromatograms of PAH in asphalt aggregate (method CEN/TS 16181)

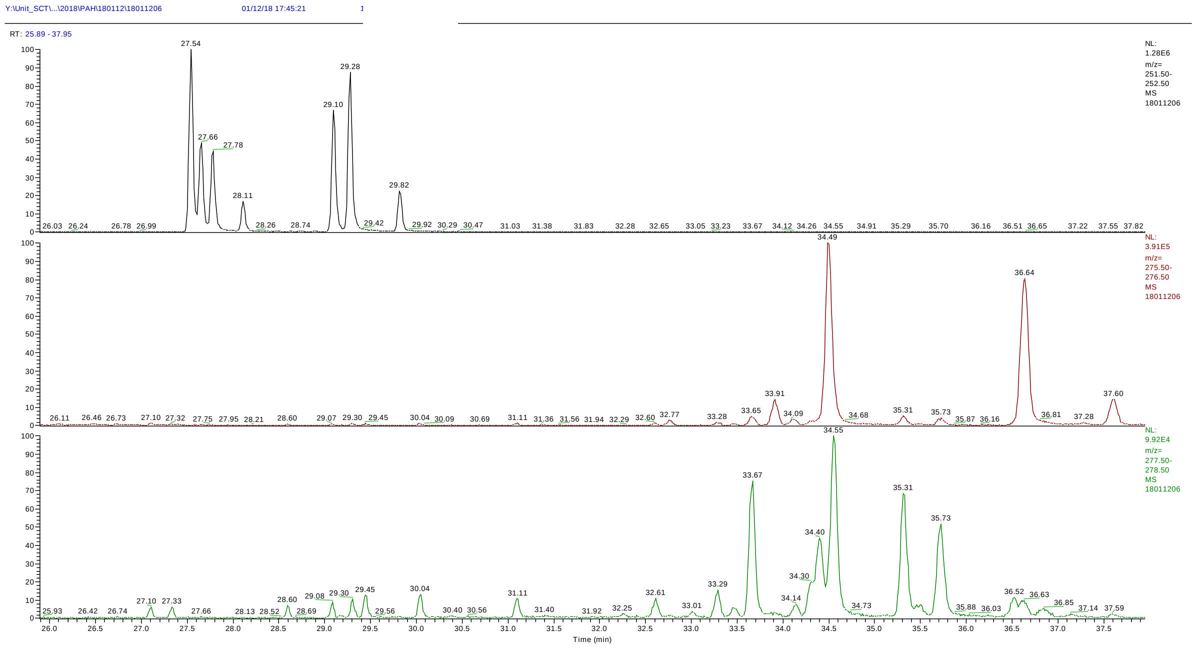
- Naftalene; acenaftylene; acenaftene; fluorene



- Fenanthrene and Anthracene; fluorantheen and pyrene; benzo(a)Anthracene and chryseen



- Benzo(b)fluoranthene, benzo(k)fluoranthene and benzo(a)pyrene; indeno(1,2,3,c,d)pyrene and benzo(g,h,i)perylene; dibenzo(a,h)anthracene



3.3. DETERMINATION OF PAH IN RECYCLED MIXED AGGREGATES WITH METHOD CEN/TS 16181

3.3.1. SAMPLE

A sample of recycled mixed aggregates was received from Theo Pauw BV. A first particle size reduction was done by SGS Intron. The sample was subsequently ground by VITO to particles <1 mm.

3.3.2. ANALYSIS

- 2.5 g of grinded sample was mixed with drying agent (Celite) and spiked with internal standards
- The dried sample was PLE extracted (Dionex ASE) with toluene using the following settings:
    Heat : 5 min
    Static: 5 min
    Flush % : 60% volume
    Purge: 100 sec
    Temperature: 100 °C
    Pressure: 2030 psi
- The extract was concentrated to 1 ml using a TurboVap at 40 °C
- The injection standards were added and the extract was analysed with GC/MS

3.3.3. RESULTS

→ Repeatability

The sample was analysed in five fold. The results are given in Table 10. For some PAH (acenaphthylene, acenaphthene, fluorene and dibenzo(ah)anthracene) the measured concentrations were lower than the detection limit and the CV_r could not be calculated. For the other PAH the repeatability was lower than 15% except for the most volatile PAH where the repeatability was between 20% and 30%.

→ Check on method performance

The recoveries of the internal standards in each sample were calculated using the calibration standard as a reference (100%). The results are given in Table 11. The average recovery of the internal standards were for all replicates higher than 75% and met the requirement of method CEN/TS 16181. For the more volatile PAH (D8-naphthalene to D10-phenanthrene) the recoveries were generally lower than the requirement of the method (60%). For D8-naphthalene the recovery in replicate n° 2 was unacceptable low (18%). The low recoveries of the volatile internal standards indicate losses during extract concentration. Because of the high boiling point of the solvent (toluene), the TurbpoVap was operated at 40°C and volatile PAH were also evaporated.

→ Sensitivity

The sensitivity of the method was calculated with S/N and was for most PAH 0.06 mg/kg. This is higher than the detection limit of method CEN/TS 16181 (0.01 mg/kg). The reason for the higher detection limit is the low sample intake of 2.5 g, which was choosen because of the high expected PAH concentrations in the sample. For samples with low PAH concentrations, it is possible to raise the sample intake to 20 g. The detection limit will then be around 0.008 mg/kg, which is lower than the detection limit of the method (0.01 mg/kg).

3.3.4. COMMENTS

The %RSD of the method using PLE extraction with toluene and measurement with GC/MS for the analysis of PAH in asphalt aggregate is too high for the volatile PAH (naphthalene to anthracene). Also the recovery of the volatile internal standards can be too low because of losses during the concentration of the extract. For recycled mixed aggregates it is advised to do the extraction by shaking with acetone/petroleum ether. With this extraction technique it was demonstrated for asphalt aggregate that better repeatabilities (lower %RSD) are obtained for the volatile PAH.

3.3.5. CHROMATOGRAMS

The GC/MS ion chromatograms of PAH in recycled mixed aggregates are shown in Figure 6.

3.3.6. CONCLUSION

Method EN 16181, using PLE extraction with toluene, is not suited for the analysis of PAH in recycled mixed aggregates. Extraction by shaking with acetone/petroleum ether and measurement with GC/MS is advised, because this procedure gave acceptable results for the analysis of PAH in asphalt aggregate. As with asphalt aggregate, it is advised to lower the requirement for the recoveries of the internal standards (e.g. to 50%).

Table 10: Measured concentrations of PAH in recycled mixed aggregates using method CEN/TS 16181

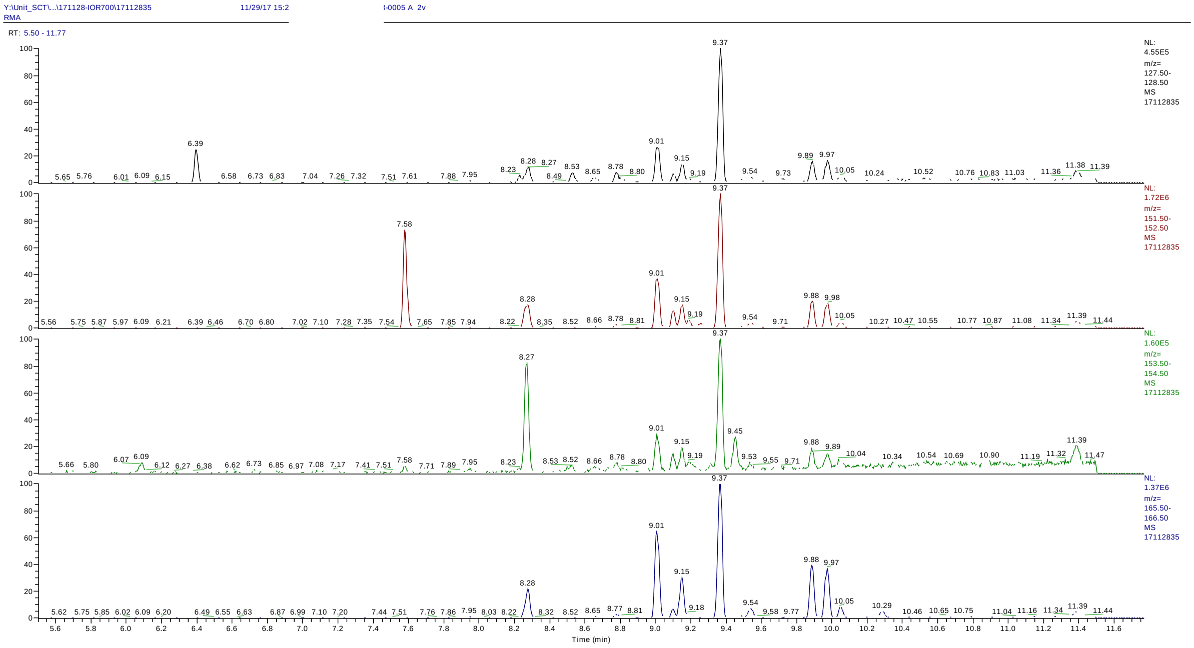
Replicate n°	**1** mg/kg	**2** mg/kg	**3** mg/kg	**4** mg/kg	**5** mg/kg	**Average** mg/kg	**St.Dev.** mg/kg	**CV_r** %
Naphthalene	0,065	0,107	0,065	0,068	< 0.06	0,08	0,02	27,0
Acenaphthylene	< 0.06	< 0.06	< 0.06	< 0.06	< 0.06	-	-	-
Acenaphthene	< 0.06	< 0.06	< 0.06	< 0.06	< 0.06	-	-	-
Fluorene	< 0.06	< 0.06	< 0.06	0,068	< 0.06	-	-	-
Phenanthrene	0,273	0,305	0,331	0,470	0,263	0,328	0,084	25,5
Anthracene	0,097	0,084	0,062	0,114	0,074	0,086	0,020	23,5
Fluoranthene	0,439	0,462	0,430	0,572	0,398	0,460	0,067	14,5
Pyrene	0,383	0,396	0,395	0,511	0,357	0,408	0,059	14,6
Benzo(a)anthracene	0,221	0,239	0,212	0,281	0,196	0,230	0,033	14,2
Chrysene	0,277	0,296	0,302	0,351	0,251	0,295	0,037	12,5
Benzo(b)fluoranthene	0,182	0,21	0,203	0,218	0,183	0,199	0,016	8,1
Benzo(k)fluoranthene	0,104	0,107	0,117	0,121	0,094	0,109	0,011	9,7
Benzo(a)pyrene	0,185	0,216	0,191	0,237	0,183	0,202	0,023	11,6
Indeno(1,2,3,c,d)pyrene	0,127	0,144	0,137	0,146	0,130	0,137	0,008	6,1
Dibenzo(a,h)anthracene	< 0.06	< 0.06	< 0.06	< 0.06	< 0.06	-	-	-
Benzo(g,h,i)perylene	0,136	0,154	0,147	0,157	0,129	0,145	0,012	8,2

Table 11: Recoveries of the internal standards in recycled mixed aggregates using method CEN/TS 16181

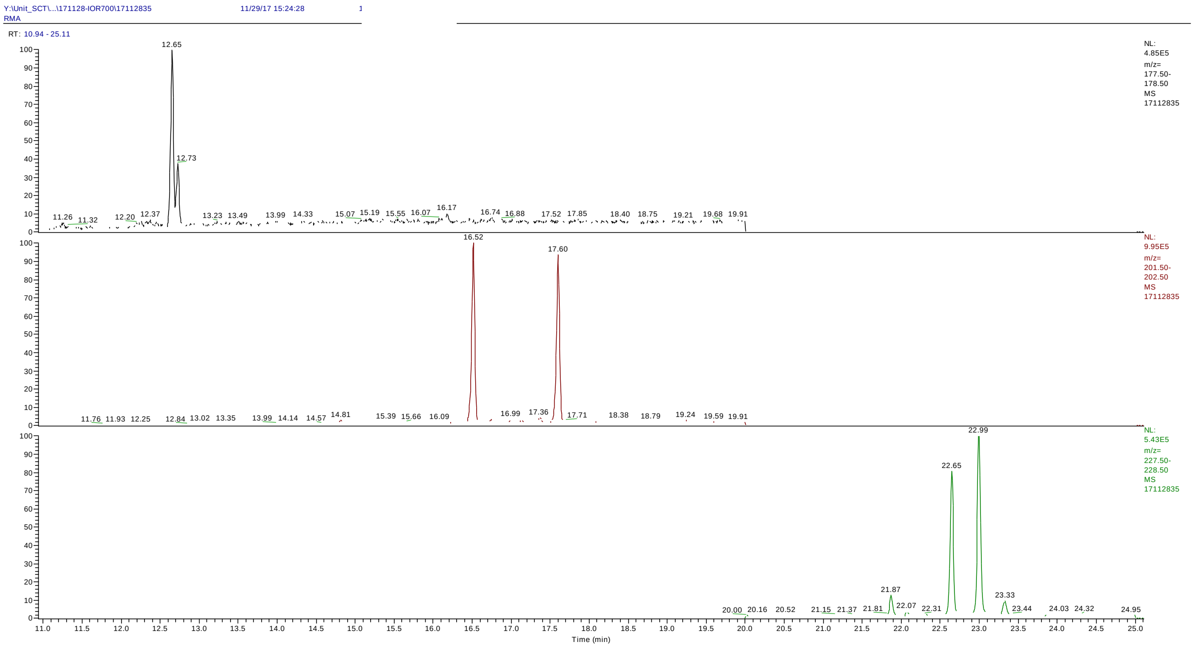
Replicate n°	**1** %	**2** %	**3** %	**4** %	**5** %
D8-naphthalene	41	18	38	37	31
D8-acenaphthylene	47	23	48	45	40
D10-acenaphthene	92	28	91	63	68
D10-fluorene	56	33	53	50	48
D10-phenanthrene	68	53	61	57	57
D10-anthracene	75	60	67	61	63
D10-fluoranthene	92	86	95	86	84
D10-pyrene	95	88	98	88	87
D12-benzo(a)anthracene	101	98	112	97	95
D12-chrysene	103	98	112	98	95
D12-benzo(b)fluoranthene	90	89	90	89	90
D12-benzo(k)fluoranthene	90	91	91	89	91
D12-benzo(a)pyrene	89	90	89	86	90
D12-indeno(1,2,3,c,d)pyrene	93	93	95	92	95
D14-dibenzo(a,h)anthracene	93	92	94	93	95
D12-benzo(g,h,i)perylene	99	96	99	96	100
Average recovery	83	71	83	77	77

Figure 6: GC/MS ion chromatograms of PAH in recycled mixed aggregates (method CEN/TS 16181)

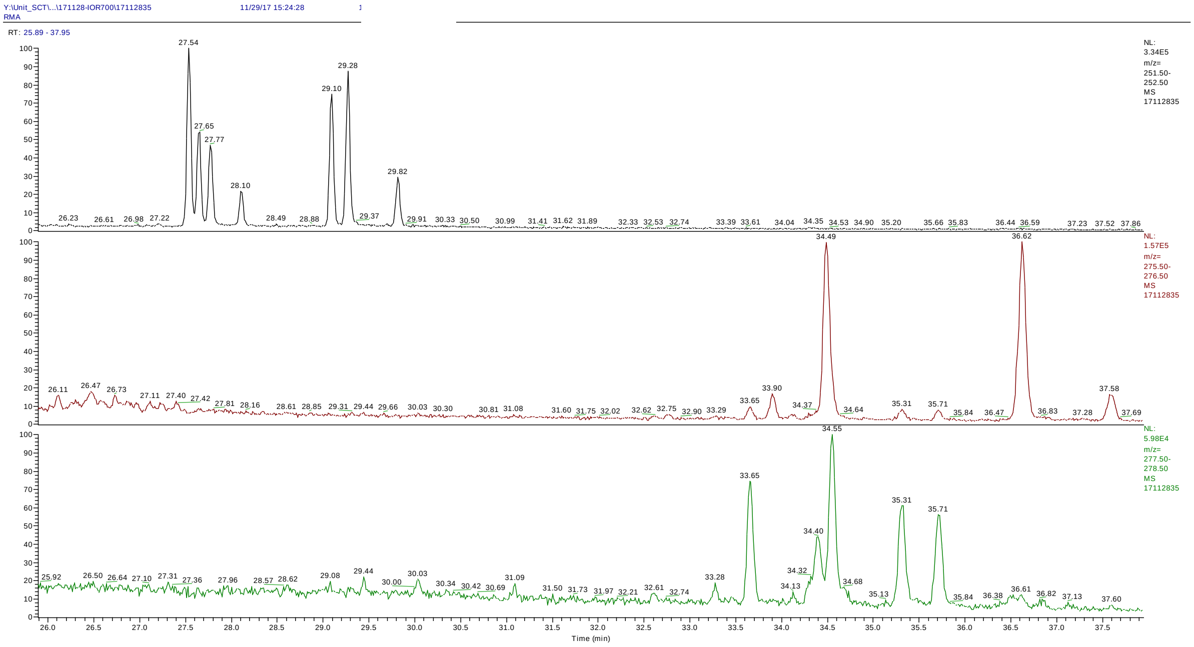
- Naftalene; acenaftylene; acenaftene; fluorene



- Fenanthrene and Anthracene; fluorantheen and pyrene; benzo(a)Anthracene and chryseen



- Benzo(b)fluoranthene, benzo(k)fluoranthene and benzo(a)pyrene; indeno(1,2,3,c,d)pyrene and benzo(g,h,i)perylene; dibenzo(a,h)anthracene



3.4. NEN 7331 - BITUMEN AND BITUMEN CONTAINING MATERIALS – DETERMINATION OF THE CONTENT OF POLYCYCLIC AROMATIC HYDROCARBONS (PAH) – GAS-CHROMATOGRAPHIC METHOD WITH MASS SPECTROMETRIC DETECTION

3.4.1. METHOD DESCRIPTION

A summary of NEN 7331 (PAH part) and modifications done by VITO is given in Table 12. In annex C of method NEN 7331 a high inter-laboratory reproducibility and a large systematic deviation is mentioned. Therefore VITO decided to apply isotope dilution and used 16 deuterated internal standards for recovery correction instead of 3. The method was applied for asphalt aggregate, roofing felt and rubber crumbs. The method was used for the determination of the following PAH:

Naphthalene
Acenaphthylene
Acenaphthene
Fluorene
Phenanthrene
Anthracene
Fluoranthene
Pyrene
Benzo(a)anthracene
Chrysene
Benzo(b)fluoranthene
Benzo(k)fluoranthene
Benzo(a)pyrene
Indeno(1,2,3,c,d)pyrene
Dibenzo(a,h)anthracene
Benzo(g,h,i)perylene

3.4.2. MEASUREMENT CONDITIONS APPLIED BY VITO

Instrument settings:

Hardware	Instrument GC-column	Thermo Quest Trace GC Thermo DSQ MS Agilent VF-17MS 30 m lenght, 0.25 mm ID, 0.25 um FT
Injector parameters	Injection volume Injection modus Injection temperature Pulse pressure Pulse time Purge flow Purge time	0.5 µl Pulsed splitless 300 °C 300 kPa 1.0 min 30 ml/min 1.0 min
GC parameters	Carrier gas Initial temperature Initial time Rate #1 Final temperature #1	Helium - const flow 1 ml/min 75 °C 1.0 min 15 °C/min 210 °C

	Hold time #1	0 min
	Rate #2	5.0 °C/min
	Final temperature #2	310 °C
	Hold time #2	13 min
MS parameters	Mode	Segmented scan
	Source temperature	250 °C
	Interface temperature	310 °C
	Solvent delay	5.5 min
Segments	m/z	Time
	120 – 180	5.5 – 11.5 min
	170 – 220	11.5 – 20 min
	210 - 250	20 – 25 min
	240 – 300	25 min – run end

Internal standards and ions used for quantitation:

Component	m/z	Internal standard	m/z
Naphthalene	128	D8-naphthalene	136
Acenaphthylene	152	D8-acenaphthylene	160
Acenaphthene	153	D10-acenaphthene	163
Fluorene	166	D10-fluorene	176
Phenanthrene	178	D10-phenanthrene	188
Anthracene	178	D10-anthracene	188
Fluoranthene	202	D10-fluoranthene	212
Pyrene	202	D10-pyrene	212
Benzo(a)anthracene	228	D12-benzo(a)anthracene	240
Chrysene	228	D12-chrysene	240
Benzo(b)fluoranthene	252	D12-benzo(b)fluoranthene	264
Benzo(k)fluoranthene	252	D12-benzo(k)fluoranthene	264
Benzo(a)pyrene	252	D12-benzo(a)pyrene	264
Indeno(1,2,3,c,d)pyrene	276	D12-indeno(1,2,3,c,d)pyrene	288
Dibenzo(a,h)anthracene	278	D14-dibenzo(a,h)anthracene	292
Benzo(g,h,i)perylene	276	D12-benzo(g,h,i)perylene	288
		D10-methylnaphthalene*	152
		D12-perylene*	264

*injection standards

3.4.3. CALIBRATION DIAGRAMS

Six calibration solutions of PAH were prepared in a concentration range of 0.02 to 4.2 µg/ml (except benzo(k)fluoranthene: 0.03 to 5.6 µg/ml). Internal standards (deuterated PAH) and injection standards (D10-methylnaphthalene and D12-perylene) were added to the calibration solutions in a fixed concentration of 0.8 µg/ml. The calibration curves are given in Figure 7 and are linear over the injected range, except for naphthalene and benzo(ghi)perylene which are linear from 0.07 µg/ml to 4.23 µg/ml.

In case of 20 g intake these concentrations correspond to a sample concentration of 0.2 to 42 mg/kg (except for benzo(k)fluoranthene: 0.3 to 56 mg/kg, and for naphthalene and benzo(ghi)perylene 0.7 to 42 mg/kg).

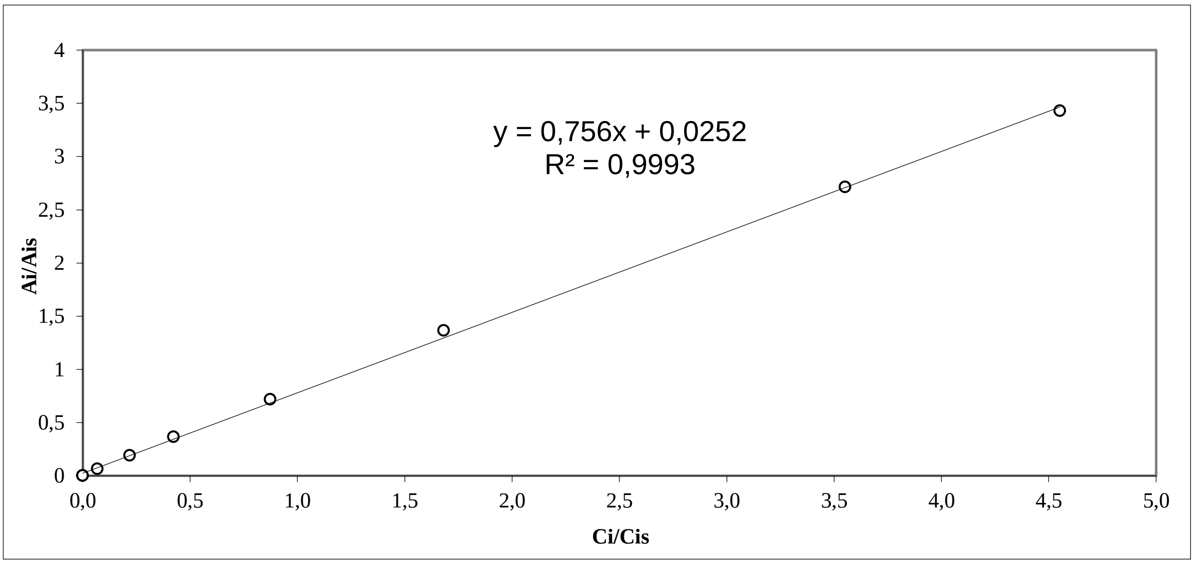
For calibration purposes a calibration solution was injected before and after the measurement of the samples. The calibration solution contains 0.7 – 2.5 mg/l per PAH and 0.8 µg/l per internal standard. The average relative response factor of the PAH in these solutions was used to calculate the PAH concentration in the sample.

Table 12: Summary of NEN 7331 and method applied by VITO

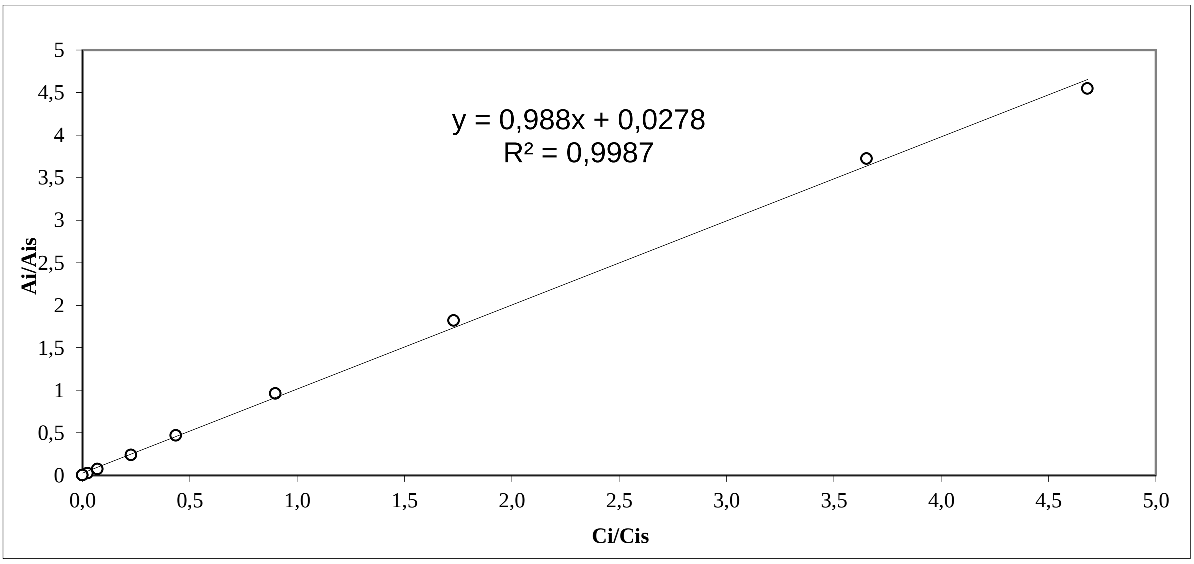
#	Sample Parameter list Method to be used	Short Description of the method to be used	Short description of the VITO Method	Method differences	Comment
14	Asphalt aggregate Asphalt concrete Roofing felt Rubber crumbs PAH NEN 7331 PAH part	- Matrix: bitumen and bitumen containing material - Intake: 10 – 20 g - IS: 3 labelled PAH - Pretreatment: cryogenic grinding - Extraction: soxhlet with petroleum ether - Clean-up: precipitation of the maltenes with ACN or hexane/DMSO partitioning (+optional alumina column) - Measurement: GC-MS - LOQ: 0.1 – 1.5 mg/kg	- Matrix: asphalt aggregate, asphalt concrete, roofing felt, rubber crumbs - Intake: 10 g - IS: 16 labelled PAH - Pretreatment: cryogenic grinding - Extraction: soxhlet with petroleumether - Clean-up: precipitation of the maltenes with ACN - Measurement: GC-MS	- VITO applies isotope dilution and uses 16 deuterated internal standards for recovery correction instead of 3	

Figure 7: Calibration diagrams of the PAH (method NEN 7331)

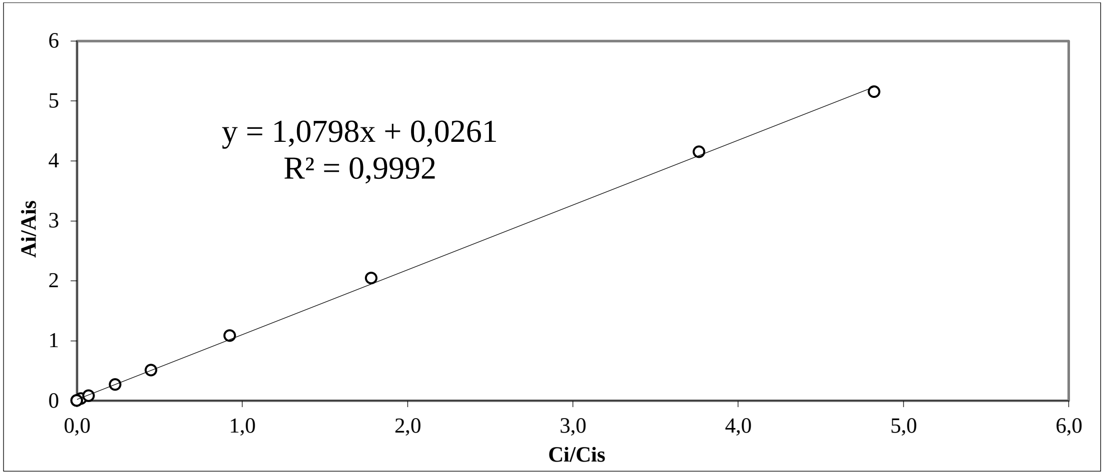
- Naftalene



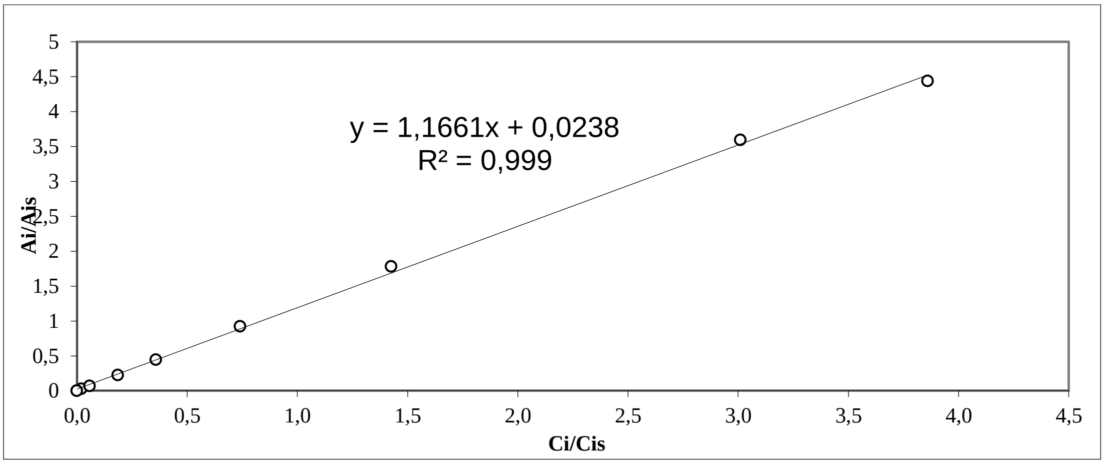
- Acenaphthylene



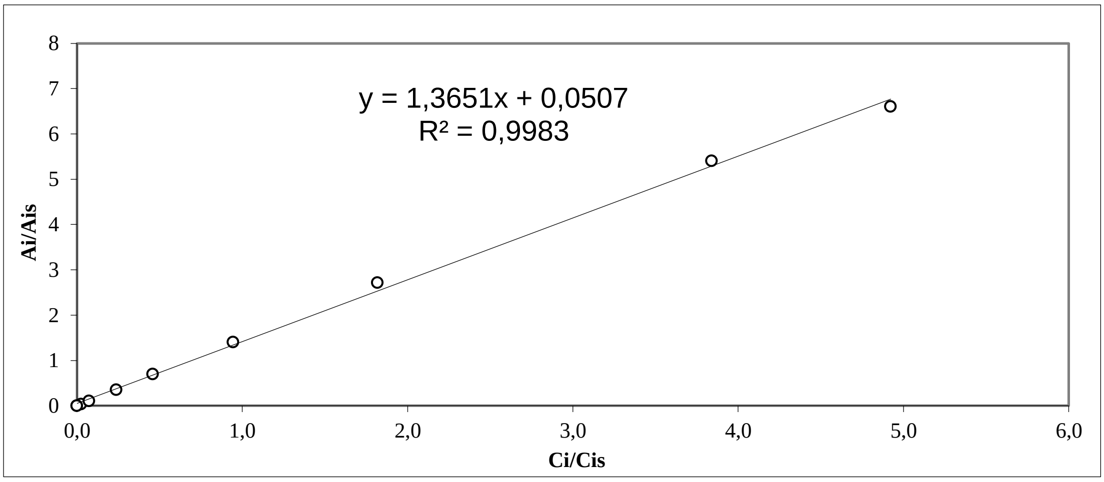
- Acenaphthene



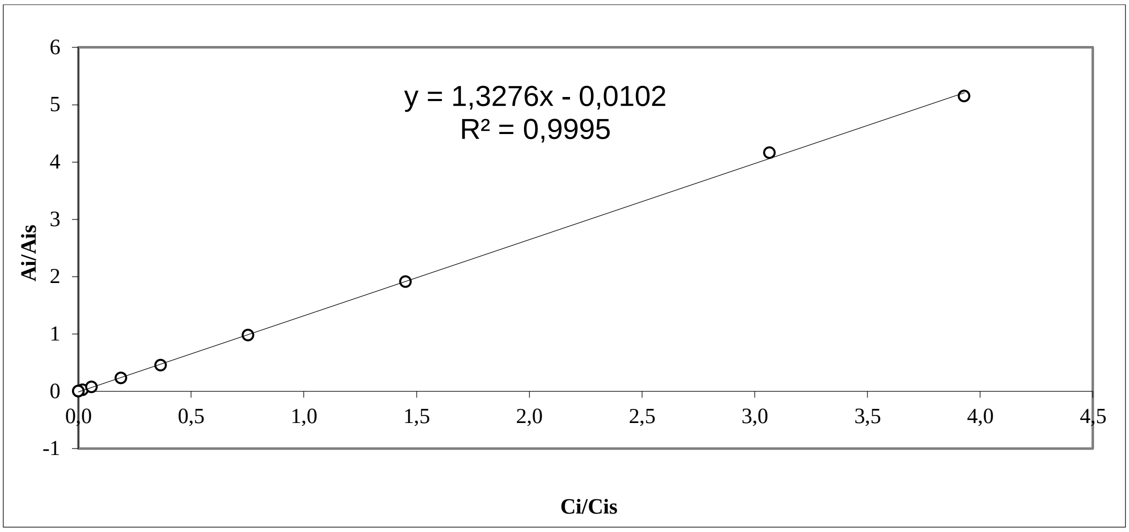
- Fluorene



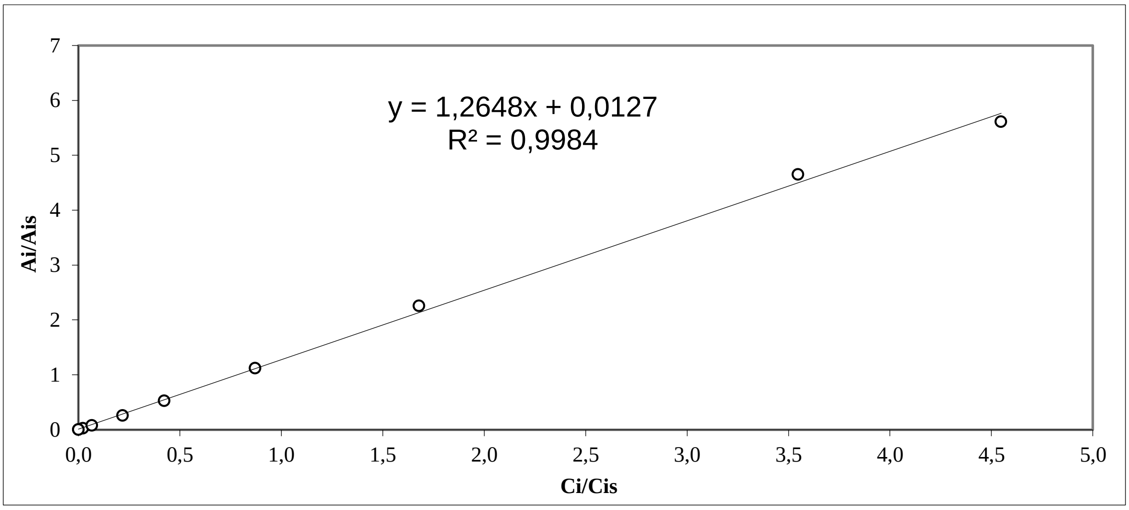
- Phenanthrene



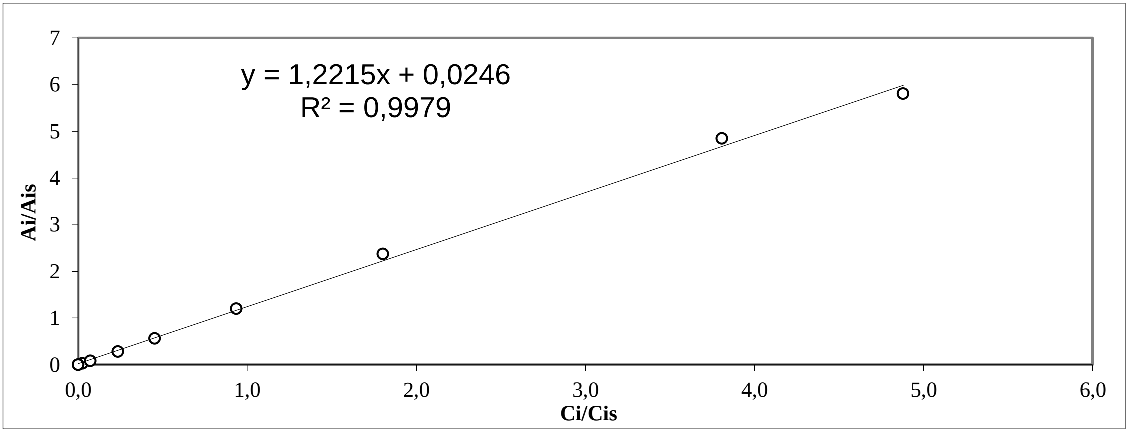
- Anthracene



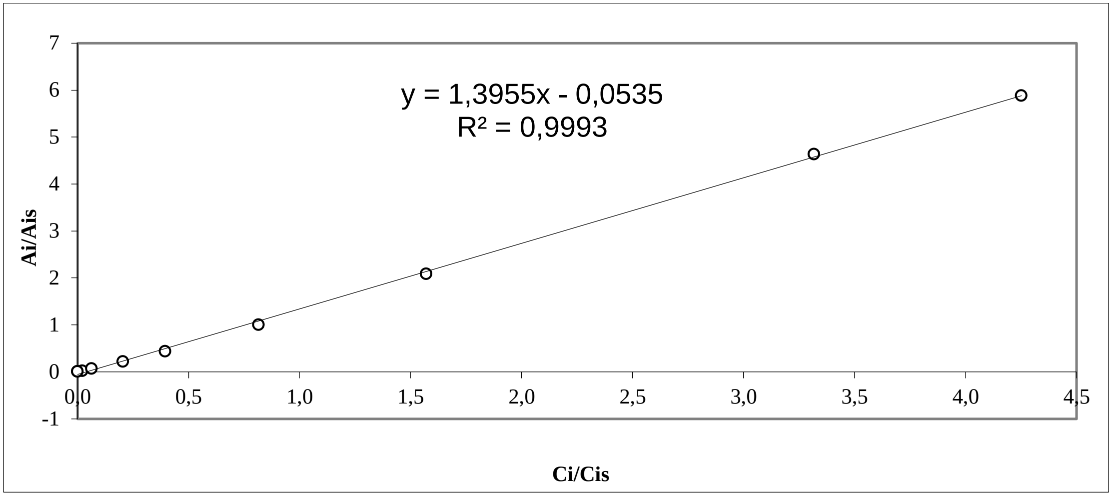
- Fluoranthene



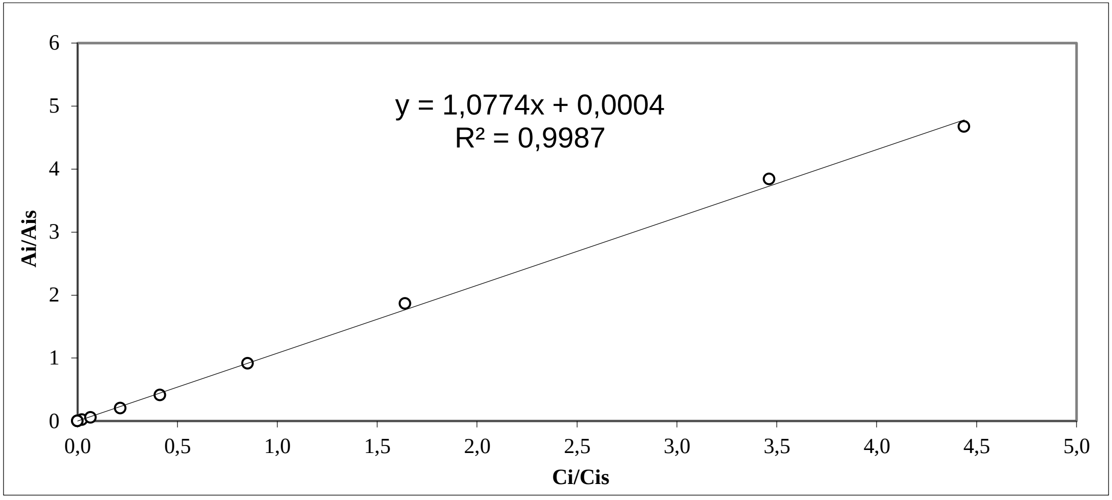
- Pyrene



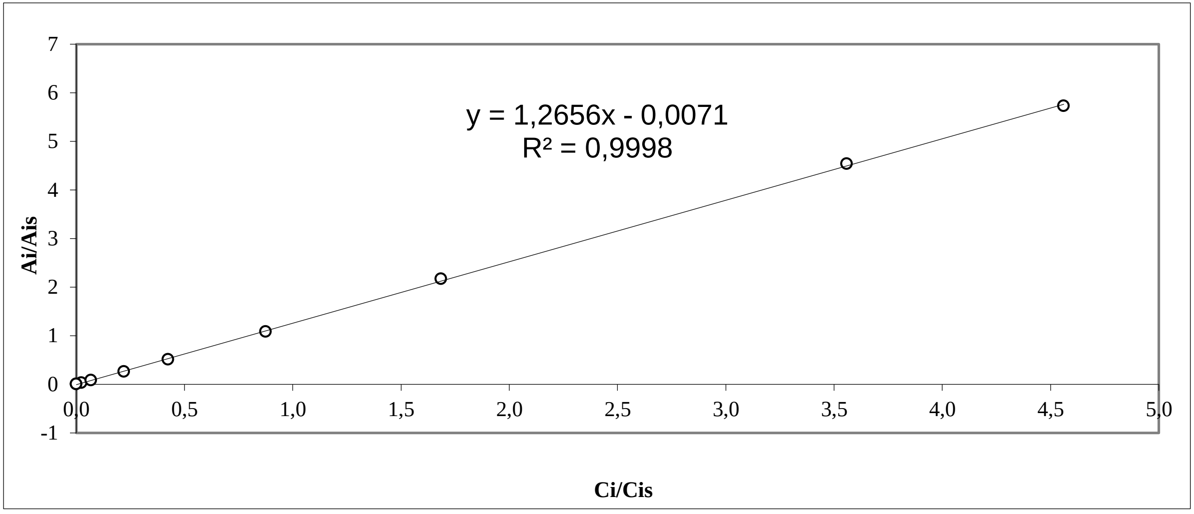
- Benzo(a)anthracene



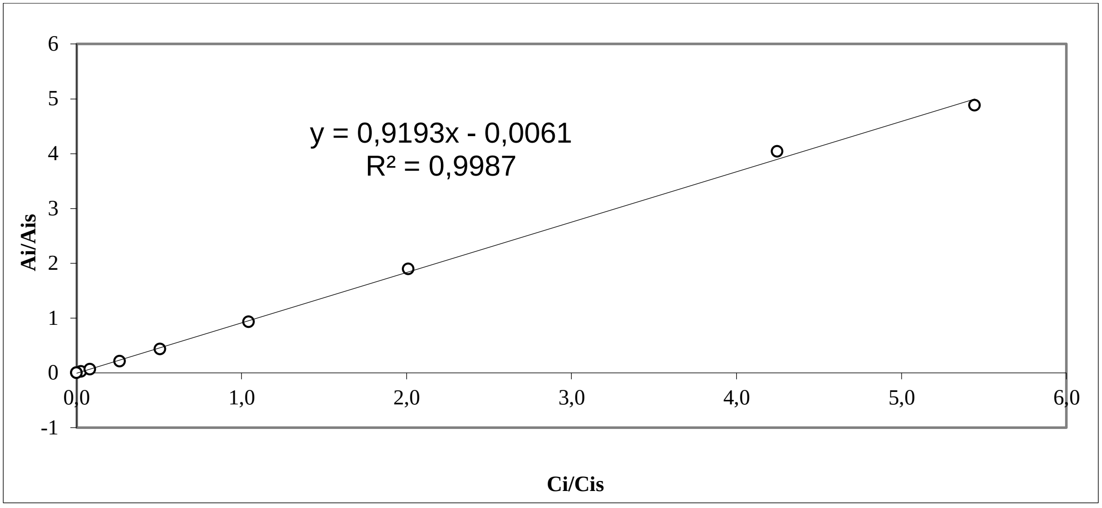
- Chrysene



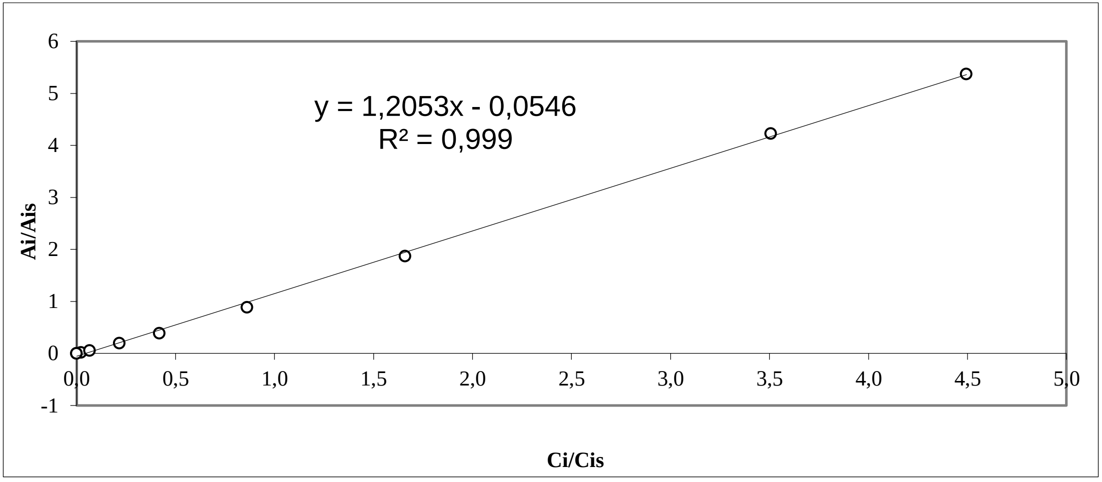
- Benzo(b)fluoranthene



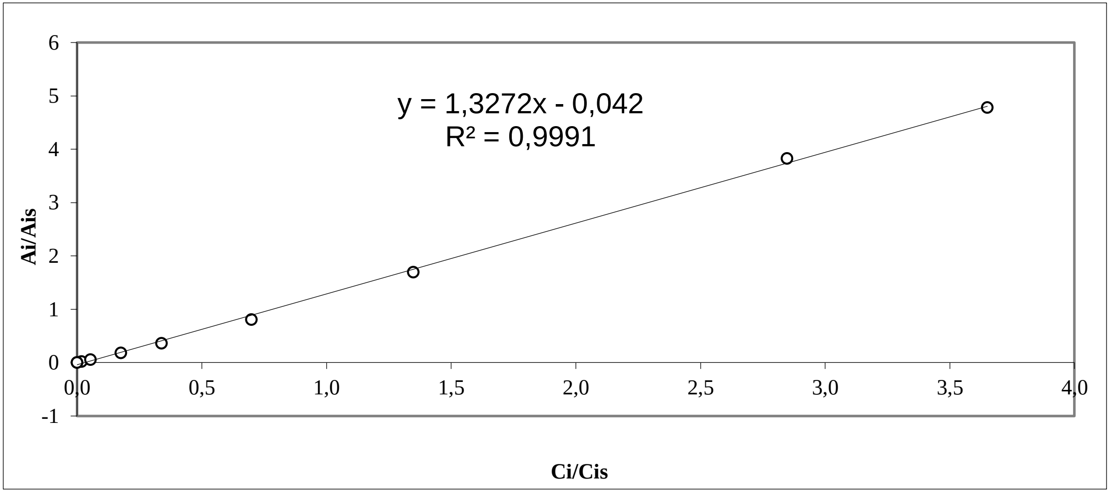
- Benzo(k)fluoranthene



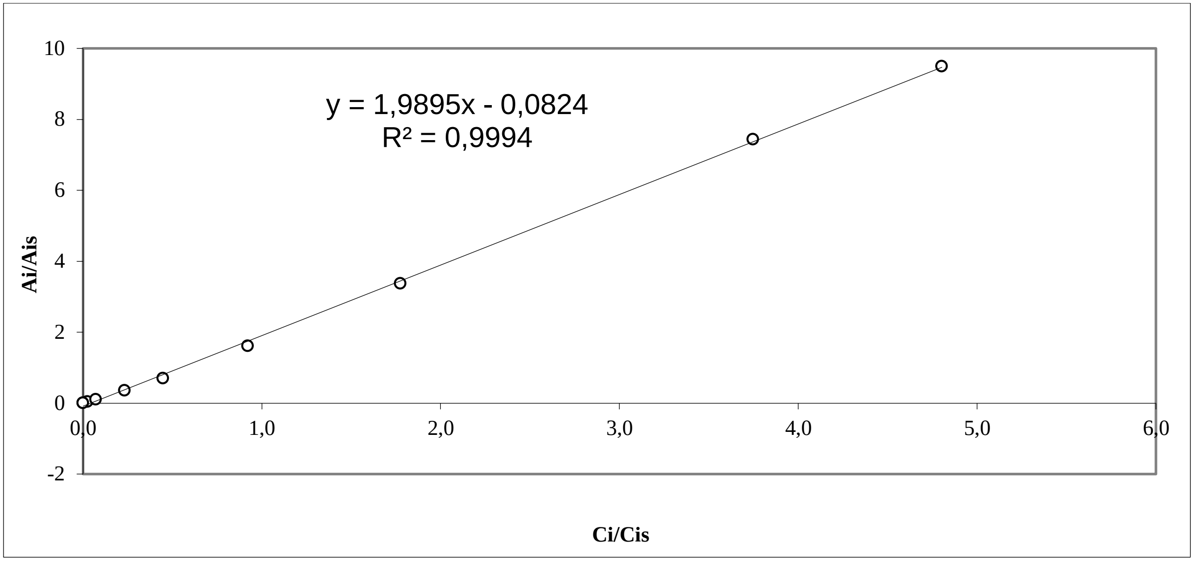
- Benzo(a)pyrene



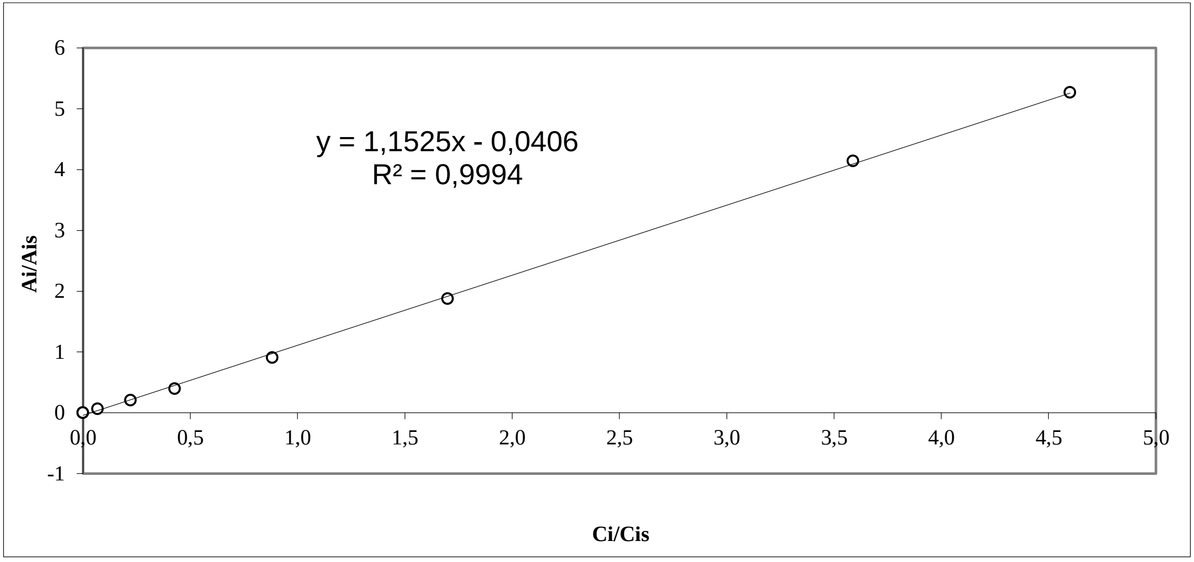
- Indeno(123cd)pyrene



- Dibenzo(ah)anthracene



- Benzo(ghi)perylene



3.5. DETERMINATION OF PAH IN ASPHALT AGGREGATE WITH METHOD NEN 7331

3.5.1. SAMPLE

Asphalt aggregate was received from REKO. A first particle size reduction was done by SGS Intron. The sample was subsequently ground by VITO to particles <1 mm.

3.5.2. ANALYSIS

- 10-20 g of grinded sample was soxhlet extracted with 200 ml petroleum ether during 16h
- 2 ml of the extract was transferred to a vial and internal standards (deuterated PAH) were added
- 3 ml acetonitrile was added to the extract and the petroleum ether phase was evaporated under a gentle stream of nitrogen
- The remaining acetonitrile phase was transferred to a second vial (the first vial was rinced twice with acetonitrile)
- 2 ml toluene was added and the extract was concentrated to ca. 1.5 ml under a gentle stream of nitrogen
- The injection standards were added to the final extract
- Due to the high PAH concentrations in the sample, the extract was diluted 20 times before it was analysed with GC/MS

3.5.3. RESULTS

→ Repeatability

The sample was analysed in five fold. The results are given in Table 13. The repeatability (expressed as relative standard deviation) is for most PAH lower than 5% and for all PAH lower than 10%.

→ Check on method performance

The recoveries of the internal standards in each sample were calculated using the calibration standard as a reference (100%). The results are given in Table 14. The recoveries for D8-naphthalene are higher than the minimum required by the method (50%). For D10-anthracene the method requires a minimum recovery of 70%. In replicate 1 and replicate 5 the recovery is lower (resp. 55% and 66%). The lower recoveries are no problem in case isotope dilution is used.

→ Sensitivity

The sensitivity of the method was calculated with S/N using the response of acenaphthylene in the sample. The LOD for acenaphthylene was 0.37 mg/kg. This is lower than the detection limit of method NEN 7331 for roofing materials (0.5 – 1.5 mg/kg) but higher than the detection limit of the method in clay pigeons (0.1 mg/kg – 1.4 mg/kg). However the final extract was diluted 20 times because of the high PAH content of the sample. In case of less PAH contaminated samples the dilution is not necessary and the LOD will meet easily the requirements of the method.

3.5.4. COMMENTS

The repeatability and the LOD of method NEN 7331 using soxhlet extraction and clean-up with acetonitrile is acceptable for the analysis of PAH in asphalt aggregate. It is advised to use more than three internal standards (preferably all 16) and the minimum recovery of the internal standards should be lowered to 50%.

3.5.5. CHROMATOGRAMS

The GC-MS ion chromatograms of PAH in asphalt aggregate are shown in Figure 8.

3.5.6. CONCLUSION

Method NEN 7331 is suited for the analysis of PAH in asphalt aggregate. It is advised to apply more than three internal standards (preferably all 16 deuterated PAH).

Table 13: Measured concentrations of PAH in asphalt aggregate using method NEN 7331

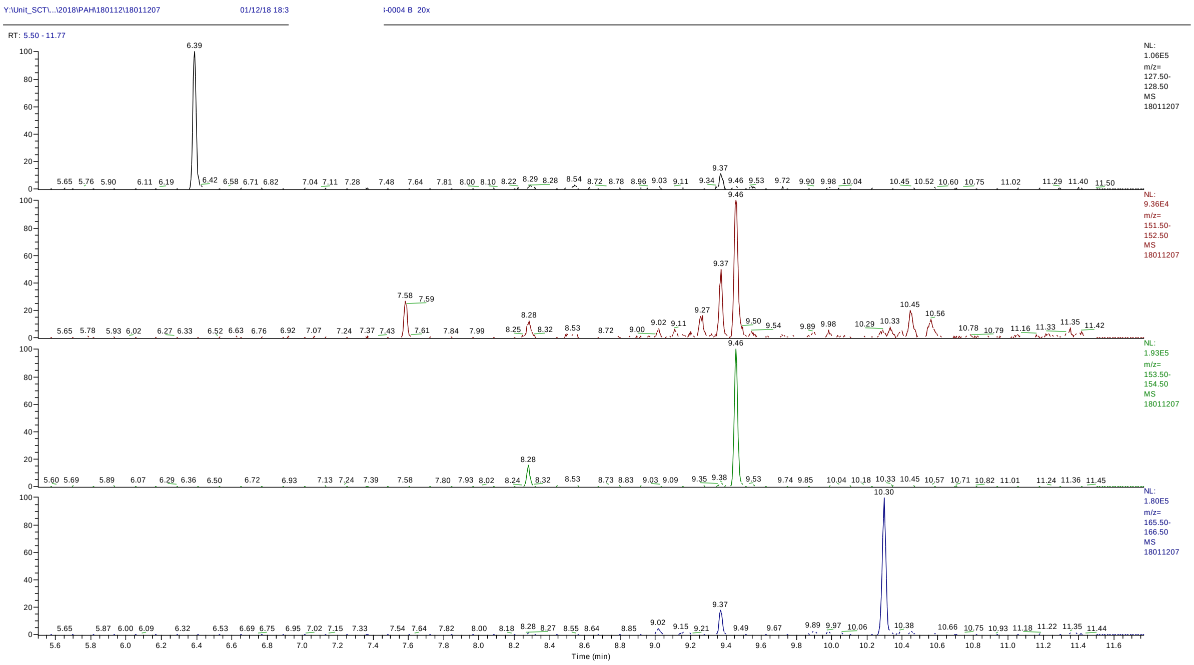
Replicate n°	**1** mg/kg	**2** mg/kg	**3** mg/kg	**4** mg/kg	**5** mg/kg	**Average** mg/kg	**St.Dev.** mg/kg	**CV$_r$** %
Naphthalene	4,68	4,53	4,41	4,83	4,15	4,52	0,26	5,8
Acenaphthylene	0,736	0,609	0,625	0,701	0,646	0,66	0,05	8,1
Acenaphthene	7,66	7,85	8,35	8,36	7,74	7,99	0,34	4,2
Fluorene	7,9	8,19	7,94	8,42	7,94	8,08	0,22	2,8
Phenanthrene	84,7	87,9	85,7	85,1	79,4	84,6	3,14	3,7
Anthracene	17,20	17,20	17,90	18,5	16,6	17,48	0,73	4,2
Fluoranthene	206	207	201	204	193	202,2	5,63	2,8
Pyrene	128	127	133	133	123	128,0	4,27	3,3
Benzo(a)anthracene	93,1	96,8	94,7	97,7	92,9	95,04	2,16	2,3
Chrysene	106	103	108	107	102	105,2	2,59	2,5
Benzo(b)fluoranthene	79,2	79,9	78,1	80,7	73,8	78,3	2,71	3,5
Benzo(k)fluoranthene	41,4	44	45,9	46,5	45,6	44,7	2,05	4,6
Benzo(a)pyrene	81,9	84,4	89,2	83,5	82,1	84,2	2,97	3,5
Indeno(1,2,3,c,d)pyrene	42,0	47,1	45,3	44,2	42,9	44,3	2,01	4,5
Dibenzo(a,h)anthracene	11,3	11	10,3	11,5	10,9	11,00	0,46	4,2
Benzo(g,h,i)perylene	40,6	40	39,5	40,8	40,3	40,2	0,51	1,3

Table 14: Recoveries of the internal standards in asphalt aggregate using method NEN 7331

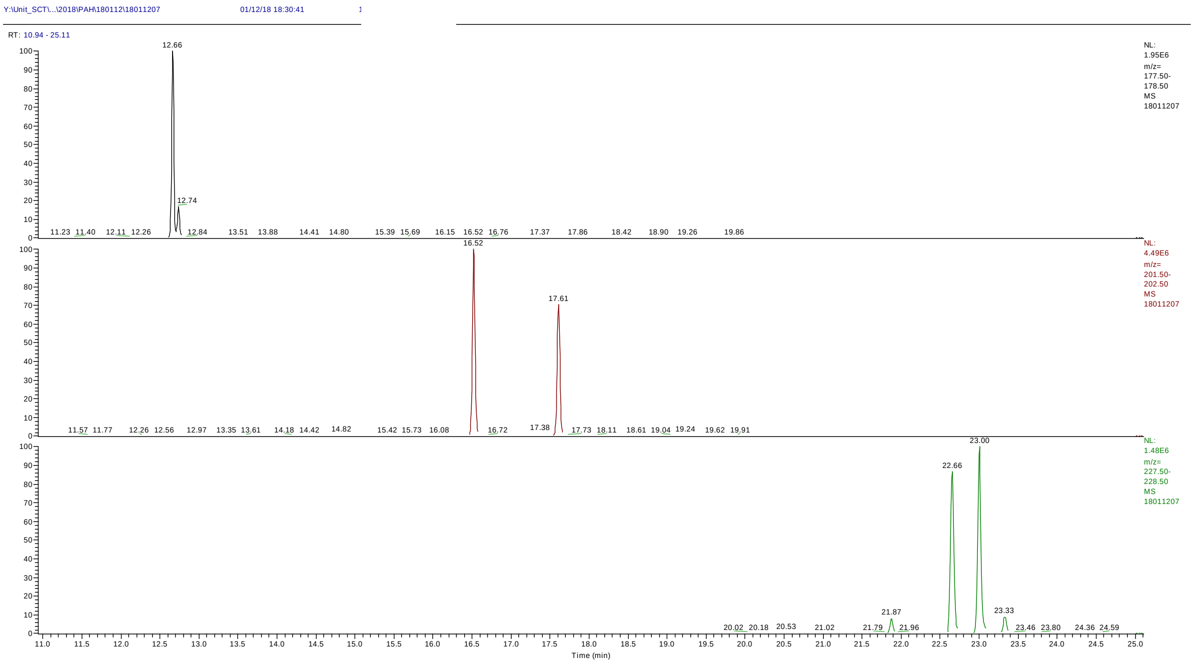
Replicate n°	**1** %	**2** %	**3** %	**4** %	**5** %
D8-naphthalene	89	89	86	84	83
D8-acenaphthylene	66	72	74	73	74
D10-acenaphthene	76	77	74	72	71
D10-fluorene	63	76	75	74	71
D10-phenanthrene	57	80	75	74	70
D10-anthracene	55	75	73	72	66
D10-fluoranthene	60	84	79	77	71
D10-pyrene	61	94	90	85	79
D12-benzo(a)anthracene	64	102	97	90	81
D12-chrysene	55	85	85	78	69
D12-benzo(b)fluoranthene	106	96	97	88	97
D12-benzo(k)fluoranthene	84	94	93	84	88
D12-benzo(a)pyrene	90	100	98	93	97
D12-indeno(1,2,3,c,d)pyrene	84	87	83	83	87
D14-dibenzo(a,h)anthracene	83	82	79	77	82
D12-benzo(g,h,i)perylene	90	86	89	84	90
Average recovery	74	86	84	81	80

Figure 8: GC/MS ion chromatograms of PAH in asphalt aggregate (method NEN 7331)

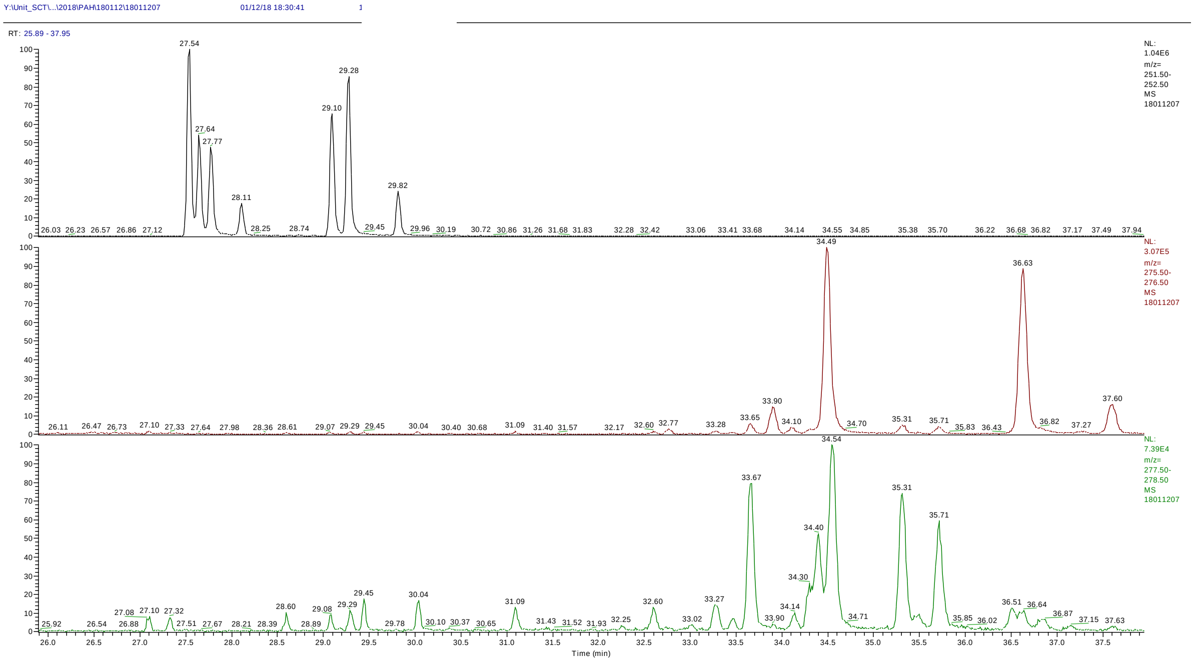
- Naftalene; acenaftylene; acenaftene; fluorene



- Fenanthrene and anthracene; fluoranthene and pyrene; benzo(a)anthracene and chrysene



- Benzo(b)fluoranthene, benzo(k)fluoranthene and benzo(a)pyrene; indeno(1,2,3,c,d)pyrene and benzo(g,h,i)perylene; dibenzo(a,h)anthracene



3.6. DETERMINATION OF PAH IN ROOFING (BITUMEN SHINGLES) WITH METHOD NEN 7331

3.6.1. SAMPLE

A roofing sample was received from Dakenshop.

3.6.2. ANALYSIS

- The sample was cut into small pieces using a pair of scissors
- 10 g of the sample was then soxhlet extracted with 200 ml petroleum ether during 16h
- 2 ml of the extract was transferred to a vial and internal standards (deuterated PAH) were added
- 3 ml acetonitrile was added to the extract and the petroleum ether phase was evaporated under a gentle stream of nitrogen
- The remaining acetonitrile phase was transferred to a second vial (the first vial was rinced twice with acetonitrile)
- 2 ml toluene was added and the extract was concentrated to ca. 1.5 ml under a gentle stream of nitrogen
- The injection standards were added to the final extract

3.6.3. RESULTS

→ Repeatability

The sample was analysed in five fold. The results are given in Table 15. The repeatability (expressed as relative standard deviation) is for most PAH lower than 10%. For benzo(k)fluoranthene and indeno(1,2,3,c,d)pyrene the repeatability is slightly higher (resp. 10.8% and 12.2%).

→ Check on method performance

The recoveries of the internal standards in each sample were calculated using the calibration standard as a reference (100%). The results are given in Table 16. For each internal standard the recovery is higher than 70%. For D12-benzo(a)anthracene the upper limit of 120% is slightly exceeded. This is no problem because isotope dilution was applied.

→ Sensitivity

The sensitivity of the method was calculated with S/N using the response of dibenzo(a,h)anthracene in the sample. The LOD for dibenzo(a,h)anthracene was 0.20 mg/kg. This is lower than the detection limit of method NEN 7331 for roofing materials (0.5 – 1.5 mg/kg).

3.6.4. COMMENTS

The repeatability and the LOD of method NEN 7331 using soxhlet extraction and clean-up with acetonitrile is acceptable for the analysis of PAH in roofing shingles. It is advised to use more than three internal standards (preferably all 16) and to raise the upper limit for the recovery of the internal standards to e.g. 130%.

3.6.5. CHROMATOGRAMS

The GC/MS ion chromatograms of PAH in roofing shingles are shown in Figure 9.

3.6.6. CONCLUSION

Method NEN 7331 is suited for the analysis of PAH in roofing. It is advised to apply more than three internal standards (preferably all 16 deuterated PAH) and to change the upper limit of the recovery requirement of the internal standards to 130%.

Table 15: Measured concentrations of PAH in roofing using method NEN 7331

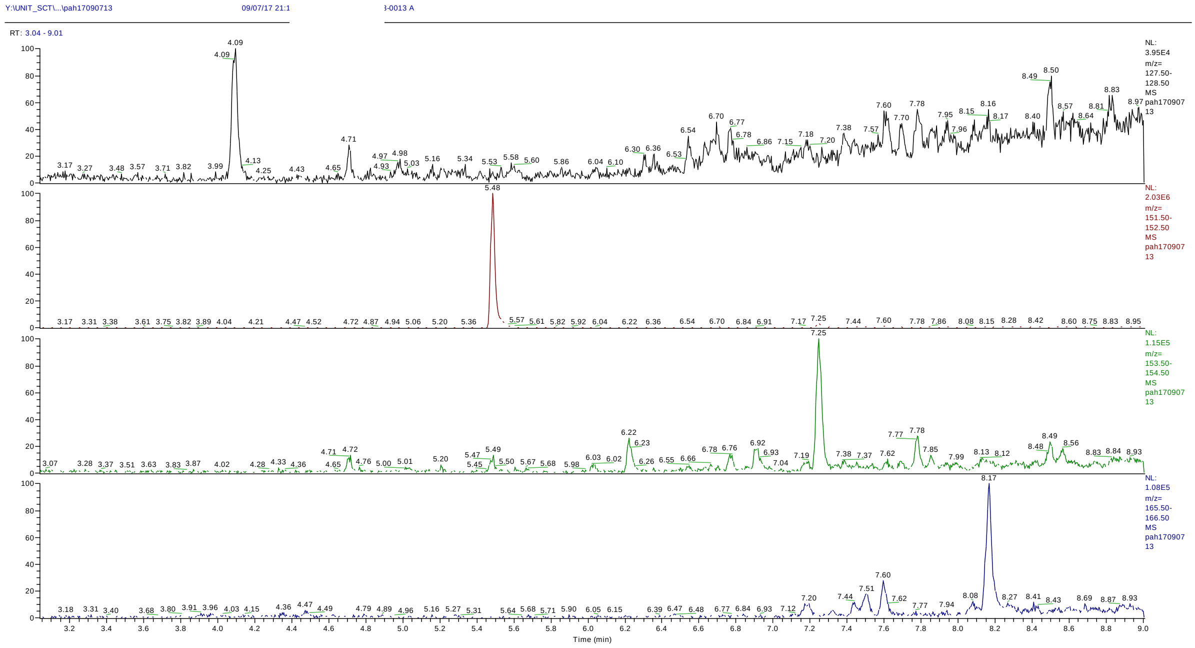
Replicate n°	**1** mg/kg	**2** mg/kg	**3** mg/kg	**4** mg/kg	**5** mg/kg	**Average** mg/kg	**St.Dev.** mg/kg	**CV_r** %
Naphthalene	0,352	0,396	0,403	0,424	0,422	0,40	0,03	7,3
Acenaphthylene	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	-	-	-
Acenaphthene	1,21	1,17	1,14	1,2	1,18	1,18	0,03	2,3
Fluorene	1,03	1,07	1,07	1,030	1,03	1,05	0,02	2,1
Phenanthrene	7,67	7,6	7,71	7,650	7,63	7,65	0,04	0,5
Anthracene	0,761	0,779	0,784	0,848	0,758	0,79	0,04	4,6
Fluoranthene	2,66	2,72	2,81	2,68	2,82	2,74	0,07	2,7
Pyrene	2,48	2,5	2,65	2,47	2,68	2,56	0,10	3,9
Benzo(a)anthracene	1,13	1,19	1,23	1,17	1,29	1,20	0,06	5,1
Chrysene	1,18	1,27	1,46	1,33	1,43	1,33	0,12	8,6
Benzo(b)fluoranthene	1,28	1,33	1,4	1,16	1,5	1,33	0,13	9,6
Benzo(k)fluoranthene	0,438	0,468	0,496	0,430	0,557	0,48	0,05	10,8
Benzo(a)pyrene	1,220	1,140	1,210	1,150	1,210	1,19	0,04	3,2
Indeno(1,2,3,c,d)pyrene	0,643	0,634	0,777	0,686	0,833	0,71	0,09	12,2
Dibenzo(a,h)anthracene	0,416	0,443	0,497	0,489	0,533	0,48	0,05	9,7
Benzo(g,h,i)perylene	3,28	3,30	3,40	3,37	3,42	3,35	0,06	1,8

Table 16: Recoveries of the internal standards in roofing using method NEN 7331

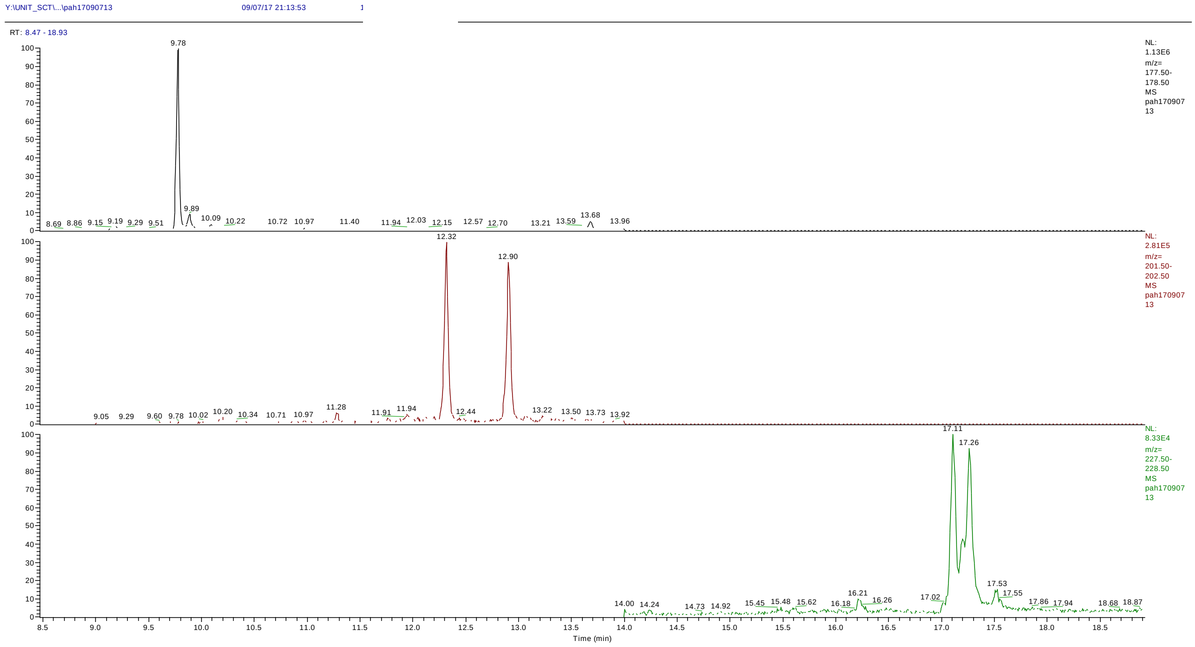
Replicate n°	**1** %	**2** %	**3** %	**4** %	**5** %
D8-naphthalene	93	86	89	87	85
D8-acenaphthylene	84	90	95	96	94
D10-acenaphthene	82	88	94	95	92
D10-fluorene	83	89	95	95	95
D10-phenanthrene	85	93	99	98	102
D10-anthracene	84	91	100	98	101
D10-fluoranthene	89	95	102	98	104
D10-pyrene	92	97	103	102	108
D12-benzo(a)anthracene	91	103	113	110	123
D12-chrysene	91	102	108	107	116
D12-benzo(b)fluoranthene	90	91	87	91	90
D12-benzo(k)fluoranthene	81	86	81	82	84
D12-benzo(a)pyrene	89	95	90	91	92
D12-indeno(1,2,3,c,d)pyrene	80	84	78	77	79
D14-dibenzo(a,h)anthracene	77	83	81	78	81
D12-benzo(g,h,i)perylene	78	78	74	74	73
Average recovery	86	91	93	92	95

Figure 9: GC/MS ion chromatograms of PAH in roofing shingles (method NEN 7331)

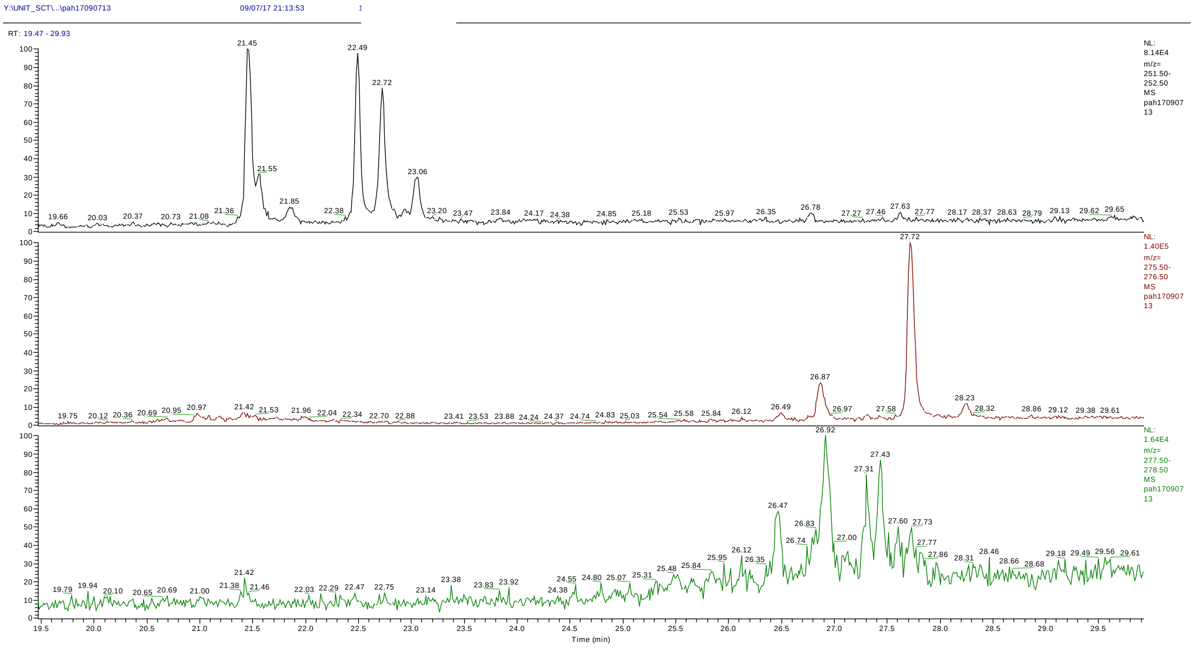
- Naftalene; acenaftylene; acenaftene; fluorene



- Fenanthrene and anthracene; fluoranthene and pyrene; benzo(a)anthracene and chrysene



- Benzo(b)fluoranthene, benzo(k)fluoranthene and benzo(a)pyrene; indeno(1,2,3,c,d)pyrene and benzo(g,h,i)perylene; dibenzo(a,h)anthracene



3.7. DETERMINATION OF PAH IN RUBBER CRUMBS WITH METHOD NEN 7331

3.7.1. SAMPLE

A sample of rubber crumbs was received from SGS Intron. A particle size reduction was done by SGS Intron.

3.7.2. ANALYSIS

- 20 g of the sample was then soxhlet extracted with 200 ml petroleum ether during 16h
- 2 ml of the extract was transferred to a vial and internal standards (deuterated PAH) were added
- 3 ml acetonitrile was added to the extract and the petroleum ether phase was evaporated under a gentle stream of nitrogen
- The remaining acetonitrile phase was transferred to a second vial (the first vial was rinced twice with acetonitrile)
- 2 ml toluene was added and the extract was concentrated to ca. 1.5 ml under a gentle stream of nitrogen
- The injection standards were added to the final extract

3.7.3. RESULTS

→ Repeatability

The sample was analysed in five fold. The results are given in Table 17. The repeatability (expressed as relative standard deviation) is for most PAH lower than 5%. For the heavier PAH (benzo(k)fluoranthene to benzo(g,h,i)perylene) the %RSD is higher and ranges from 9.0% to 13.1%.

→ Check on method performance

The recoveries of the internal standards in each sample were calculated using the calibration standard as a reference (100%). The results are given in Table 18. For the more volatile PAH (upto D12-chrysene) the recoveries are lower than 70% (but higher than 50%). For the heavier PAH (from D12-benzo(b)fluoranthene) the recoveries are generally higher than 70%. Because isotope dilution is applied, the recoveries are acceptable.

→ Sensitivity

The sensitivity of the method was calculated with S/N using the response of naphthalene in the sample. The LOD for naphthalene was 0.03 mg/kg. This is lower than the detection limit of method NEN 7331 for roofing materials (0.5 – 1.5 mg/kg) and for clay pigeons (0.1 to 1.4 mg/kg)

3.7.4. COMMENTS

The repeatability and the LOD of method NEN 7331 using soxhlet extraction and clean-up with acetonitrile is acceptable for the analysis of PAH in rubber crumbs. It is advised to use more than three internal standards (preferably all 16) and to lower the lower limit for the recovery of the internal standards to e.g. 50%.

3.7.5. CHROMATOGRAMS

The GC/MS ion chromatograms of PAH in rubber crumbs are shown in Figure 10.

3.7.6. CONCLUSION

Method NEN 7331 is suited for the analysis of PAH in rubber crumbs. It is advised to apply more than three internal standards (preferably all 16 deuterated PAH) and to change the lower limit of the recovery requirement of the internal standards to 50%.

Table 17: Measured concentrations of PAH in rubber crumbs using method NEN 7331

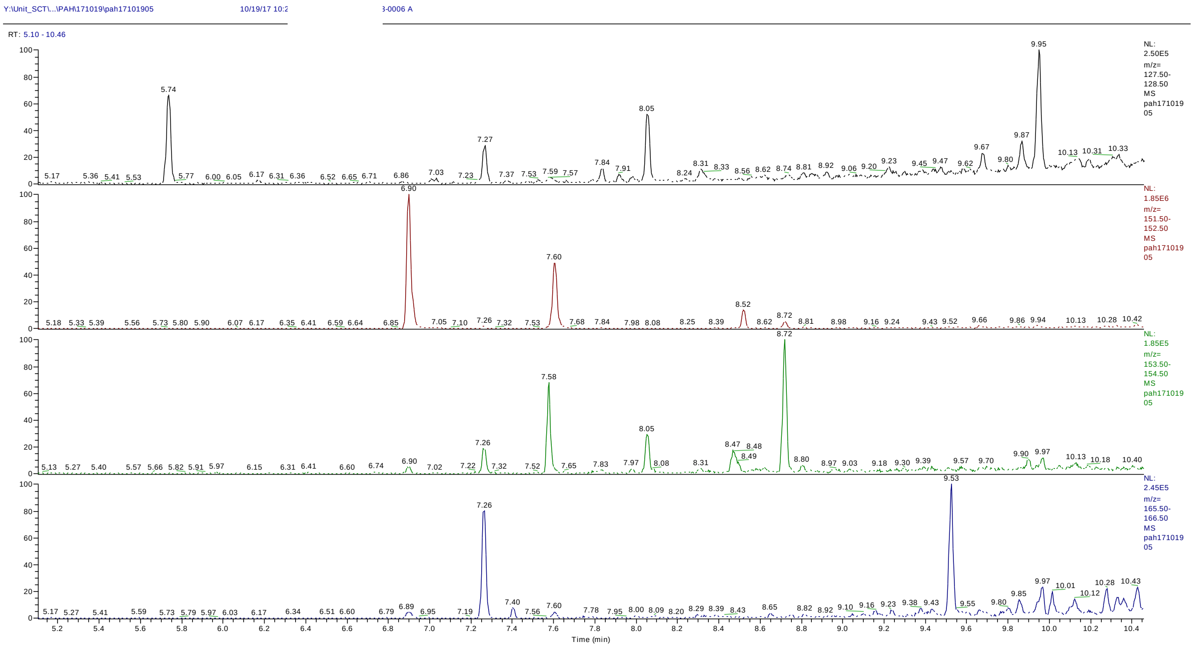
Replicate n°	**1** mg/kg	**2** mg/kg	**3** mg/kg	**4** mg/kg	**5** mg/kg	**Average** mg/kg	**St.Dev.** mg/kg	**C.V.** %
Naphthalene	0,49	0,48	0,51	0,49	0,48	0,49	0,01	2,7
Acenaphthylene	0,85	0,84	0,85	0,82	0,84	0,84	0,01	1,4
Acenaphthene	1,11	1,12	1,1	1,14	1,11	1,12	0,02	1,4
Fluorene	1,27	1,24	1,21	1,24	1,25	1,24	0,02	1,7
Phenanthrene	7,68	7,72	7,67	7,7	7,5	7,66	0,09	1,2
Anthracene	1,340	1,310	1,340	1,35	1,19	1,31	0,07	5,1
Fluoranthene	9,63	9,74	9,67	9,72	9,68	9,69	0,04	0,4
Pyrene	28,2	28,2	28,5	28,6	28,2	28,34	0,19	0,7
Benzo(a)anthracene	1,08	1,08	1,13	1,15	1,07	1,10	0,04	3,2
Chrysene	3,14	3,21	3,26	3,19	3,16	3,19	0,05	1,5
Benzo(b)fluoranthene	1,22	1,21	1,25	1,20	1,14	1,20	0,04	3,4
Benzo(k)fluoranthene	0,40	0,40	0,41	0,42	0,32	0,39	0,04	10,6
Benzo(a)pyrene	1,50	1,47	1,73	1,61	1,37	1,54	0,14	9,0
Indeno(1,2,3,c,d)pyrene	0,74	0,63	0,85	0,83	0,67	0,74	0,10	13,0
Dibenzo(a,h)anthracene	< 0.06	< 0.06	< 0.06	< 0.06	< 0.06	-	-	-
Benzo(g,h,i)perylene	5,89	5,43	7,39	7,00	5,91	6,32	0,83	13,1

Table 18: Recoveries of the internal standards in rubber crumbs using method NEN 7331

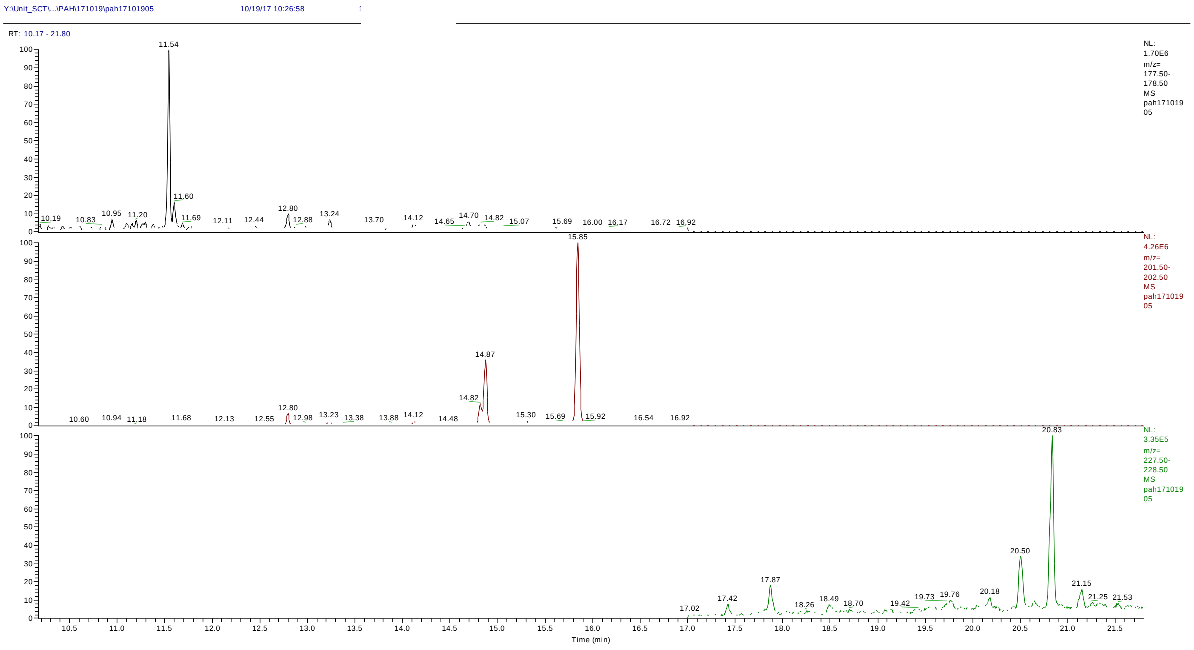
Replicate n°	**1** %	**2** %	**3** %	**4** %	**5** %
D8-naphthalene	58	61	62	64	61
D8-acenaphthylene	55	59	60	62	58
D10-acenaphthene	51	55	55	55	52
D10-fluorene	53	58	58	58	55
D10-phenanthrene	54	58	58	58	55
D10-anthracene	58	63	62	65	58
D10-fluoranthene	55	60	60	61	56
D10-pyrene	55	59	59	59	54
D12-benzo(a)anthracene	53	62	60	63	57
D12-chrysene	54	60	60	62	56
D12-benzo(b)fluoranthene	86	94	95	98	90
D12-benzo(k)fluoranthene	85	92	95	98	91
D12-benzo(a)pyrene	87	91	94	92	94
D12-indeno(1,2,3,c,d)pyrene	87	76	78	64	93
D14-dibenzo(a,h)anthracene	87	78	81	64	98
D12-benzo(g,h,i)perylene	87	71	73	59	96
Average recovery	66	68	69	68	70

Figure 10: GC/MS ion chromatograms of PAH in rubber crumbs (method NEN 7331)

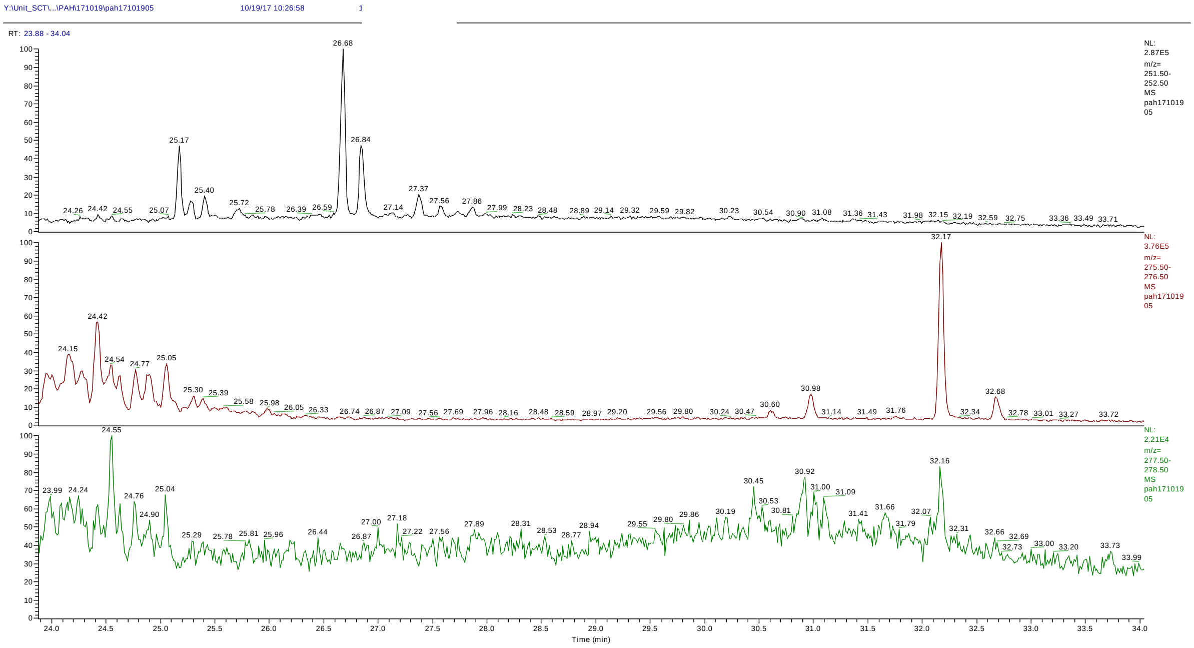
- Naftalene; acenaftylene; acenaftene; fluorene



- Fenanthrene and anthracene; fluoranthene and pyrene; benzo(a)anthracene and chrysene



- Benzo(b)fluoranthene, benzo(k)fluoranthene and benzo(a)pyrene; indeno(1,2,3,c,d)pyrene and benzo(g,h,i)perylene; dibenzo(a,h)anthracene



3.8. COMPARISON OF METHODS CEN/TS 16181 AND NEN 7331

PAH in asphalt aggregate were analysed with two methods: CEN/TS 16181 and NEN 7331. The average concentration and the relative standard deviation of each PAH with both methods are listed in Table 19. For most PAH the average concentrations are slightly lower using method NEN 7331, but the repeatabilities (%RSD) of this method are much better than when using CEN/TS 16181. The higher repeatability values of method CEN/TS 16181 were also observed for PAH in recycled mixed aggregates. Therefore it is advised to retain only method NEN 7331 for the analysis of PAH in construction materials.

Table 19: PAH in asphalt aggregate - comparison of results obtained with 2 different methods

	CEN/TS 16181		**NEN 7331**	
	Average conc. mg/kg	**CV_r** %	**Average conc.** mg/kg	**CV_r** %
Naftalene	4,7	22,1	4,5	5,8
Acenaftylene	0,5	10,0	0,7	8,1
Acenaftene	6,2	12,7	8,0	4,2
Fluorene	7,9	12,8	8,1	2,8
Fenanthrene	95,3	13,6	84,6	3,7
Anthracene	17,2	15,3	17,5	4,2
Fluoranthene	252	11	202	2,8
Pyrene	151	10	128	3,3
Benzo(a)anthracene	114	14	95,0	2,3
Chrysene	123	11	105	2,5
Benzo(b)fluoranthene	88,5	10,2	78,3	3,5
Benzo(k)fluoranthene	44,1	6,9	44,7	4,6
Benzo(a)pyrene	76,5	8,2	84,2	3,5
Indeno(1,2,3,c,d)pyrene	41,1	8,7	44,3	4,5
Dibenzo(a,h)anthracene	9,3	9,8	11,0	4,2
Benzo(g,h,i)perylene	41,8	11,4	40,2	1,3

CHAPTER 4 DETERMINATION OF THE CONTENT OF BTEX IN CONSTRUCTION PRODUCTS

4.1. NEN 7331 - Bitumen and bitumen containing materials – Determination of the content of benzene, toluene, ethylbenzene and xylene (BTEX) – gas-chromatographic method with mass spectrometric detection

4.1.1. Method description

A summary of NEN 7331 (BTEX part) and modifications done by VITO is given in Table 20. The method was applied for asphalt aggregate. The method was used for the determination of the following BTEX:

Benzene
Toluene
Ethylbenzene
m/p-Xylene
o-Xylene

4.1.2. Measurement conditions applied by VITO

Instrument settings:

Hardware	Instrument	Thermo Trace GC Thermo DSQ MS
	GC-column	Agilent VOC 30 m lenght, 0.20 mm ID, 1.2 um FT
Headspace parameters	Equilibration temperature	70 °C
	Equilibration time	30 min
	Injection method	Syringe
Injector parameters	Injection volume	1 ml gas phase
	Injection modus	Split
	Injection temperature	275 °C
	Split flow	10 ml/min
GC parameters	Carrier gas	Helium - const flow 1 ml/min
	Initial temperature	35 °C
	Initial time	1.0 min
	Rate #1	5 °C/min
	Final temperature #1	175 °C
	Hold time #1	0 min
MS parameters	Mode	Selected Ion Monitoring (SIM)
	Source temperature	220 °C
	Interface temperature	255 °C

Ions	Component	m/z
	Benzene	78, 77
	Toluene	91, 92
	Ethylbenzene	106, 91
	Xylenes	106, 91
	D10-ethylbenzene	98, 116

4.1.3. CALIBRATION DIAGRAMS

Six calibration solutions of BTEX were prepared in a concentration range of 1.7 to 56 µg/l per component. The concentration of the internal standard D10-ethylbebzene was constant (6.25 µg/l). The calibration curves are given in Figure 11 and are linear over the injected range.

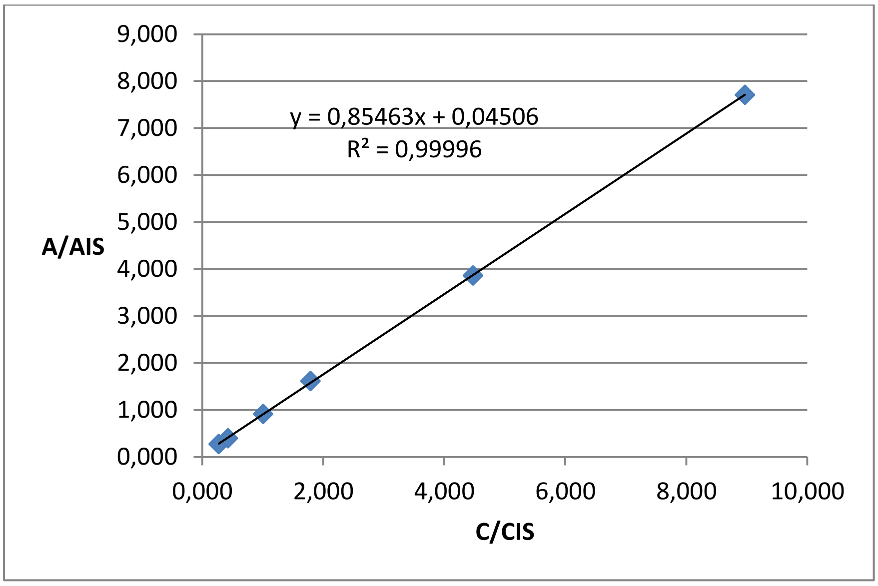
If 10 g sample is extracted with 50 ml methanol, and the methanol solution is diluted 10 times with water before the measurement, the linear range corresponds to a sample concentration of 0.08 mg/kg to 2.8 mg/kg (except for the sum of m/p-xylene: 0.16 to 5.6 mg/kg).

Table 20: Summary of NEN 7331 and method applied by VITO

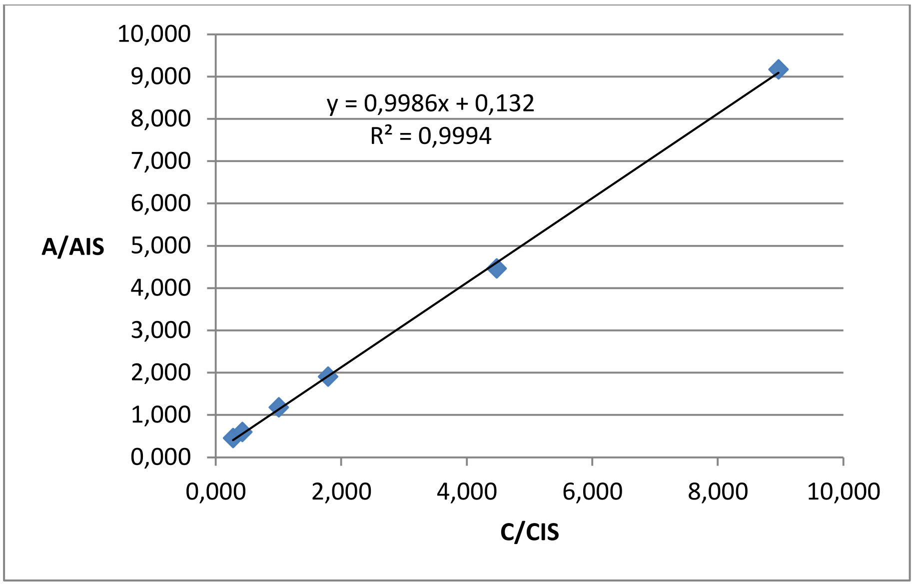
Sample Parameter list Method to be used	Short Description of the method to be used	Short description of the VITO Method	Method differences	Comment
Asphalt aggregate BTEX NEN 7331 BTEX part	- Matrix: bitumen and bitumen containing material - Intake: 10 g - IS: D10-Ethylbenzene - Pretreatment: cryogenic grinding - Extraction: agitation with MeOH, dilution of the extract in water - Measurement: Purge&Trap – GC-MS - LOQ: 0.1 mg/kg	- Matrix: asphalt aggregate - Intake: 10 g - IS: Ethylbenzene-D10 - Pretreatment: cryogenic grinding - Extraction: agitation with MeOH, dilution of the extract in water - Measurement: Headspace - GC-MS	- VITO applies headspace instead of purge&trap	- headspace is a little bit less sensitive than purge&trap but requires less sample handling and there is less chance of carry-over

Figure 11: Calibration diagrams of the BTEX (method NEN7331)

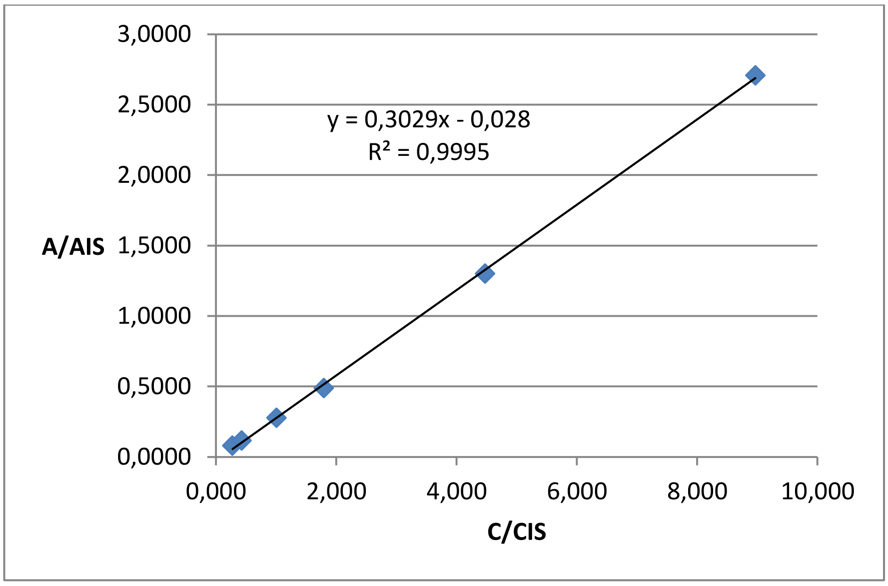
- Benzene



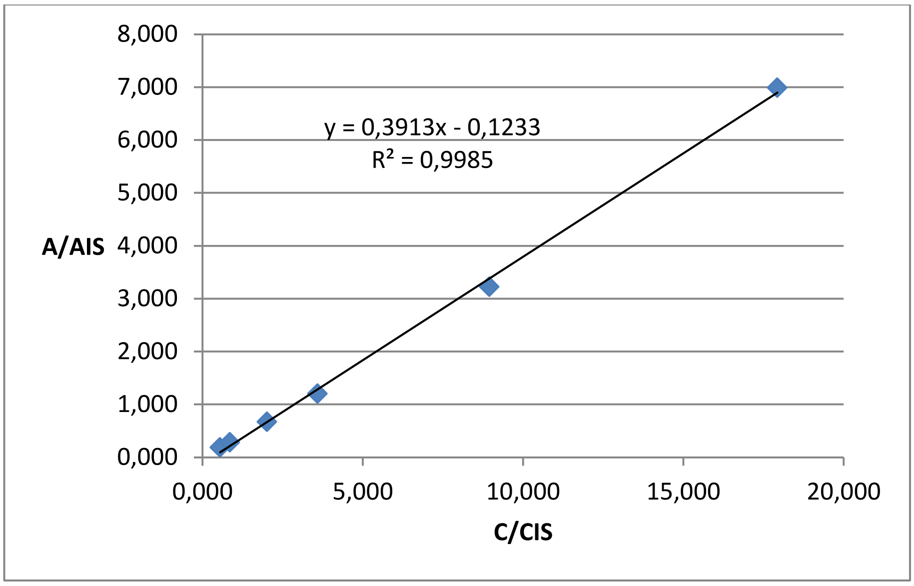
- Toluene



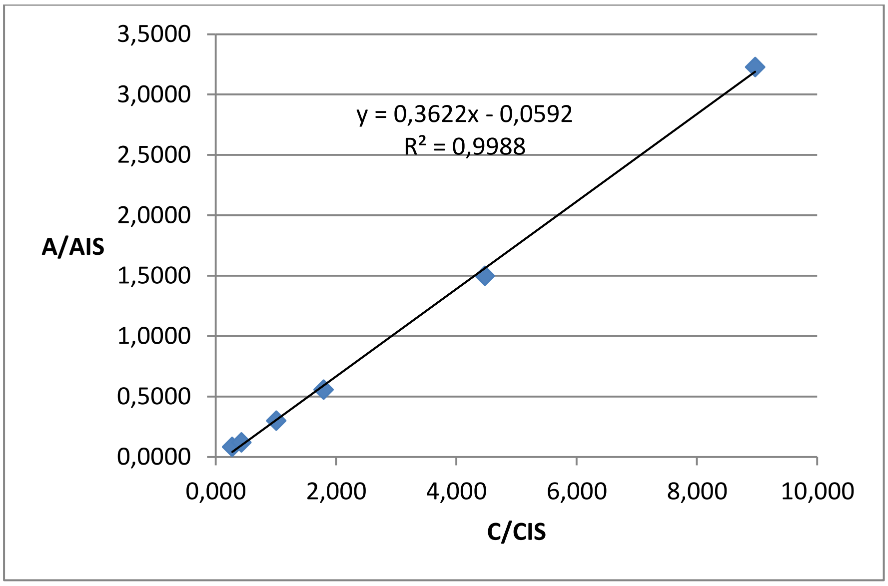
- Ethylbenzene



- m/p-Xylene



- o-Xylene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A/AIS
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R² = 0,9988
0,000
2,000
4,000
6,000
8,000
10,000
C/CIS

4.2. DETERMINATION OF BTEX IN ASPHALT AGGREGATE WITH METHOD NEN 7331

4.2.1. SAMPLE

Asphalte aggregate was received from REKO. Particle size reduction was done by SGS Intron.

4.2.2. ANALYSIS

- 10 g of grinded sample was added to 50 ml of methanol in a 250 ml extraction bottle
- Internal standard (D10-ethylbenzene) was added and the bottle was shaken for 24h
- 0.5 ml of the methanol extract was transferred to a headspace vial containing 4.5 ml water and 1.5 g sodium chloride
- The vial was closed and heated for 30 min at 70 °C
- 1 ml of the gas phase was injected in the GC/MS

4.2.3. RESULTS

→ Repeatability

The sample was analysed in five fold. The results are given in Table 21. The repeatability could not be calculated because all the results were lower than the method detection limit (0.08 mg/kg per component).

→ Check on method performance

The recoveries of the internal standard in each sample was calculated using the calibration standard as a reference (100%). The results are given in Table 22. The recoveries of D10-ethylbenzene ranges from 92.9% to 99.0% and meets the requirement of the method (80-110%). The repeatability of the recovery was 2.4%.

→ Sensitivity

The sensitivity of the method was calculated with the lowest calibration standard. The LOD is 0.08 mg/kg per component and complies with the LOD of method NEN 7331 (0.1 mg/kg).

4.2.4. COMMENTS

The repeatability could not be calculated because the sample did not contain measurable concentrations of BTEX. The recovery of the internal standard and the LOD were within the limits of method NEN 7331. The LOD of the method are amply sufficient with regard to the limit values for construction materials in national regulations (1 – 6 mg/kg depending on the compound and country[3]).

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[3] I. Velzeboer and A. van Zomeren, End of Waste criteria for inert aggregates in member states, ECN-E-17-010 (2017) / personal communication by J. Bartling, Deutsches Institut für Bautechnik.

4.2.5. CONCLUSION

Because the BTEX concentrations were below the LOD, the repeatability could not be calculated. However, the recovery and repeatability of the internal standard were very good. Based on this information, and because the LOD of the method is much lower than the limit values in national regulations, the method is found acceptable for the analysis of BTEX in asphalt aggregate samples.

Table 21: Measured concentrations of BTEX in asphalt aggregate using method NEN 7331

Replicate n°	**1** mg/kg	**2** mg/kg	**3** mg/kg	**4** mg/kg	**5** mg/kg	**Average** mg/kg	**St.Dev.** mg/kg	**C.V.** %
Benzene	< 0.08	< 0.08	< 0.08	< 0.08	< 0.08	-	-	-
Toluene	< 0.08	< 0.08	< 0.08	< 0.08	< 0.08	-	-	-
Ethylbenzene	< 0.08	< 0.08	< 0.08	< 0.08	< 0.08	-	-	-
m/p-Xylene	< 0.16	< 0.16	< 0.16	< 0.16	< 0.16	-	-	-
o-Xylene	< 0.08	< 0.08	< 0.08	< 0.08	< 0.08	-	-	-

Table 22: Recovery of the internal standard in asphalt aggregate using method NEN 7331

Replicate n°	**1** %	**2** %	**3** %	**4** %	**5** %
D10-ethylbenzene	92,9	97,1	96,4	94,8	99,0

CHAPTER 5 DETERMINATION OF THE CONTENT OF PCB IN CONSTRUCTION PRODUCTS

5.1. EN 16167 - SOIL, TREATED BIOWASTE AND SLUDGE - DETERMINATION OF POLYCHLORINATED BIPHENYLS (PCB) BY GAS CHROMATOGRAPHY WITH MASS SELECTIVE DETECTION (GC-MS) AND GAS CHROMATOGRAPHY WITH ELECTRON-CAPTURE DETECTION (GC-ECD)

5.1.1. METHOD DESCRIPTION

A summary of EN 16167 and modifications done by VITO is given in Table 23.

The method was used for the determination of the following PCB congeners:
PCB-28, PCB-52, PCB-101, PCB-118, PCB-138, PCB-153 and PCB-180

5.1.2. MEASUREMENT CONDITIONS

Instrument:	Thermo Trace GC, Trace DSQ
Column :	VF1701, 30m x 0.25 mm x 0.25 µm
Carrier gas:	He, ct flow 1 mL/min
Injection:	1 µl splitless with surge injector temperature: 300 °C 1 min. splitless time surge pressure 300 kPa
GC-program:	125°C (1 min) -> 320°C (20°C/min), total run time 15 min
MS conditions:	source temp. 250°C EI, 70 eV SIM mode SIM ions

window	start time	masses
1	6,0	256,258,260,268,270,272,290,292,302,304
2	8,2	326,328,338,340,360,362,372,374
3	9,7	360,362,372,374,394,396,406,408

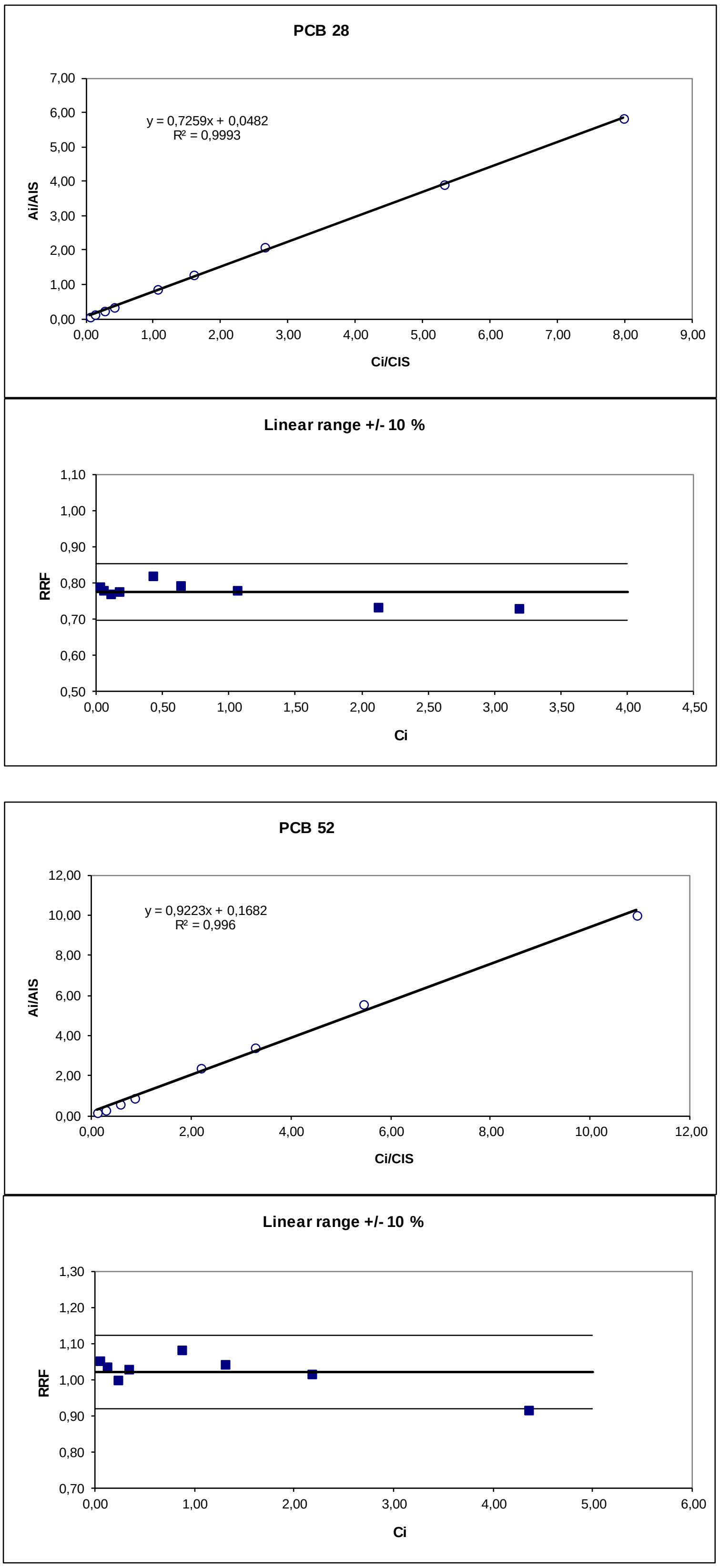
5.1.3. CALIBRATION DIAGRAMS

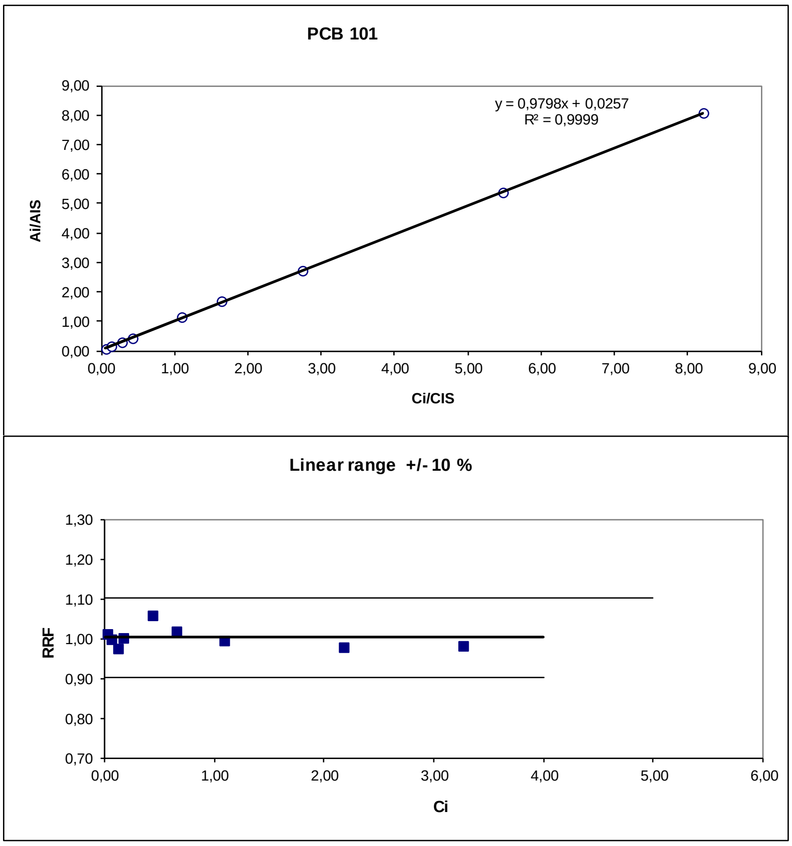
Calibration solutions were prepared in the concentration range of 0,02-3 µg/mL. Calibration diagrams (internal standard method) are given in Figure 12. The internal standards (all corresponding ^{13}C-labelled congeners) were added in a concentration of 0.3 µg/mL. Linearity is obtained for all compounds. The linear working range of 0.02-3 µg/mL corresponds to a working range of 1-150 µg/kg in case of 10 g intake and 0.5 mL final extract volume.

Table 23: Summary of EN 16167 and method applied by VITO

Samples Parameter list	Short Description of the method to be used	Departures from method by VITO and comments
Recycled mixed aggregates PCB-28, 52, 101, 118, 138, 153, 180	- Matrix: sludge, soil, treated biowaste - Intake: 2 – 20 g - IS: non-labelled PCB (ECD) or labelled PCB (MS) - Extraction: - agitation with acetone and petroleum ether or - soxhlet with petroleum ether or - PLE with petroleum ether - Clean-up: - silica, alumina, florisil or acid/base silica column - DMF/heptane partitioning - acid wash - GPC - sulphur removal with TBA sulfite or pyrogenic copper or silica with silver nitrate - Measurement: GC-ECD or GC-MS - LOQ: 1 µg/kg d.m.	- Intake: 10 g - IS: labelled PCB congeners (isotope dilution) - Extraction: PLE with acetone/hexane - Clean-up: acid/base silica followed by DMSO/hexane partitioning - Measurement: GC-MS

Figure 12: Calibration diagrams for PCB congeners




PCB 101
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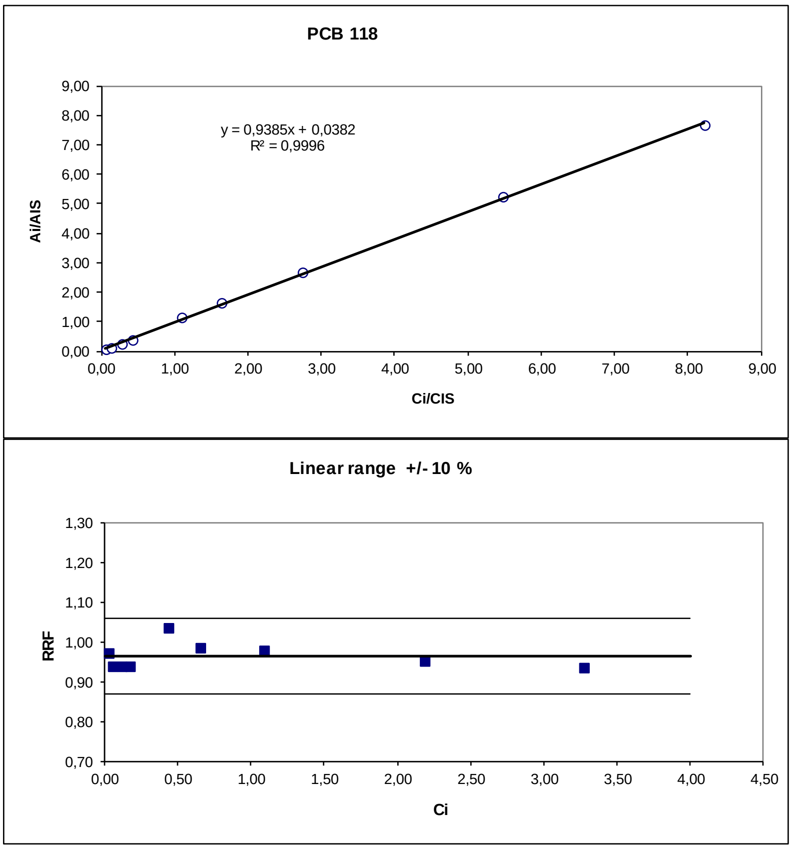
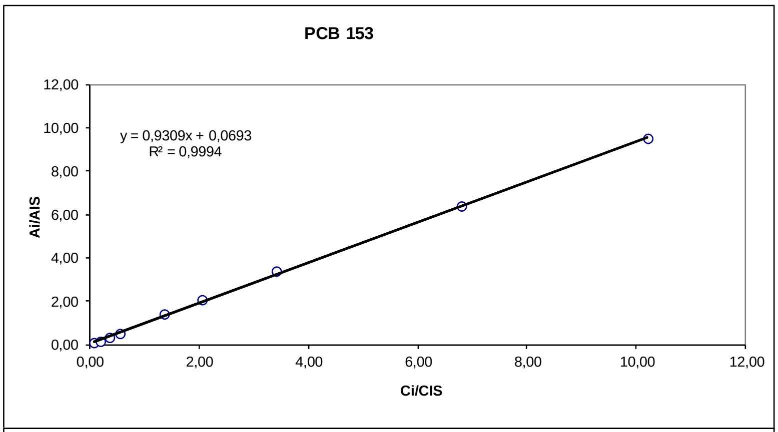
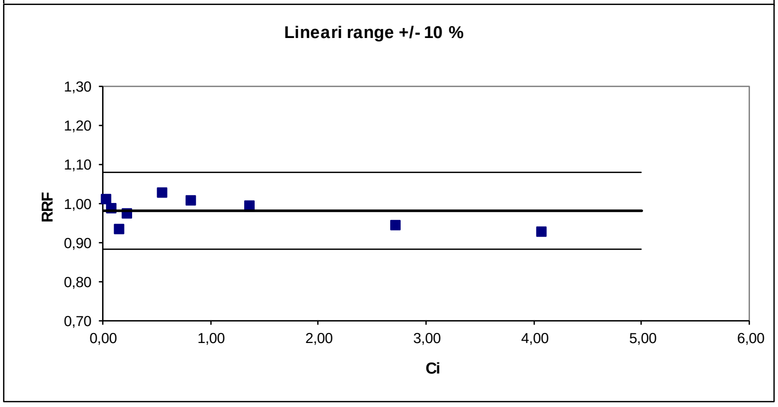
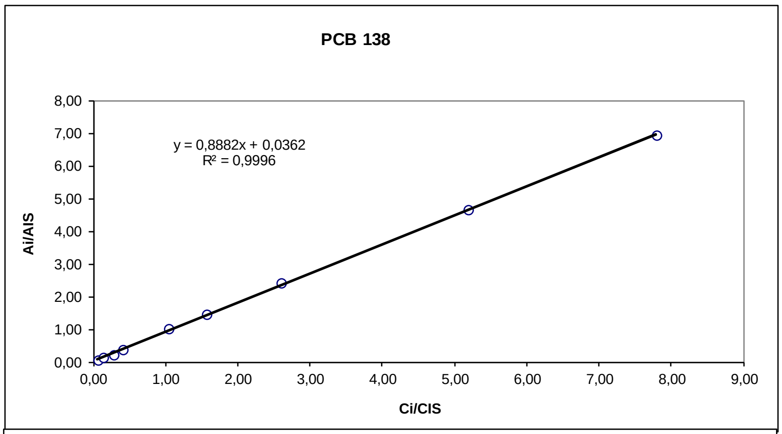
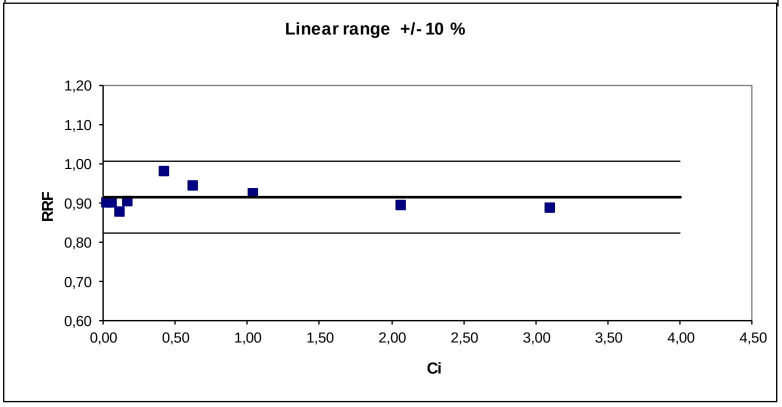
R² = 0,9999
Ai/AIS
9,00
8,00
7,00
6,00
5,00
4,00
3,00
2,00
1,00
0,00
0,00
1,00
2,00
3,00
4,00
5,00
6,00
7,00
8,00
9,00
Ci/CIS
Linear range +/- 10 %
RRF
1,30
1,20
1,10
1,00
0,90
0,80
0,70
0,00
1,00
2,00
3,00
4,00
5,00
6,00
Ci

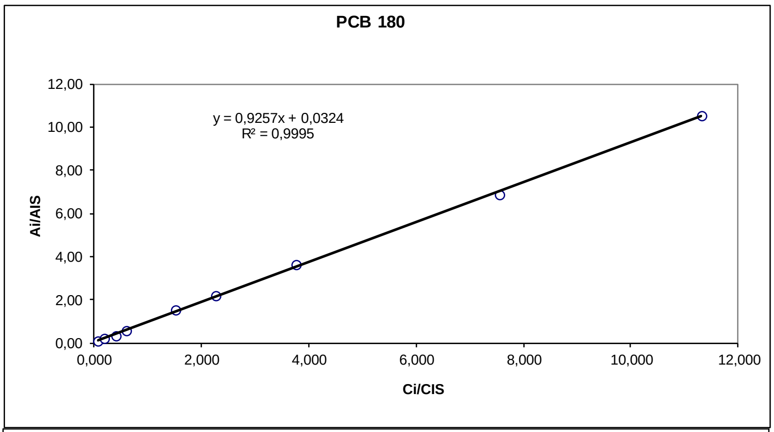

PCB 118
y = 0,9385x + 0,0382
R² = 0,9996
Ai/AIS
9,00
8,00
7,00
6,00
5,00
4,00
3,00
2,00
1,00
0,00
0,00
1,00
2,00
3,00
4,00
5,00
6,00
7,00
8,00
9,00
Ci/CIS
Linear range +/- 10 %
RRF
1,30
1,20
1,10
1,00
0,90
0,80
0,70
0,00
0,50
1,00
1,50
2,00
2,50
3,00
3,50
4,00
4,50
Ci

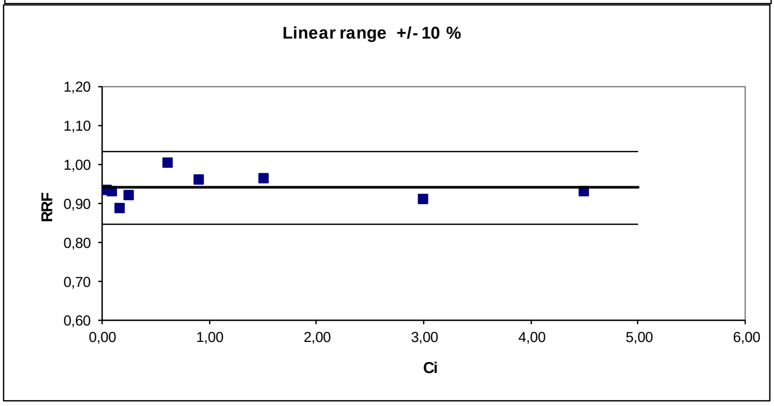

PCB 153
y = 0,9309x + 0,0693
R² = 0,9994
Ai/AIS
12,00
10,00
8,00
6,00
4,00
2,00
0,00
0,00
2,00
4,00
6,00
8,00
10,00
12,00
Ci/CIS


Lineari range +/- 10 %
RRF
1,30
1,20
1,10
1,00
0,90
0,80
0,70
0,00
1,00
2,00
3,00
4,00
5,00
6,00
Ci


PCB 138
y = 0,8882x + 0,0362
R² = 0,9996
Ai/AIS
8,00
7,00
6,00
5,00
4,00
3,00
2,00
1,00
0,00
0,00
1,00
2,00
3,00
4,00
5,00
6,00
7,00
8,00
9,00
Ci/CIS


Linear range +/- 10 %
RRF
1,20
1,10
1,00
0,90
0,80
0,70
0,60
0,00
0,50
1,00
1,50
2,00
2,50
3,00
3,50
4,00
4,50
Ci


PCB 180
y = 0,9257x + 0,0324
R² = 0,9995
Ai/AIS
Ci/CIS
12,00
10,00
8,00
6,00
4,00
2,00
0,00
0,000
2,000
4,000
6,000
8,000
10,000
12,000


Linear range +/- 10 %
RRF
Ci
1,20
1,10
1,00
0,90
0,80
0,70
0,60
0,00
1,00
2,00
3,00
4,00
5,00
6,00

5.2. DETERMINATION OF THE CONTENT OF PCBS IN RECYCLED MIXED AGGREGATES

5.2.1. SAMPLE

A sample of recycled mixed aggregates was received from Theo Pauw BV. A first particle size reduction was done by SGS Intron. The sample was subsequently ground by VITO to particles <1 mm.

5.2.2. ANALYSIS

- 10 g sample and 5 g Celite were brought into a PLE thimble and spiked with 100 ng of each ^{13}C-PCB congener.
- The sample was extracted with acetone/hexane 50/50 using a PLE extractor.
- The extract was evaporated and solvent changed to 1 mL hexane.
- The extract was transferred to a chromatographic column containing 2 g silica 33 % NaOH 1N, 5 g silica 44 % H_2SO_4 and 1 g Na_2SO_4 and the PCB congeners were eluted with 30 mL hexane.
- The eluate was concentrated to 15 mL and subsequently extracted 3 times with 25 mL DMSO.
- 100 mL water was added to the combined DMSO extracts and the PCB congeners were back extracted with 2 times 50 mL hexane.
- The combined hexane extracts were concentrated to 0.5 mL and after addition of injection standard (PCB-178) injected into a GC-MS.

5.2.3. COMMENTS

The PLE extraction was carried out with acetone/hexane (instead of petroleum ether) as there was no risk for coextraction of plastic material.

VITO applied an additional clean up step using DMSO/hexane partitioning to remove interfering hydrocarbons; this clean up step is equivalent to the DMF/petroleum ether partitioning described in EN 16167.

5.2.4. CHROMATOGRAMS

Chromatograms (TIC and ion chromatograms) are given in Figure 13 for an extract of recycled mixed aggregates.

5.2.5. RESULTS

→ Repeatabilities

The results of the replicate determinations (n = 6) of the content of PCB congeners in recycled mixed aggregates are given in Table 24. The product contains PCB congeners in concentrations varying from 0.3 to 25 µg/kg dm, with a total PCB content of 80 µg/kg dm. Good repeatabilities are obtained for all congeners; for PCB-28 one outlier value has been omitted for the repeatability calculation.

→ **Recoveries**

PCB recoveries were determined for a spiked sandy soil, which was analysed using the same analytical procedure. The recovery values are tabulated in Table 25. The recoveries are between 80 and 100%, with exception of PCB-28 for which a somewhat lower recovery of 72% was observed.

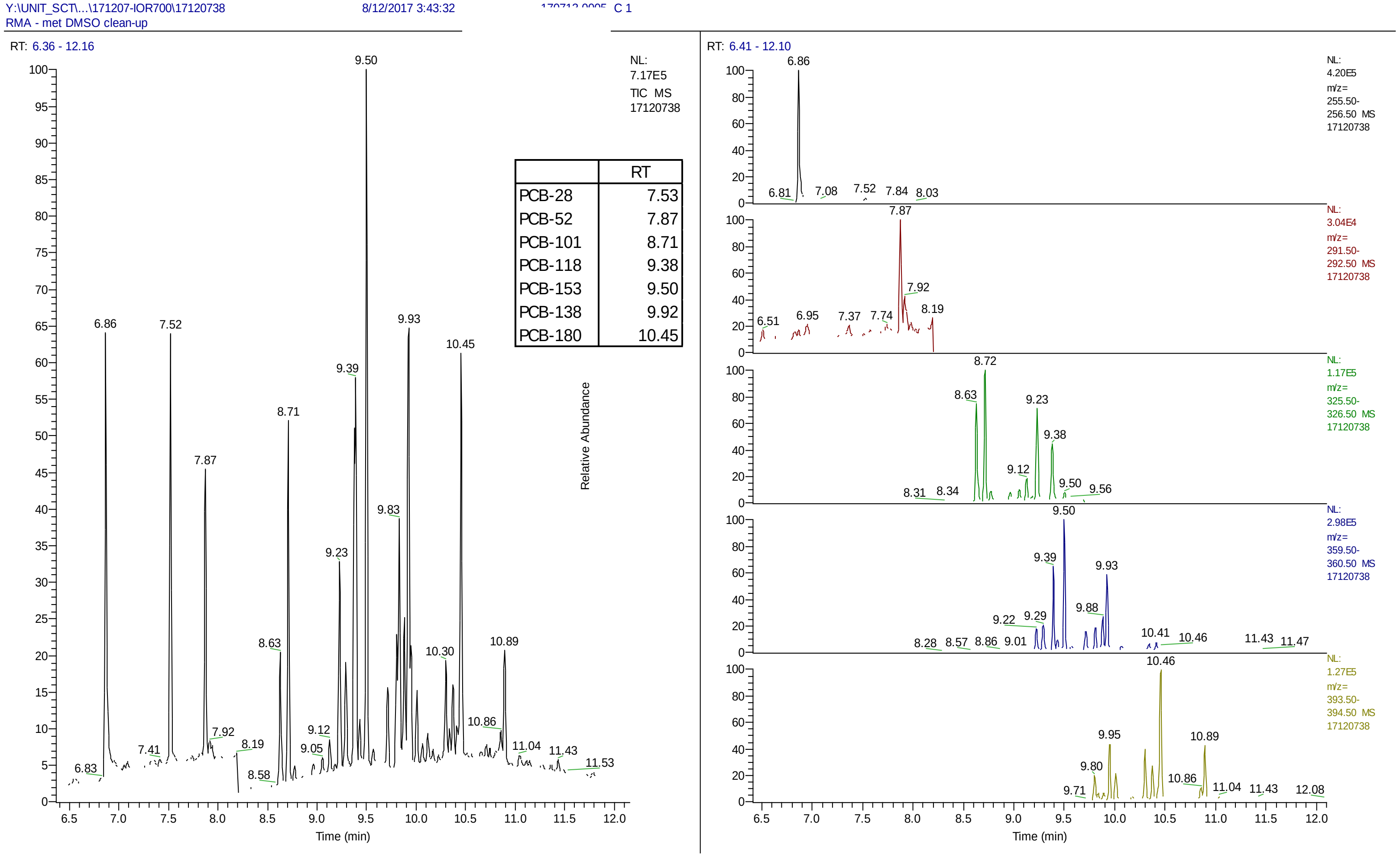
→ **Sensitivity**

The LOD depends on sample intake and final extact volume. On the basis of the calibration characteristics LOD's below 1 ug/kg are achievable in case of a concentration factor of 20. LOD's were also calculated on the basis of signal-to-noise ratios registered in the ion chromatograms of a recycled mixed aggregate extract (concentration corresponding to 3 times the noise). The LOD values are given in Table 26 and are below the limit of application of the standard (1 µg/kg).

5.3. CONCLUSION

Standard EN 16167 is suited for the analysis of PCB's in construction materials. The method is repeatable and the low limit of application of 1 µg/kg of the standard can be achieved. The standard does not need an adaptation.

Figure 13: Total ion and ion chromatograms for PCB congeners in an extract of recycled mixed aggregates



	RT
PCB-28	7.53
PCB-52	7.87
PCB-101	8.71
PCB-118	9.38
PCB-153	9.50
PCB-138	9.92
PCB-180	10.45

Table 24: Measured concentrations for PCB congeners in recycled mixed aggregates

congener	***170713-0005 C1*** µg/kg dm	***170713-0005 C2*** µg/kg dm	***170713-0005 C3*** µg/kg dm	***170713-0005 C4*** µg/kg dm	***170713-0005 C5*** µg/kg dm	***170713-0005 C6*** µg/kg dm	***Average*** µg/kg dm	***CVr*** %
PCB-28	0,297	0,308	0,295	0,294	0,358	~~0,504~~	0,310	9
PCB-52	0,821	0,896	1,17	0,814	0,902	1,19	0,965	18
PCB-101	9,21	10,1	9,38	10,5	8,81	10,6	9,77	7,5
PCB-118	3,80	3,92	3,95	4,38	3,59	4,80	4,08	11
PCB-153	23,8	24,7	25,0	28,2	24,2	29,1	25,8	8,7
PCB-138	19,9	21,3	18,0	23,7	19,2	24,6	21,1	12
PCB-180	19,1	19,4	19,2	23,1	19,7	22,4	20,5	8,8
sum PCB's	76,9	80,6	76,9	91,0	76,8	93,2	82,6	9,2

Table 25: PCB recovery values for a spiked soil

congener	***QC sample*** µg/kg dm	***Theor.conc.*** µg/kg ds	***Recovery*** %
PCB-28	3,00	4,15	72
PCB-52	3,95	4,66	85
PCB-101	3,68	3,81	97
PCB-118	9,15	9,36	98
PCB-153	3,14	3,69	85
PCB-138	7,24	7,22	100
PCB-180	1,73	2,1	83
sum PCB's	31,9	35,0	91

Table 26: LOD-values for PCB congeners calculated on the basis of signal-to-noise ratios for a sample extract

Congener	***LOD*** µg/kg
PCB 28	0,14
PCB 52	0,25
PCB 101	0,11
PCB 118	0,11
PCB 153	0,32
PCB 138	0,36
PCB 180	0,28

CHAPTER 6 DETERMINATION OF THE CONTENT OF POLYBROMINATED DIPHENYL ETHERS (PBDE) IN CONSTRUCTION PRODUCTS

6.1. EN ISO 22032 - WATER QUALITY -- DETERMINATION OF SELECTED POLYBROMINATED DIPHENYL ETHERS IN SEDIMENT AND SEWAGE SLUDGE -- METHOD USING EXTRACTION AND GAS CHROMATOGRAPHY/MASS SPECTROMETRY

6.1.1. METHOD DESCRIPTION

A summary of EN ISO 22032 and modifications done by VITO is given in Table 27.

The method was used for the determination of the following BDE congeners:

BDE-47
BDE-99
BDE-100
BDE-153
BDE-154
BDE-183
BDE-205
BDE-209

6.1.2. MEASUREMENT CONDITIONS

Hardware	Instrument	HP 6890 Series GC System Agilent 5975C inert XL EI/CI MSD
	GC-column	Restek RTX1614 15 m, 0.25 mmID, 0.10 um df
Injector parameters	Injection volume	1 µl
	Injection modus	Pulsed splitless
	Injection temperature	110 °C
	Final temperature	320 °C
	Pressure	0.44 psi
	Pulse pressure	2.1 psi
	Pulse time	1.25 min
	Purge flow	50 ml/min
	Purge time	1.25 min
GC parameters	Carrier gas	He - const flow 1 ml/min
	Initial temperature	90°C
	Initial time	2 min
	Rate #1	25°C/min
	Final temperature #1	200°C

	Hold time #1 Rate #2 Final temperature #2 Hold time #2	5 min 15°C/min 330 °C 12 min
MS parameters	Mode Tune file Gain factor Resulting EM voltage Source temperature Interface temperature Solvent delay	SIM atune.u 5 1576 V 245 °C 330 °C 3 min
SIM parameters	m/z	Component
	405.8; 407.8	BDE-28
	325.9; 485.7	BDE-47
	405.7; 563.6	BDE-99
	405.7; 563.6	BDE-100
	483.7; 643.5	BDE-153
	483.7; 643.5	BDE-154
	561.6; 721.4	BDE-183
	639.5; 641.5	BDE-205
	797.7; 799.7	BDE-209
	417.8; 575.6	13C-BDE-28
	339.9; 497.7	13C-BDE-47
	417.7; 576.6	13C-BDE-99
	495.7; 497.7	13C-BDE-153
	573.6; 575.6	13C-BDE-183
	811.4; 813.4	13C-BDE-209

6.1.3. CALIBRATION DIAGRAMS

Calibration solutions were prepared in the concentration range of 0,025-1 µg/mL (except BDE-209 0.1-3.5 µg/mL) . Calibration diagrams are given in Figure 14. Linearity is obtained for all compounds. The linear working ranges are:

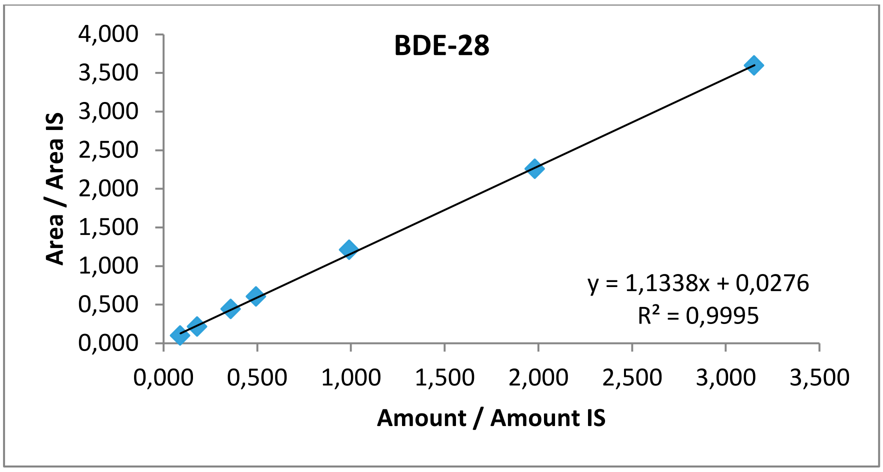
- All BDE’s except BDE-205 and BDE-209: 0,025 – 1 µg/mL(extract concentration)
- BDE-205: 0,05 – 0,6 µg/mL
- BDE-209: 0,2 – 3,5 µg/mL

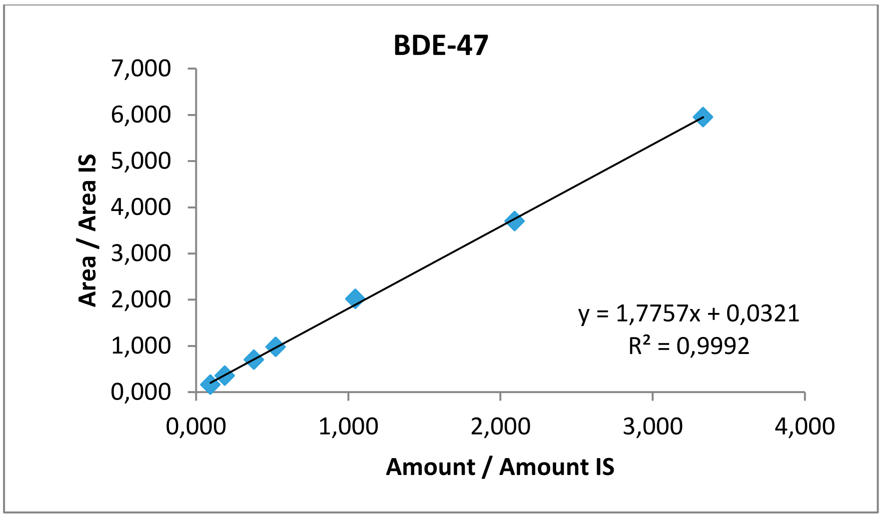
In case of 1 g intake and 50 ml final extract volume these concentrations correspond to:
- All BDE’s except BDE-205 and BDE-209: 1 – 50 mg/kg plastic product
- BDE-205: 2 – 30 mg/kg
- BDE-209: 10 – 175 mg/kg

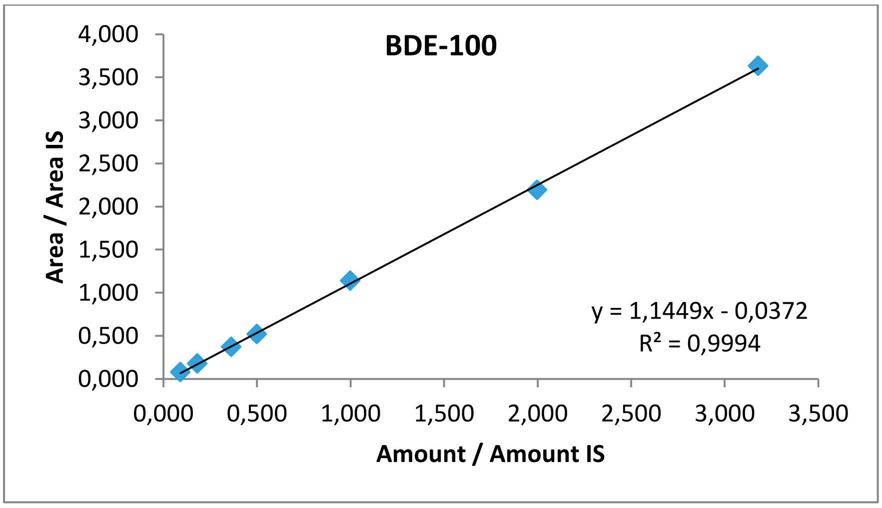
Table 27: Summary of EN ISO 22032 and method applied by VITO

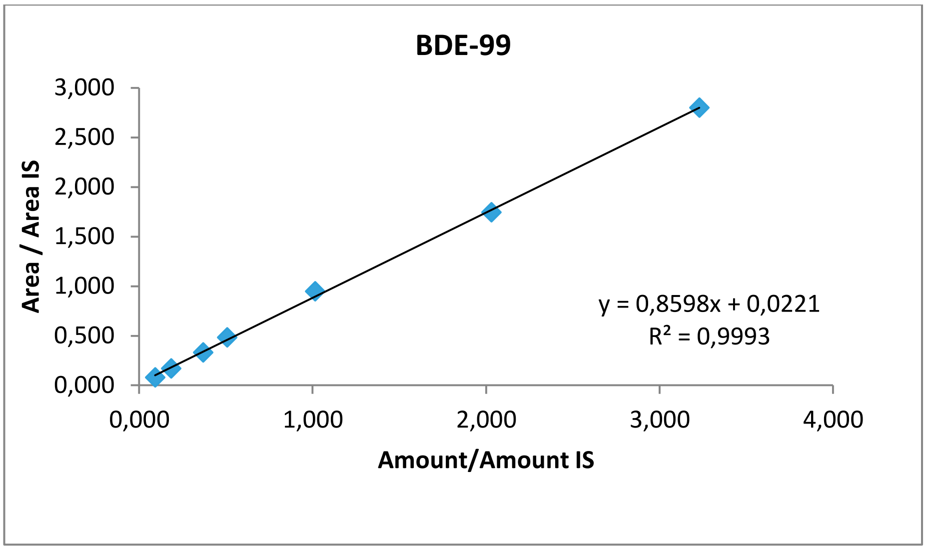
Samples Parameter list	Short Description of the method to be used	Departures from method by VITO and comments
Plastic product (CRM, HDPE) BDE-47, 99, 100, 153, 154, 183, 205, 209	- Matrix: sediment, sewage sludge - Intake: 5-10 g (freeze dried, ground) - IS: EI-MS: ^{13}C-BDEs (47, 99, 153, 183, 209); NCI-MS: BDE-77, BDE-181 and ^{13}C-BDE-209 - Extraction: Soxhlet with toluene or acetone/hexane or iso-octane, 24h (remark: BDEs are light sensitive) - Clean-up (optional): multilayer silica (NaOH, H_2SO_4, $AgNO_3$); basic alumina; GPC; final volume 100 µL - Measurement: GC-EI-MS, GC-NCI-MS - LOQ: GC-EI-MS: 0.05-25 µg/kg (non-deca); 0.3-100 µg/kg (deca) GC-NCI-MS: LOQ's are approx. 10 times lower	- VITO analyses also BDE-28, using ^{13}C-BDE-28 as IS - VITO sample intake: 1 g (cryogenically ground) - VITO used toluene as extraction solvent; PE dissolves in hot toluene - VITO added the IS after the soxhlet extraction (to an aliquot of the 50 ml extract) because of high BDE concentrations - VITO did not apply clean-up and the measurement was done by GC-EI-MS

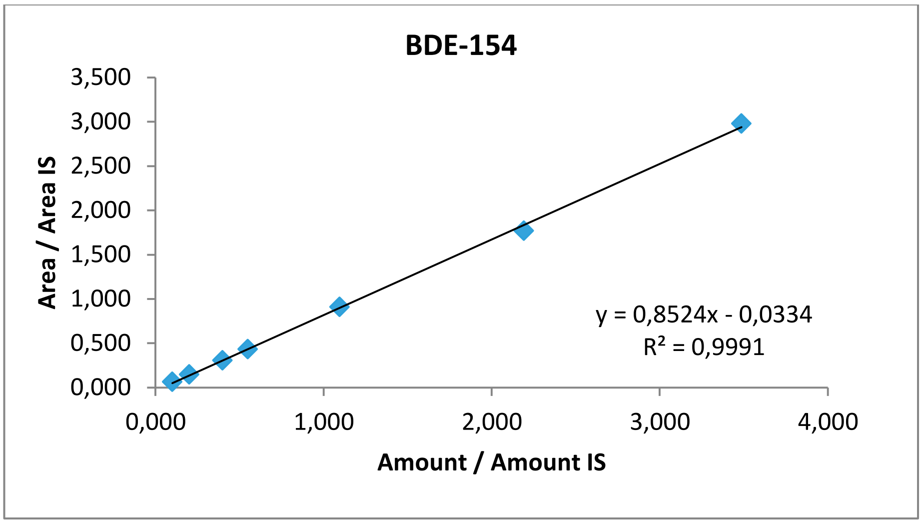
Figure 14: Calibration diagrams for BDE congeners (concentrations in µg/mL)

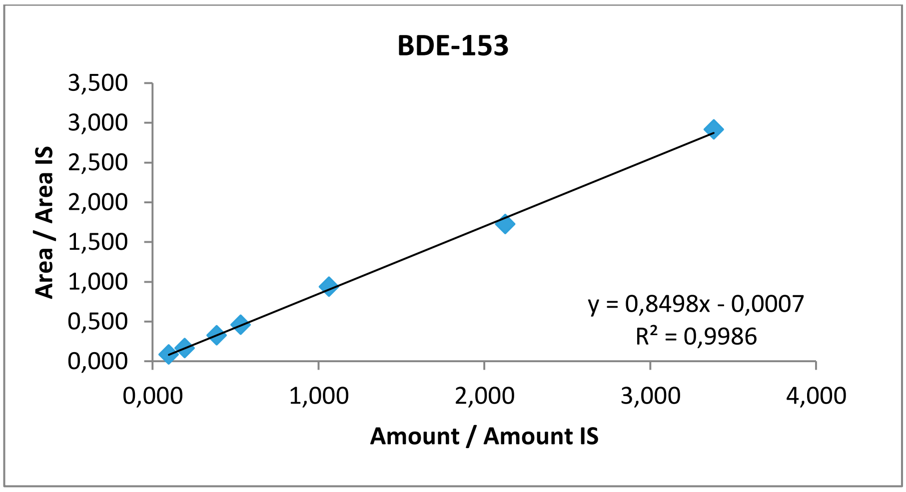


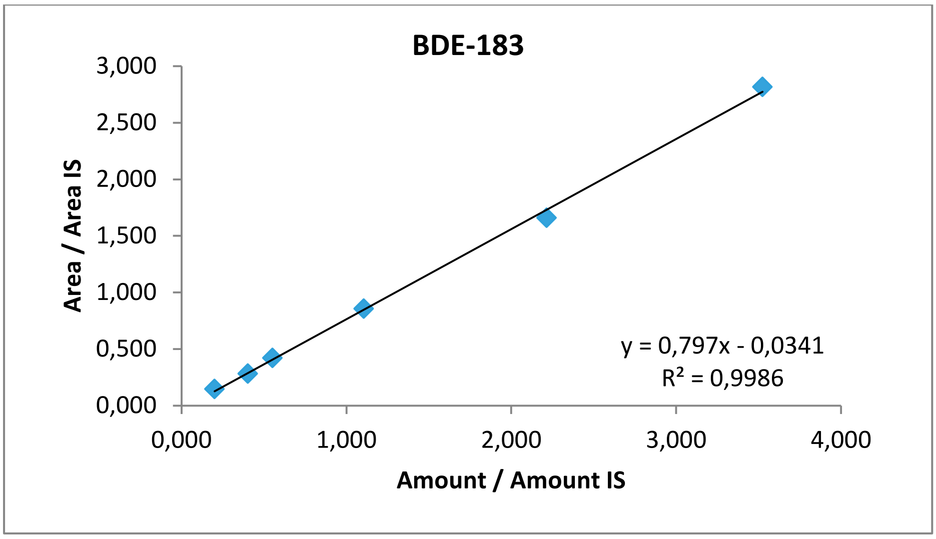


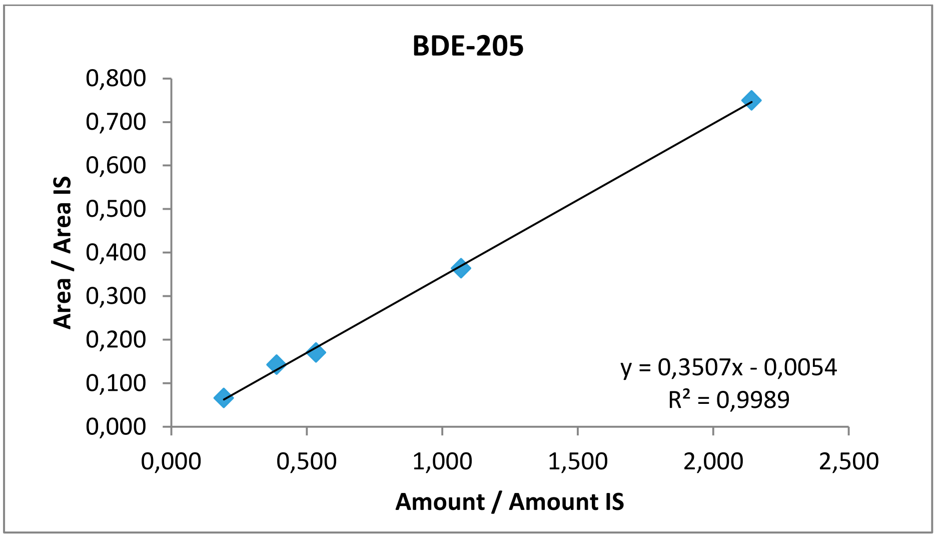


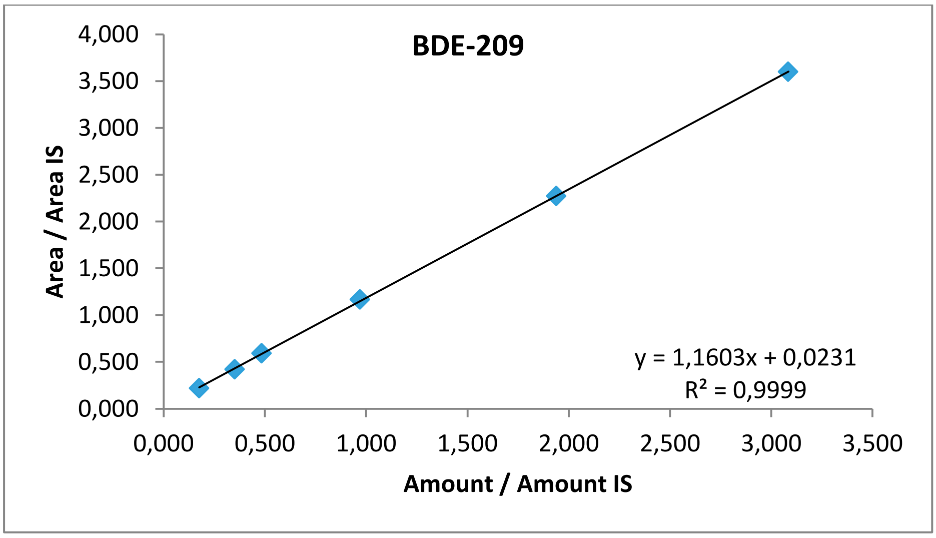

BDE-99
Area / Area IS
3,000
2,500
2,000
1,500
1,000
0,500
0,000
0,000
1,000
2,000
3,000
4,000
Amount/Amount IS
y = 0,8598x + 0,0221
R² = 0,9993


BDE-154
Area / Area IS
3,500
3,000
2,500
2,000
1,500
1,000
0,500
0,000
0,000
1,000
2,000
3,000
4,000
Amount / Amount IS
y = 0,8524x - 0,0334
R² = 0,9991


BDE-153
Area / Area IS
3,500
3,000
2,500
2,000
1,500
1,000
0,500
0,000
0,000
1,000
2,000
3,000
4,000
Amount / Amount IS
y = 0,8498x - 0,0007
R² = 0,9986


BDE-183
Area / Area IS
3,000
2,500
2,000
1,500
1,000
0,500
0,000
0,000
1,000
2,000
3,000
4,000
Amount / Amount IS
y = 0,797x - 0,0341
R² = 0,9986


BDE-205
Area / Area IS
0,800
0,700
0,600
0,500
0,400
0,300
0,200
0,100
0,000
0,000
0,500
1,000
1,500
2,000
2,500
Amount / Amount IS
y = 0,3507x - 0,0054
R² = 0,9989


BDE-209
Area / Area IS
4,000
3,500
3,000
2,500
2,000
1,500
1,000
0,500
0,000
0,000
0,500
1,000
1,500
2,000
2,500
3,000
3,500
Amount / Amount IS
y = 1,1603x + 0,0231
R² = 0,9999

6.2. DETERMINATION OF SELECTED PBDE IN PLASTIC MATERIAL

6.2.1. SAMPLE

The sample (ERM-EC590, 20 g) was received from JRC-Geel (Belgium). The sample consisted of polyethylene pellets, containing 1-500 mg/kg of each congener. The pellets were cryogenically grinded to particle sizes <1 mm using a ultracentrifugal mill (Retsch ZM 10).

6.2.2. ANALYSIS

- 1 g of grinded sample was brought in a soxhlet thimble and extracted with toluene during 24 h.
- Prior to extraction a solution of PCB-180 (50 µg) was added as extraction standard.
- During the extraction the PE material dissolved in hot toluene and was removed from the Soxhlet thimble
- After cooling of the extract at room temperature, the polyethylene precipitated from the solution as a white solid. The solid was removed from the solution by filtration (Whatman filter paper) and the solution was collected in weighed amber vials.
- 1 mL of the extract was taken and IS solution was added (300 ng of non-deca-BDE’s, 1000 ng of BDE-209)

6.2.3. COMMENTS

None

6.2.4. CHROMATOGRAMS

Chromatograms of BDE congeners are given for a polyethylene extract in Figure 15.

6.2.5. RESULTS

→ Repeatabilities

The results of the replicate determinations of BDE congeners in polyethylene are given in Table 28. The results show very good repeatabilities for all congeners; the %RSD varies from 4 to 8%.

→ Recoveries

The recoveries of the BDE congeners were determined by comparing the measured average concentrations with the certified values of ERM-EC590 (see Table 29). The recoveries were between 80 and 100 %. The higher BDE-47 recovery is due to a contribution of coeluting PCB-180, which was added as extraction standard.

→ **Sensitivities**

LOD values were determined on the basis of the signal-to-noise ratios registered for the lowest calibration solution. The following LOD's were calculated, assuming 1 g intake and 50 mL final extract:

- non-deca-BDE: 0,1-1 mg/kg
- deca-BDE: 3 mg/kg

Lower values will be obtained in case of larger intakes and concentration of the extracts to smaller volumes. With 10 g intake and 100 µL final volume the following LODs are theoretically achievable:

- non-deca-BDE: 0,02-0,2 µg/kg
- deca-BDE: 0,6 µg/kg

These values are similar to those mentioned in the umbrella standard TS 00351024 (0,05-0,3 µg/kg). The real LOD's will however strongly depend on matrix interferences and the question is if it is relevant to be able to analyse these low concentrations in construction materials, knowing that the PBDE limit value in REACH annex XVII is 1000 mg/kg.

6.3. CONCLUSION

Method EN ISO 22032 is suited for the analysis of PBDE in plastic material.
Clean-up of the extract was for the sample studied not necessary but can be kept in the method for samples with low PBDE concentrations or for dirty samples. With regard to the LOD requirement we advice to increase the LOD values of the umbrella standard TS 00351024 with a factor 1000.

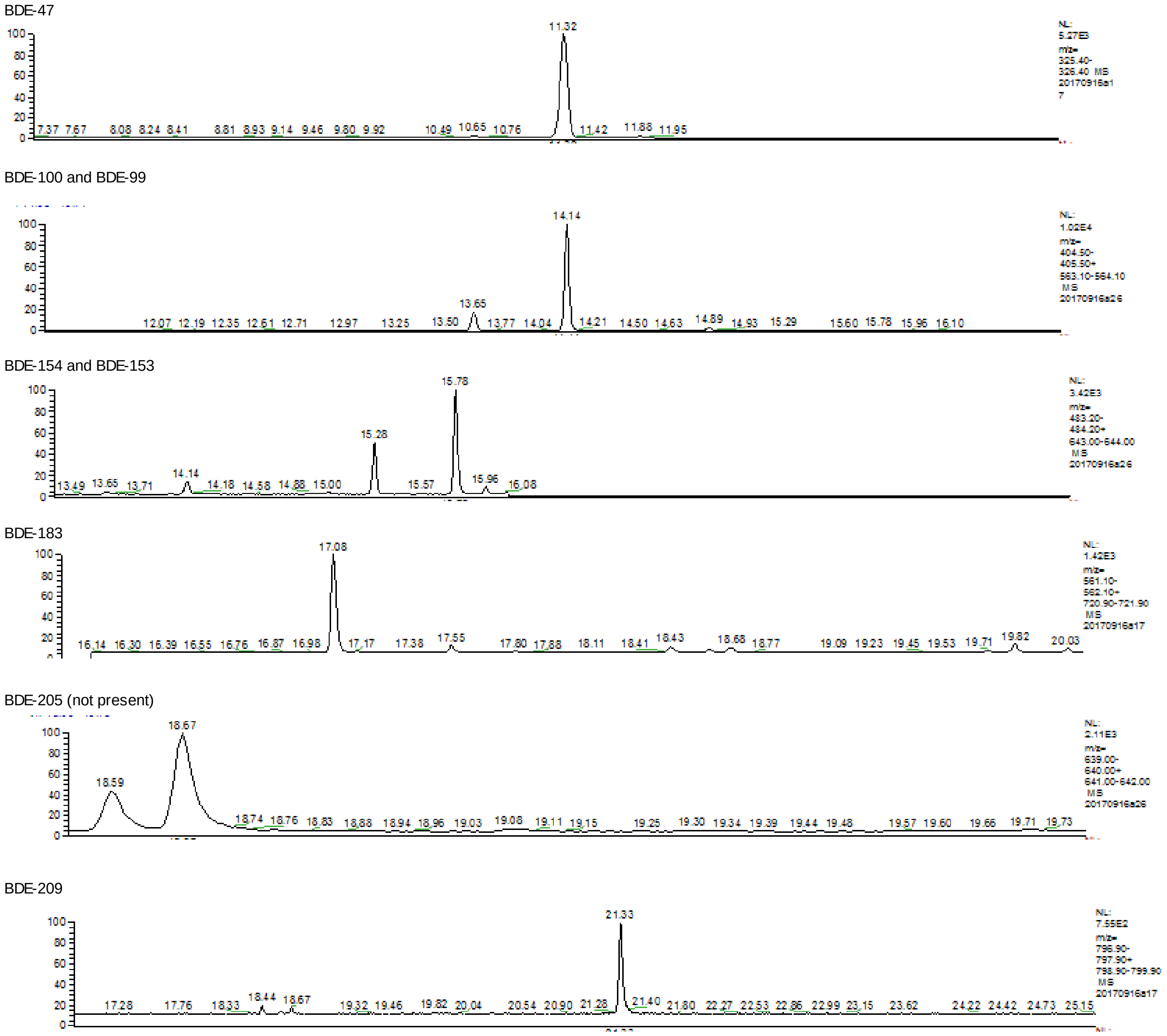
Table 28: Measured concentrations for BDE congeners in polyethylene (ERM-EC590)

Replicate n°	***1*** mg/kg	***2*** mg/kg	***3*** mg/kg	***4*** mg/kg	***5*** mg/kg	***Average*** mg/kg	***St.Dev*** mg/kg	***CV$_r$*** %
BDE-28	1,6	1,7	1,4	1,6	1,4	1,5	0,1	8,4
BDE-47	234	244	215	232	238	233	11,1	4,8
BDE-100	51,9	51,6	47,3	48,5	48,7	49,6	2,0	4,1
BDE-99	267	280	250	265	271	267	11,0	4,1
BDE-154	20,9	23,0	19,7	20,4	21,0	21,0	1,2	6,0
BDE-153	44,1	45,3	40,0	42,3	41,4	42,6	2,1	5,0
BDE-183	118	123	110	115	118	117	4,4	3,7
BDE-205	< 2	< 2	< 2	< 2	< 2	< 2	N/A	N/A
BDE-209	538	535	485	525	519	520	21,5	4,1

Table 29: Recoveries of PBDEs from plastic material

	ERM-EC590 certified values mg/kg	***Measured average conc.*** mg/kg	***Recovery*** %
BDE-28	-	1,5	-
BDE-47	230	233	101
BDE-100	63	50	79
BDE-99	300	267	89
BDE-154	26	21	81
BDE-153	47	42,6	91
BDE-183	132	117	88
BDE-205	-	< 2	-
BDE-209	650	520	80

Figure 15: Ion chromatograms of BDE congeners for a polyethylene extract



CHAPTER 7 DETERMINATION OF THE CONTENT OF DIOXINS AND FURANS (PCDD/F) AND DIOXIN-LIKE PCB'S (dl-PCB) IN CONSTRUCTION PRODUCTS

7.1. EN 16190 - SOIL, TREATED BIOWASTE AND SLUDGE - DETERMINATION OF DIOXINS AND FURANS AND DIOXIN-LIKE POLYCHLORINATED BIPHENYLS BY GAS CHROMATOGRAPHY WITH HIGH RESOLUTION MASS SELECTIVE DETECTION (HR GC-MS)

7.1.1. METHOD DESCRIPTION

A summary of the method is given in Table 30. The analyses were carried out by SGS-IAC (Antwerp). The modifications applied by SGS are given in the same table.

7.1.2. MEASUREMENT CONDITIONS

The measurement conditions applied by SGS were not communicated. They were in compliance with the requirements set for HRGC-HRMS analysis in existing dioxin standards.

7.1.3. CALIBRATION DIAGRAMS

Calibration diagrams were submitted by SGS and will be made available on request.

Table 30: Summary of EN 16190 and method applied in this study

Samples Parameter list	Short Description of the method to be used	Departures from method by SGS and comments
Rubber crumbs Polychlorodibenzodioxins Polychlorodibenzofurans Dioxin-like PCBs	- Matrix: sludge, biowaste, soil - Intake: 5 – 50 g - IS: ^{13}C-PCDDF (17) and ^{13}C-PCB (12) - Extraction: Soxhlet or equivalent - Clean-up : - GPC - multilayer column - sulphuric acid - activated carbon column - and/or alternative clean-up method - Measurement: GC-HRMS - LOQ: 1 ng/kg per congener	- Matrix : rubber crumbs - Intake: 1 g - IS: ^{13}C-PCDDF (16) and ^{13}C-PCB (12) - Extraction: soxhlet - Clean-up: multilayer and alumina column - Measurement: GC-HRMS - LOQ: 4-12.5 ng/kg per congener for dioxins 25-500 ng/kg per congener for dl-PCBs

7.2. DETERMINATION OF PCDD/F AND DL-PCB'S IN RUBBER CRUMBS

7.2.1. SAMPLE

Rubber crumbs were received from SGS Intron (Sittart, NL). The crumbs were grinded to particles <1 mm.

7.2.2. ANALYSIS

Due to the type of sample and the risk of interference by the high organic load of the rubber crumbs SGS decided to limit the intake to 1 g. As a consequence the LOD values increased with a factor 10.
Other details of the extraction and clean up method were not communicated by SGS.

7.2.3. COMMENTS

For construction products with high organic content it is recommended to reduce the intake but this implies that the limit of application of 1 ng/kg per congener as stated in EN 16690 can not be achieved.

7.2.4. CHROMATOGRAMS

Chromatograms for PCDD/F and dl-PCB congeners in rubber crumbs are given in Annex A.

7.2.5. RESULTS

The analysis reports provided by SGS are given in annex of this report.

→ Repeatabilities

The results of the replicate determinations of PCDD/F in rubber crumbs are summarized in Table 31. The results show that the rubber crumbs do not contain tetra- and pentachlorinated dioxins and furans in concentrations >2 ng/kg. 3 HxCDD congeners were detected with concentrations of 2-6 ng/kg. HpCDD/F and OCDF were found in concentrations of 6 to 100 ng/kg, OCDD in a concentration of 600 ng/kg. The repeatabilities (%RSD) range from 4 to 25% depending on congener.
The results of the replicate determinations of dl-PCB's can also be found in Table 31. The dl-PCB's are present in higher concentrations than the PCDD/F, ranging from 18 to 7600 ng/kg. With the exception of PCB-81 and PCB-126 the calculated %RSD is high: 18-27%. These values are higher than the CV_r values which can be found in table D.2 of EN 16190. The higher %RSD result from disturbed chromatograms by interfering constituents present in rubber crumbs.

→ **Sensitivity**

SGS reports LOQ-values of <2 and <7 ng/kg for resp. non-detected PCDD/F and dl-PCB congeners. These values are higher than the limit of detection of 1 ng/kg given in EN 16190, but as stated above SGS only took 1 gram of sample contrary to the recommended intake of 5-50 g. With higher intakes lower LOD's are possibly achievable depending on the degree of matrix interferences.

7.3. CONCLUSION

For the type of sample studied and on the basis of the analytical results reported by SGS it can not be directly concluded that EN 16690 is suited for the reliable determination of PCDD/F and dl-PCB in construction products. However the measured concentrations are low, total TEQ values (see Table 31) stay well below the German regulatory limit of 100 ng TEQ/kg for soil (playground) or deposition of sludge on soil. It is expected that better precision values will be obtained for construction products with higher PCDD/F and d,l-PCB concentrations, so that we recommend to accept EN 16190 as fit for purpose.

Table 31: Measured concentrations for PCDD/F and dl-PCBs in rubber crumbs

PCDD/F	**1** ng/kg	**2** ng/kg	**3** ng/kg	**4** ng/kg	**5** ng/kg	**Average** ng/kg	**CV_r** %	**Average** ng WHO TEQ /kg
2378-TCDF	< 1,7	< 1,9	< 1,8	< 1,9	< 1,8	-	-	<0,18
2378-TCDD	< 1,7	< 1,9	< 1,8	< 1,9	< 1,8	-	-	<1,8
12378-PeCDF	< 1,7	< 1,9	< 1,8	< 1,9	< 1,8	-	-	<0,054
23478-PeCDF	< 1,7	< 1,9	< 1,8	< 1,9	< 1,8	-	-	<0,54
12378-PeCDD	< 1,7	< 1,9	< 1,8	< 1,9	< 1,8	-	-	<1,8
123478-HxCDF	< 1,7	< 1,9	< 1,8	< 1,9	< 1,8	-	-	<0,18
123678-HxCDF	< 1,7	< 1,9	< 1,8	< 1,9	< 1,8	-	-	<0,18
234678-HxCDF	< 1,7	< 1,9	< 1,8	< 1,9	< 1,8	-	-	<0,18
123789-HxCDF	< 1,7	< 1,9	< 1,8	< 1,9	< 1,8	-	-	<0,18
123478-HxCDD	< 1,7	2,2	2,3	2,4	< 1,8	2,3	4,3	0,23
123678-HxCDD	5,3	6,6	9,8	9,8	7,5	7,8	25,5	0,78
123789-HxCDD	3,1	4,4	4,50	4,7	4,20	4,2	15,1	0.42
1234678-HpCDF	4,7	7,1	6,30	6,7	5,20	6	16,9	0.06
1234789-HpCDF	< 2,9	< 3,1	< 3,0	< 3,1	< 3,0		-	<0.03
1234678-HpCDD	73	92	110	110	120	101	18,4	1.01
OCDF *	9,1	~~31~~	11	9,3	10	9,9	8,7	0.003
OCDD	510	710	660	600	710	638	13,3	0.19
dl-PCB's	**1** ng/kg	**2** ng/kg	**3** ng/kg	**4** ng/kg	**5** ng/kg	**Average** ng/kg	**CV_r** %	
PCB-81	18	19	19	18	17	18,2	4,6	0,005
PCB-77	290	370	340	380	470	370	17,8	0,037
PCB-126 *	42	54	45	52	~~140~~	48,3	11,8	4,83
PCB-169	7,4	< 6,6	10	< 7,5	< 7,7	-	-	<0,24
PCB-123	110	200	150	170	180	162	21,1	0,005
PCB-118	5600	8400	7000	7800	9100	7580	17,8	0,23
PCB-114	130	190	160	170	210	172	17,6	0,005
PCB-105	2000	3000	2500	2800	3600	2780	21,3	0,08
PCB-167	450	670	540	720	770	630	21,0	0,019
PCB-156	860	1500	1100	1500	1600	1312	24,2	0,039
PCB-157	130	210	180	210	280	202	27,0	0,006
PCB-189	110	180	120	210	180	160	26,9	0,005
						Total TEQ	lower bound	7,95
							upper bound	13,3

CHAPTER 8 DETERMINATION OF THE CONTENT OF PHTHALATE ESTERS IN CONSTRUCTION PRODUCTS

8.1. CEN/TS 16183 - SLUDGE, TREATED BIOWASTE AND SOIL - DETERMINATION OF SELECTED PHTHALATES USING CAPILLARY GAS CHROMATOGRAPHY WITH MASS SPECTROMETRIC DETECTION (GC-MS)

8.1.1. METHOD DESCRIPTION

A summary of CEN/TS 16183 and modifications done by VITO is given in Table 32.

The method was used for the determination of the following compounds:

- Dimethylphthalate
- Diethylphthalate
- Dipropylphthalate
- Di-(2-methylpropyl)phthalate
- Dibutylphthalate
- Butylbenzylphthalate
- Dicyclohexylphthalate
- Di-(2-ethylhexyl)phthalate
- Dioctylphthalate
- Didecylphthalate
- Diundecylphthalate

Note that CEN/TS 16183 states that the applicability of the method to other phthalates is not excluded except the isomeric mixtures e.g. DiNP (di-isononylphthalate), but shall be verified in each case.

8.1.2. MEASUREMENT CONDITIONS APPLIED BY VITO

Instrument: Trace GC, Trace DSQ

Column:	DB-XLB 30m x 0.25 mm x 0.25 µm
Carrier gas:	He, flow 1 ml/min
Injection :	1 µl splitless with surge injector temperature 250 °C 1 mi.n splitless time surge pressure 300 kPa
GC-oven :	60 °C (1 min) ->320 °C (25 °C/min) Total run time: 15 min.
MS (SIM) :	source temp. 250°C

EI, 70 eV

Parameter	RT	mass	% m2 vs m1	% m3 vs m1
FTAL001A-DMP	5,73	163		
FTAL001B		77	19	
FTAL002A-DEP	6,42	149		
FTAL002B		177	24	
FTAL003A-DPropP	7,24	149		
FTAL003B		191	5,4	
FTAL004A-DIBP	7,62	149		
FTAL004B		223	6,0	
FTAL005A-DBP	8,03	149		
FTAL005B		205	5,8	
FTAL006A-BBP	9,59	149		
FTAL006B		91	58	
FTAL007A-DEHP	10,1	149		
FTAL007B		167	36	
FTAL007C		279		6,6
FTAL008A-DCHP	10,15	149		
FTAL008B		167	34	
FTAL008C		249		4,2
FTAL009A-DOP	10,74	149		
FTAL009B		279	5,7	
FTAL010A-DDcP	11,95	149		
FTAL010B		307	5,4	
FTAL011A-DUP	12,78	149		
FTAL011B		321	4,9	
FTAL012A-DMP-D4	5,73	167		
FTAL012B		81	16	
FTAL013A-DEP-D4	6,42	153		
FTAL013B		181	22	
FTAL014A-DIBP-D4	7,62	153		
FTAL014B		227	5,5	
FTAL015A-DBP-D4	8,03	153		
FTAL015B		209	3,9	
FTAL016A-DEHP-D4	10,1	153		
FTAL016B		171	30	
FTAL017A-DOP-D4	10,74	153		
FTAL017B		283	4,8	

8.1.3. CALIBRATION DIAGRAMS

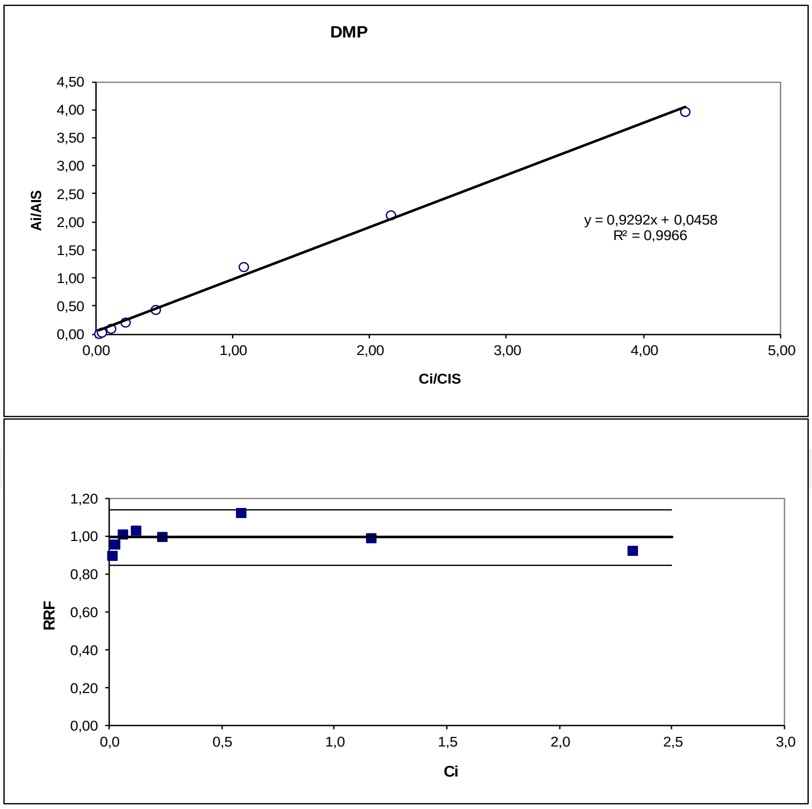
Calibration solutions were prepared in the concentration range of 0.01-2 mg/L. Calibration diagrams are given in Figure 21. Linearity is obtained for all compounds. The working ranges are:

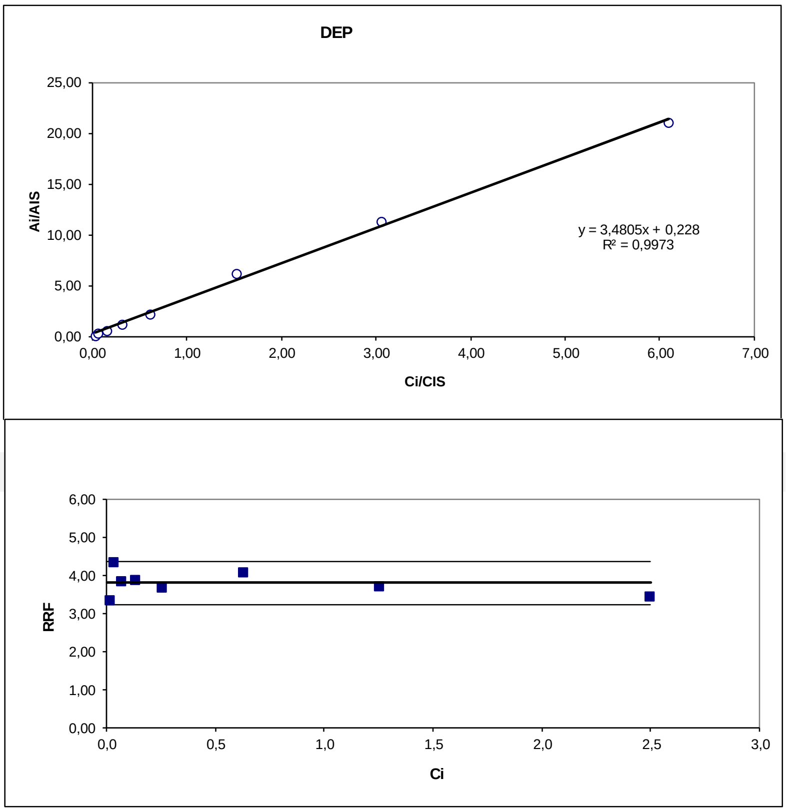
- DMP, DEP, DPP, DiBP, BBP: 0,01-2 mg/L (corresponds to 0,04-8 mg/kg sealant in case of 5 g intake and 20 mL final extract)
- DBP, DCHP, DOP: 0,02-2 mg/L
- DEHP, DDP, DUP: 0,05-2 mg/L

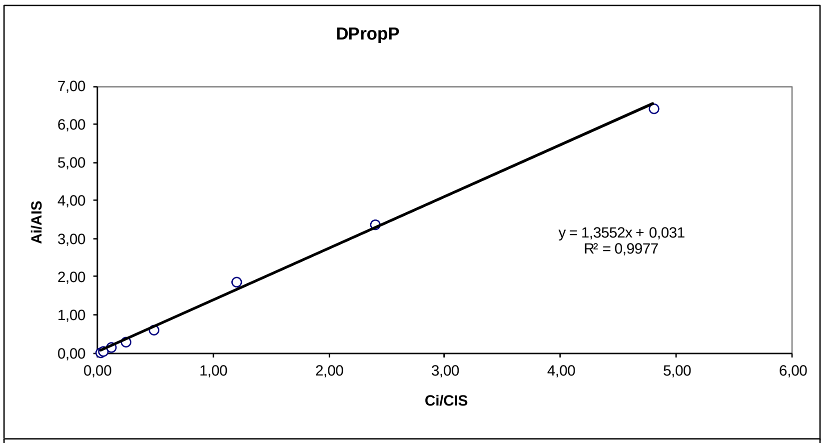
Table 32: Summary of CEN/TS 16183 and method applied by VITO

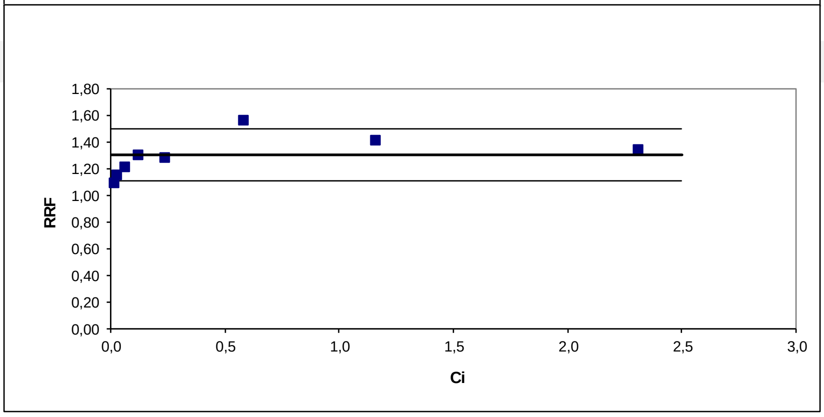
Samples Parameter list	Short description of the method	Departures from method by VITO and comments
~~PVC flooring (old)~~ Sealant 1 DMP DEP DPP DiBP DBP BBzP DCHP DEHP DOP DDP DUP	- Matrix: Sludge, treated biowaste, soil - Intake: 1-10 g - IS: ring-D_4- or ^{13}C-IS, typically 3 labelled phthalates - Extraction: drying with Na_2SO_4 or freeze drying; shaking with ethylacetate (>30 min)(remark: heating of glassware (400°C); deactivation of glassware with isooctane; don't use septa) - Clean-up (optional, to be avoided): activated aluminium oxide - Measurement: GC-MS Q m/z 149 (exc. DMP 163) - Quantification: internal standard method; LOQ: 0.1-0.5 mg/kg dm	- Intake: 5 g ground sealant (very high DiNP concentration in sealant!) - IS: D_4-DMP, D_4-DEP, D_4-DiBP, D_4-DBP, D_4-DEHP, D_4-DOP - Clean-up : n.a. - Remark: TS 16183 states: *the applicability to other phthalates is not excluded except the isomeric mixtures e.g. DiNP*

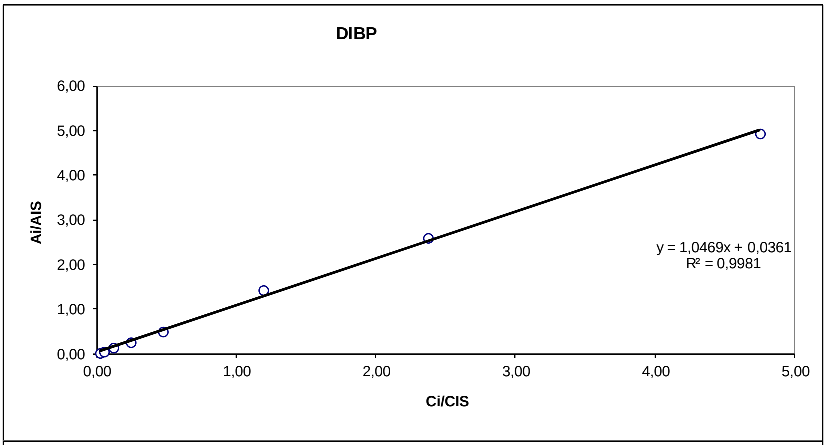
Figure 16: Calibration diagrams for phthalate esters (concentrations in mg/L)

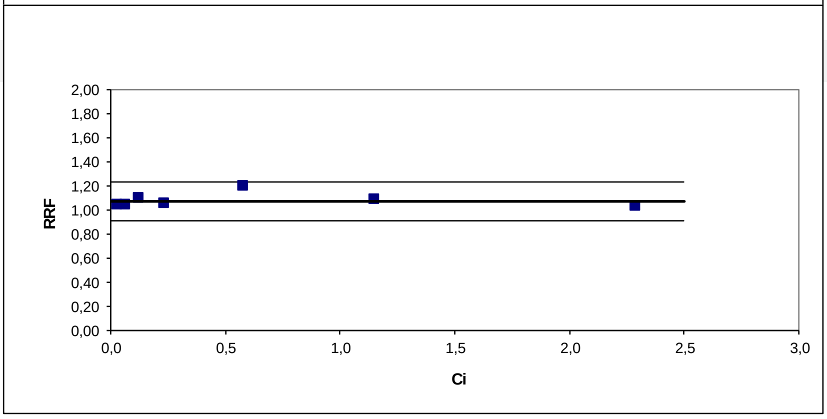





DPropP
Ai/AIS
7,00
6,00
5,00
4,00
3,00
2,00
1,00
0,00
0,00
1,00
2,00
3,00
4,00
5,00
6,00
Ci/CIS
y = 1,3552x + 0,031
R² = 0,9977


RRF
1,80
1,60
1,40
1,20
1,00
0,80
0,60
0,40
0,20
0,00
0,0
0,5
1,0
1,5
2,0
2,5
3,0
Ci


DIBP
Ai/AIS
6,00
5,00
4,00
3,00
2,00
1,00
0,00
0,00
1,00
2,00
3,00
4,00
5,00
Ci/CIS
y = 1,0469x + 0,0361
R² = 0,9981


RRF
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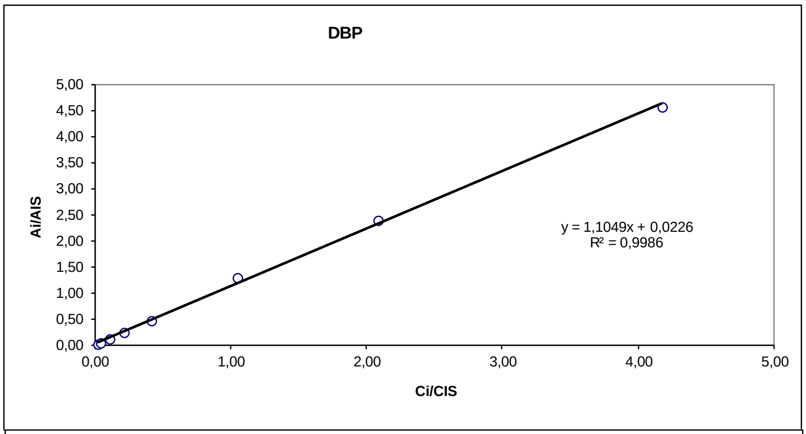
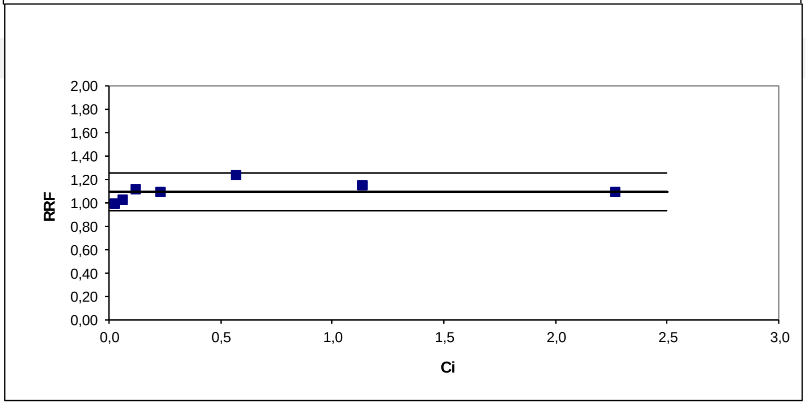
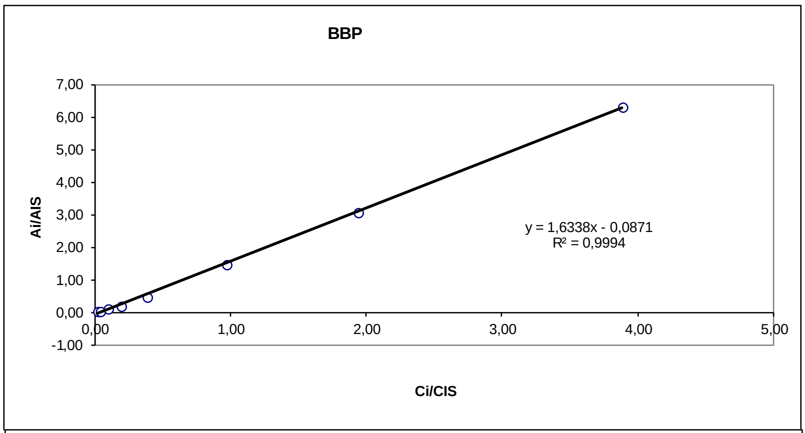
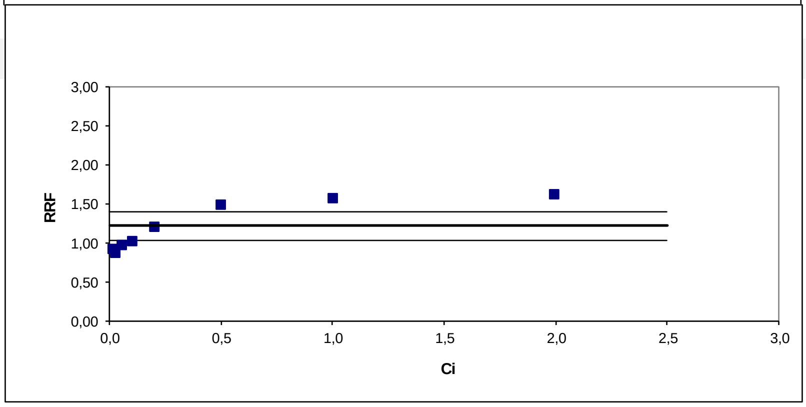
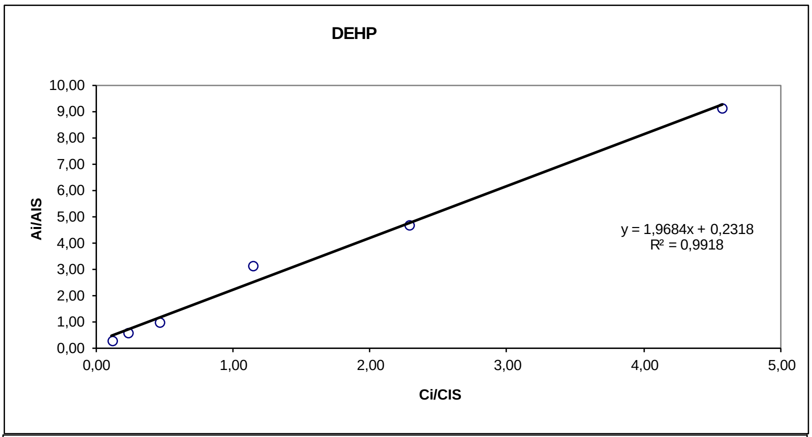
1,80
1,60
1,40
1,20
1,00
0,80
0,60
0,40
0,20
0,00
0,0
0,5
1,0
1,5
2,0
2,5
3,0
Ci

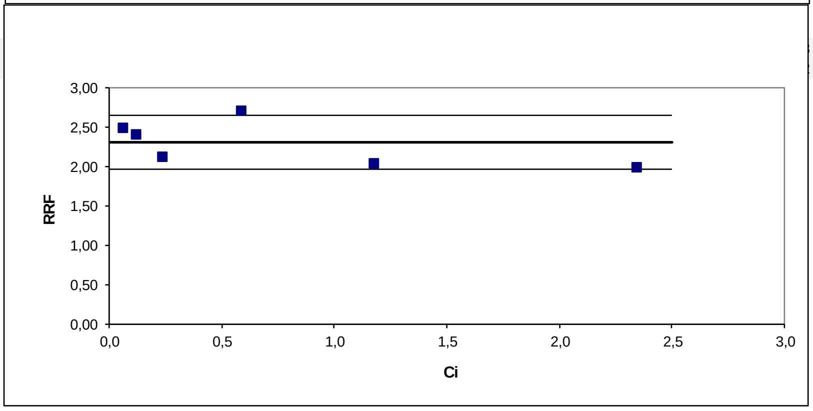

DBP
Ai/AIS
5,00
4,50
4,00
3,50
3,00
2,50
2,00
1,50
1,00
0,50
0,00
0,00
1,00
2,00
3,00
4,00
5,00
Ci/CIS
y = 1,1049x + 0,0226
R² = 0,9986

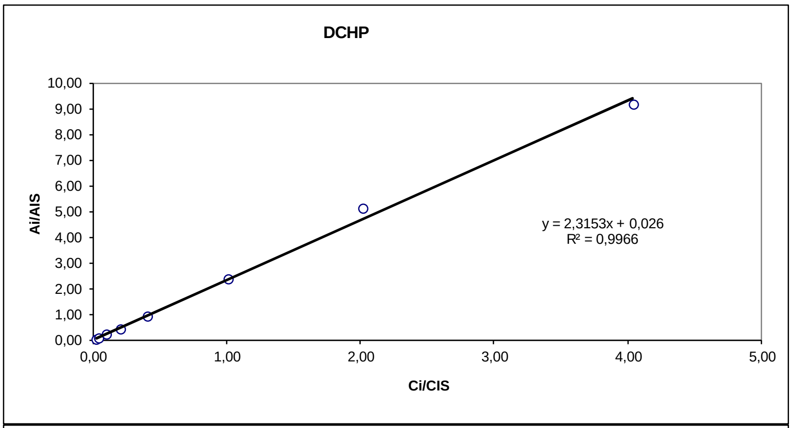

RRF
2,00
1,80
1,60
1,40
1,20
1,00
0,80
0,60
0,40
0,20
0,00
0,0
0,5
1,0
1,5
2,0
2,5
3,0
Ci

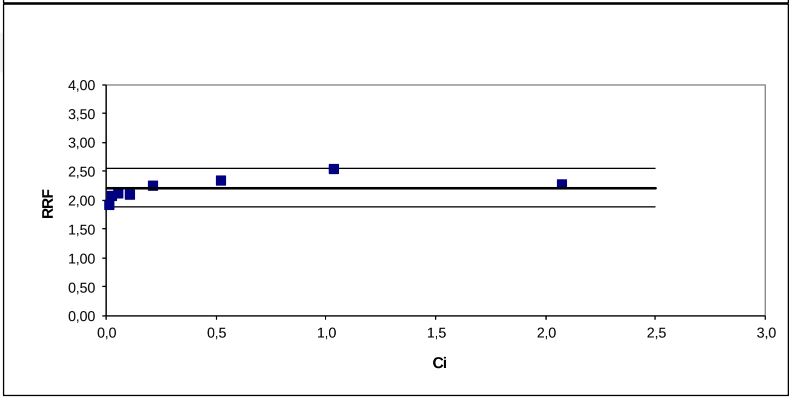

BBP
Ai/AIS
7,00
6,00
5,00
4,00
3,00
2,00
1,00
0,00
-1,00
0,00
1,00
2,00
3,00
4,00
5,00
Ci/CIS
y = 1,6338x - 0,0871
R² = 0,9994

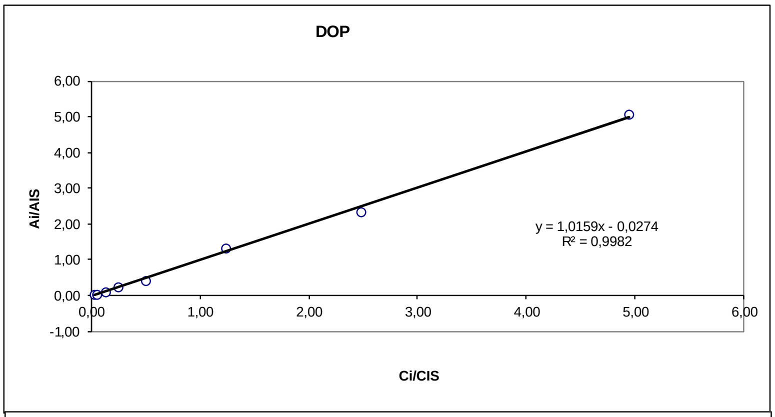

RRF
3,00
2,50
2,00
1,50
1,00
0,50
0,00
0,0
0,5
1,0
1,5
2,0
2,5
3,0
Ci


DEHP
Ai/AIS
10,00
9,00
8,00
7,00
6,00
5,00
4,00
3,00
2,00
1,00
0,00
0,00
1,00
2,00
3,00
4,00
5,00
Ci/CIS
y = 1,9684x + 0,2318
R² = 0,9918


RRF
3,00
2,50
2,00
1,50
1,00
0,50
0,00
0,0
0,5
1,0
1,5
2,0
2,5
3,0
Ci


DCHP
Ai/AIS
10,00
9,00
8,00
7,00
6,00
5,00
4,00
3,00
2,00
1,00
0,00
0,00
1,00
2,00
3,00
4,00
5,00
Ci/CIS
y = 2,3153x + 0,026
R² = 0,9966


RRF
4,00
3,50
3,00
2,50
2,00
1,50
1,00
0,50
0,00
0,0
0,5
1,0
1,5
2,0
2,5
3,0
Ci


DOP
Ai/AIS
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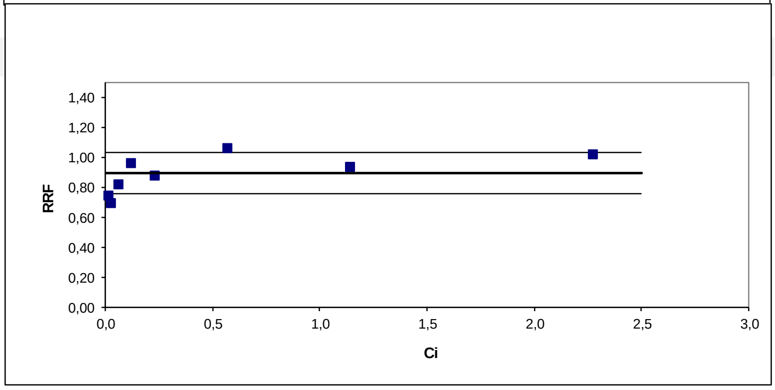
4,00
3,00
2,00
1,00
0,00
-1,00
0,00
1,00
2,00
3,00
4,00
5,00
6,00
y = 1,0159x - 0,0274
R² = 0,9982
Ci/CIS


RRF
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1,20
1,00
0,80
0,60
0,40
0,20
0,00
0,0
0,5
1,0
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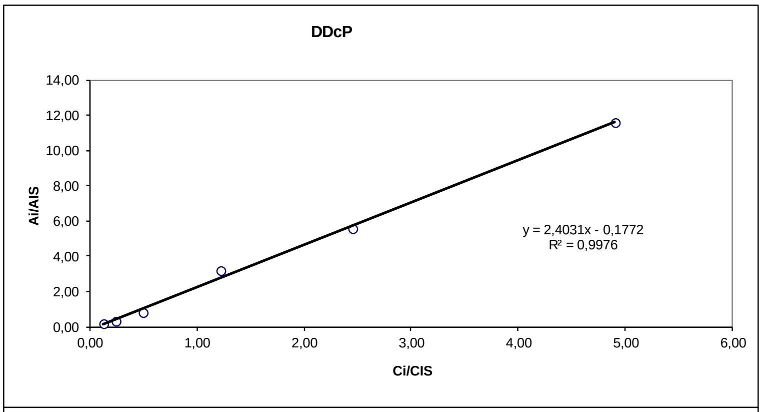
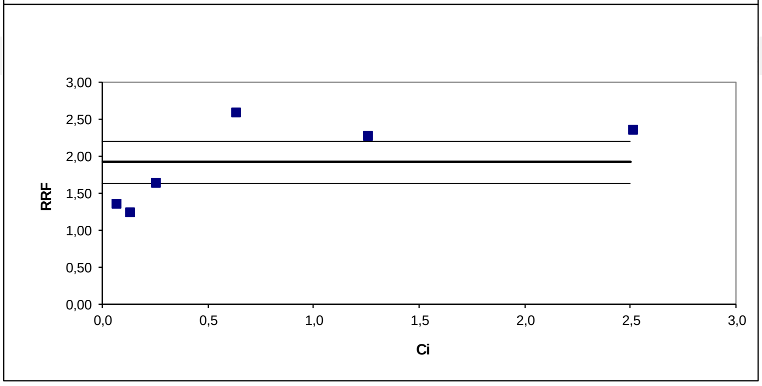
2,0
2,5
3,0
Ci


DDcP
Ai/AIS
14,00
12,00
10,00
8,00
6,00
4,00
2,00
0,00
0,00
1,00
2,00
3,00
4,00
5,00
6,00
y = 2,4031x - 0,1772
R² = 0,9976
Ci/CIS


RRF
3,00
2,50
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1,50
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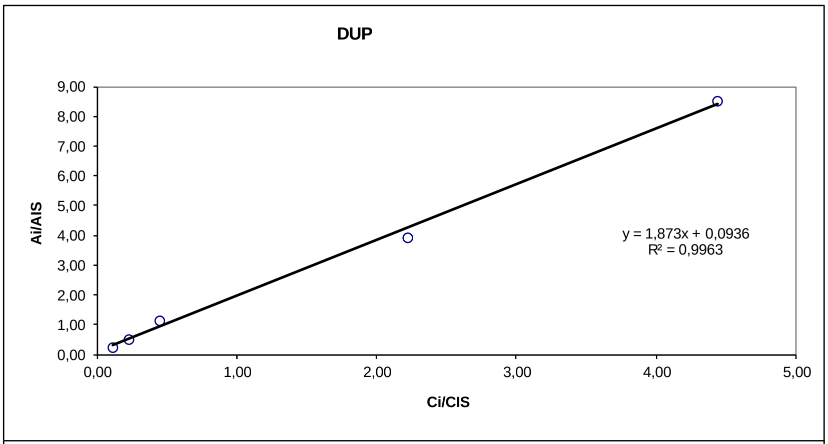
0,0
0,5
1,0
1,5
2,0
2,5
3,0
Ci


DUP
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7,00
6,00
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4,00
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2,00
1,00
0,00
Ai/AIS
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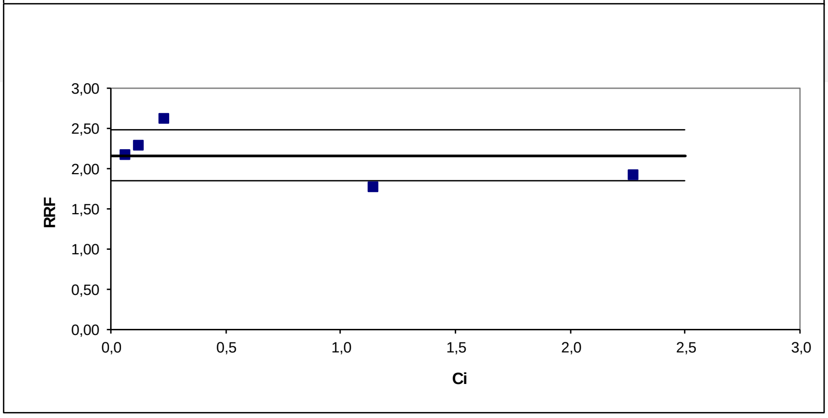
1,00
2,00
3,00
4,00
5,00
Ci/CIS
y = 1,873x + 0,0936
R² = 0,9963


3,00
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2,00
1,50
1,00
0,50
0,00
RRF
0,0
0,5
1,0
1,5
2,0
2,5
3,0
Ci

8.2. DETERMINATION OF PHTHALATES IN SEALANT 1 AND SEALANT 2

8.2.1. SAMPLE

Both sealants were received from Fraunhofer. Sealant 1 was a polyurethane kit, sealant 2 a polyacrylate kit. 5 kits of each were delivered. The contents of 2 kits were mixed. The paste was spread on a glass plate and after hardening the material was cut and grinded into pieces <1 mm.

8.2.2. ANALYSIS

- 20 ml ethylacetate was added to 5 g ground sample
- Internal standards (10 µg) were added and the mixture was shaken during 30 minutes
- The supernatant solvent was transferred to an appropriate tube for centrifugation
- Finally the extract was filtered using an Acrodisc 0.2 µm PTFE filter
- The extract was analysed using GC-MS without and after 1000 times dilution; an additional amount of internal standard was added to a part of the diluted extract

8.2.3. COMMENTS

The samples only contain minor amounts of CEN/TS 16813 phthalates, but considerable amounts of DiNP which does not belong to the scope of the standard. The very large DINP peak interferes with DEHP, DCHP, DOP, DDP and DUP.

Sonication of the extract (5 g sample in 20 ml ethyl acetate) leads to a 'cloudy' and ‘sticky’ solution. Centrifugation and filtration were necessary; several filters (acrodisc 0.5 µm) had to be used to obtain 500-1000 µl of clear filtrate. The GC-MS system got quickly dirty due to high DINP content and extracted polymer.

Because of different concentration levels of individual phthalates and DINP several extract dilutions had to be analysed using different GC-MS settings.

8.2.4. CHROMATOGRAMS

Chromatograms of phthalates are given in Figure 17 and Figure 18 for the resp. sealant extracts.

8.2.5. RESULTS

→ Repeatability

The results of the replicate determinations of phthalates in the resp. sealants are given in Table 33. Due to interference of the DEHP-d4 signal by DiNP isomers the concentrations of DEHP and DCHP in sealant 1 were calculated using DBP-d4 as internal standard. For sealant 1 all CEN/TS 16183 phthalates were found in concentrations <1 mg/kg, except BBP. The repeatabilities vary from 5 to 19 %. Sealant 2 contains low concentrations of DMP, DiBP and DBP (<1 mg/kg), but higher

concentrations of BBP and DEHP (resp. 9 and 88 mg/kg). The repeatabilities vary from 4 to 10 %, with the exception of the most volatile phthalate DMP, for which 29% RSD was calculated, due to an outlier value of 0.051 mg/kg.
In Table 34 the results calculated for DiNP are shown. The sealants contain high amounts of DiNP, resp. 40 and 10 m/m %. DiNP can be determined precisely; the repeatabilities are resp. 3 and 6% for sealant 1 and 2.

→ Recoveries

The results of matrix additions are shown in Table 35. The sealants were spiked with resp. 1 and 8 mg/kg of each phthalate. The recoveries were not quantitative, 60% on average, and method optimisation using longer extraction times, repeated extractions and/or more appropriate solvents will be needed to improve the bias in case of sealant analysis.

→ Sensitivity

The lowest concentrations of the linear range correspond to sample concentrations of 0.04 to 0.2 mg/kg, which is below the lowest mass contents mentioned in the scope of CEN/TS 16183. Typical procedural blank values are given in Table 36. For most phthalates the blank values are <0.01 mg/kg; for DEHP values of 0.02 and 0.05 mg/kg were measured.

8.3. CONCLUSION

Although repeatabilities and LOD’s can be considered to be acceptable, recovery data indicate that method optimization is needed to obtain more accurate results.

Table 33: Measured concentrations of selected phthalates in sealant 1 and 2

Sealant 1	***A***	***B***	***C***	***D***	***E***	***average***	***CV_r***
	mg/kg	*mg/kg*	*mg/kg*	*mg/kg*	*mg/kg*	*mg/kg*	*%*
DMP	0,25	0,27	0,27	0,30	0,26	0,27	6,9
DEP	0,009	0,010	0,010	0,010	0,008	0,01	10
DPP	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	
DIBP	0,072	0,061	0,057	0,054	0,066	0,062	12
DBP	0,038	0,055	0,052	0,046	0,052	0,049	14
BBP	2,6	2,6	2,7	2,9	2,9	2,74	5,5
DEHP*	0,50	0,56	0,45	0,46	0,45	0,48	10
DCHP*	0,12	0,10	0,09	0,08	0,08	0,093	19
DOP	interfered by DiNP						
DDcP	<0,03	<0,03	<0,03	<0,03	<0,03		
DUP	<0,03	<0,03	<0,03	<0,03	<0,03		

**Calculated using DBP-d4 as IS because of interfered DEHP-d4 signal*

Sealant 2	***A***	***B***	***C***	***D***	***E***	***average***	***CV_r***
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	%
DMP	0,072	0,090	0,11	0,11	0,051	0,087	29
DEP	<0,02	<0,02	<0,02	<0,02	<0,02		
DPropP	<0,01	<0,01	<0,01	<0,01	<0,01		
DIBP	0,030	0,030	0,037	0,031	0,029	0,031	10
DBP	0,026	0,023	0,022	0,022	0,023	0,023	7,1
BBP	8,9	9,1	9,1	9,0	9,8	9,18	3,9
DEHP	88	81	90	88	91	87,6	4,5
DCHP	<0,06	<0,06	<0,06	<0,06	<0,06		
DOP	interfered by DiNP						
DDcP	interfered by DiNP						
DUP	interfered by DiNP						

Table 34: Measured concentrations of DiNP in sealant 1 and 2

DiNP	***Sealant 1*** m/m %	***Sealant 2*** m/m %
A	40,3	11,6
B	39,2	11,6
C	42,0	10,5
D	40,6	11,1
E	39,2	10
Average	40,26	10,96
CV_r	2,9%	6,4%

Table 35: Recoveries of phthalates added to sealant 1 and sealant 2

Sealant 1	***spike LOW***			***spike HIGH***		
	Result mg/kg	***Theor. Conc.*** mg/kg	***Recovery*** %	***Result*** mg/kg	***Theor. Conc.*** mg/kg	***Recovery*** %
DMP	0,830	1,07	77	5,63	8,09	70
DEP	0,731	1,15	64	5,29	8,68	61
DPropP	0,700	1,05	66	4,60	7,95	58
DIBP	0,638	1,04	61	4,54	7,88	58
DBP	0,611	0,92	67	4,15	6,93	60
BBP*	0,300	0,95	31	3,90	7,21	54
DEHP*	0,320	1,08	30	3,32	8,16	41
DCHP*	0,258	1,05	25	2,56	7,90	32

**Calculated using DBP-d4 as IS because of interfered DEHP-d4 signal*

Sealant 2	***spike LOW*** ***Result*** mg/kg	***Theor. Conc.*** mg/kg	***Recovery*** %	***spike HIGH*** ***Result*** mg/kg	***Theor. Conc.*** mg/kg	***Recovery*** %
DMP	0,836	1,07	78	5,71	8,03	71
DEP	0,690	1,14	60	5,50	8,61	64
DPropP	0,640	1,05	61	4,40	7,88	56
DIBP	0,616	1,04	59	4,47	7,81	57
DBP	0,574	0,91	63	4,27	6,87	62
BBP	0,300	0,95	32	6,80	7,15	95
DEHP	*	*	*	*	*	*
DCHP	0,480	1,04	46	6,70	7,84	85

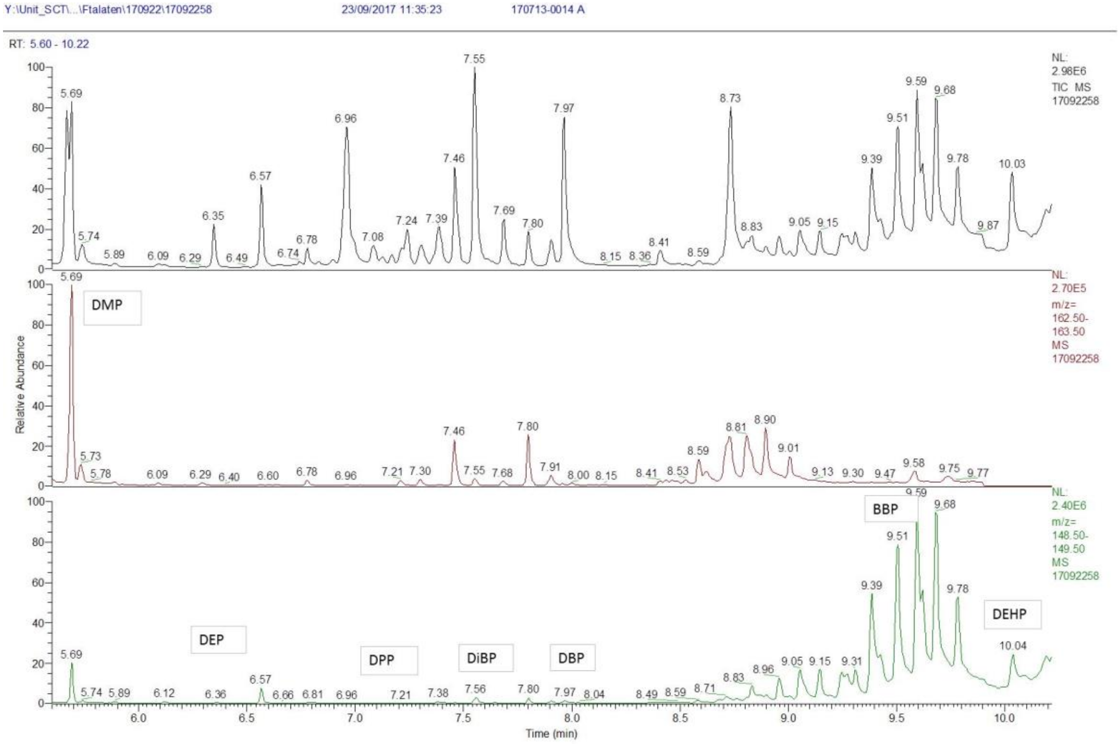
**DEHP addition low compared to orginal concentration (88 mg/kg)*

Table 36: Phthalate procedural blanks

	Blank 1 *mg/kg*	***Blank 2*** *mg/kg*
DMP	0,002	0,009
DEP	0,004	0,003
DPropP	0,006	0,003
DIBP	0,012	0,006
DBP	0,010	0,009
BBP	0,009	0,008
DEHP	0,023	0,049
DCHP	0,011	0,008
DDcP	0,014	0,003
DUP	0,019	0,005

Figure 17: TIC chromatogram and ion chromatograms for phthalates in a polyurethane sealant extract

5-10.5 min (undiluted)



10-14 min (1000 x diluted)

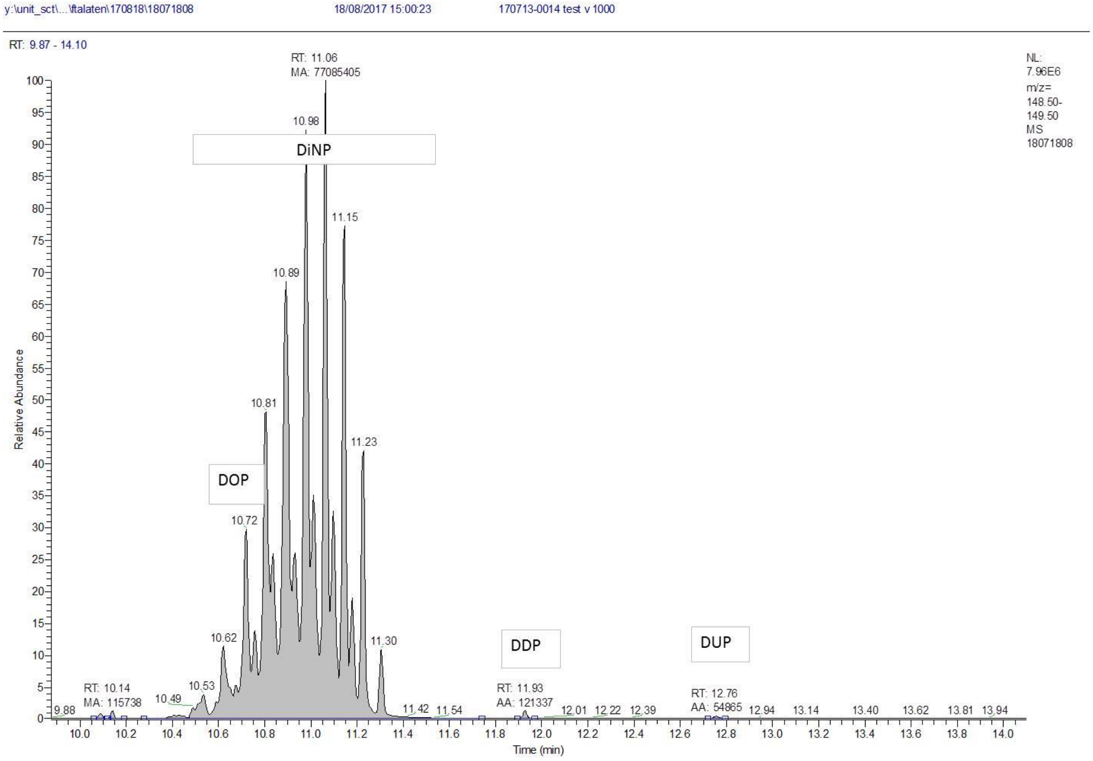
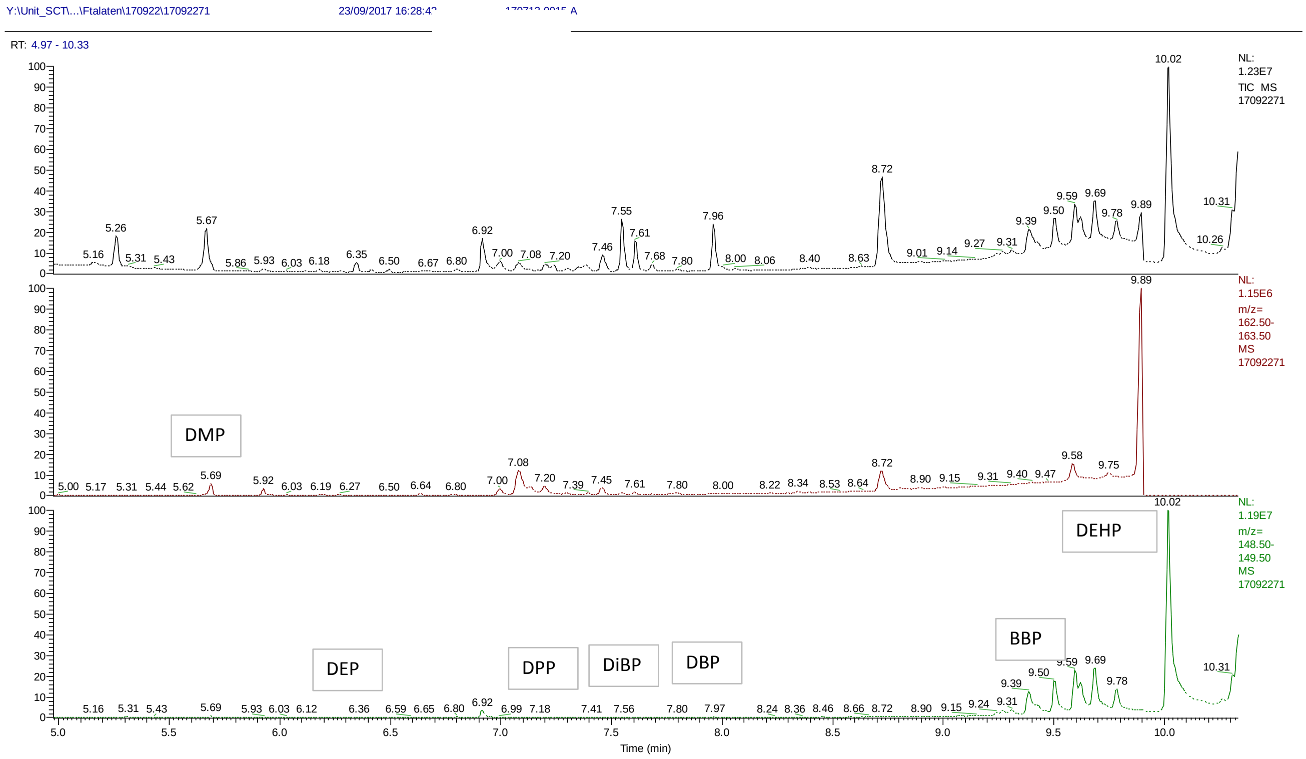
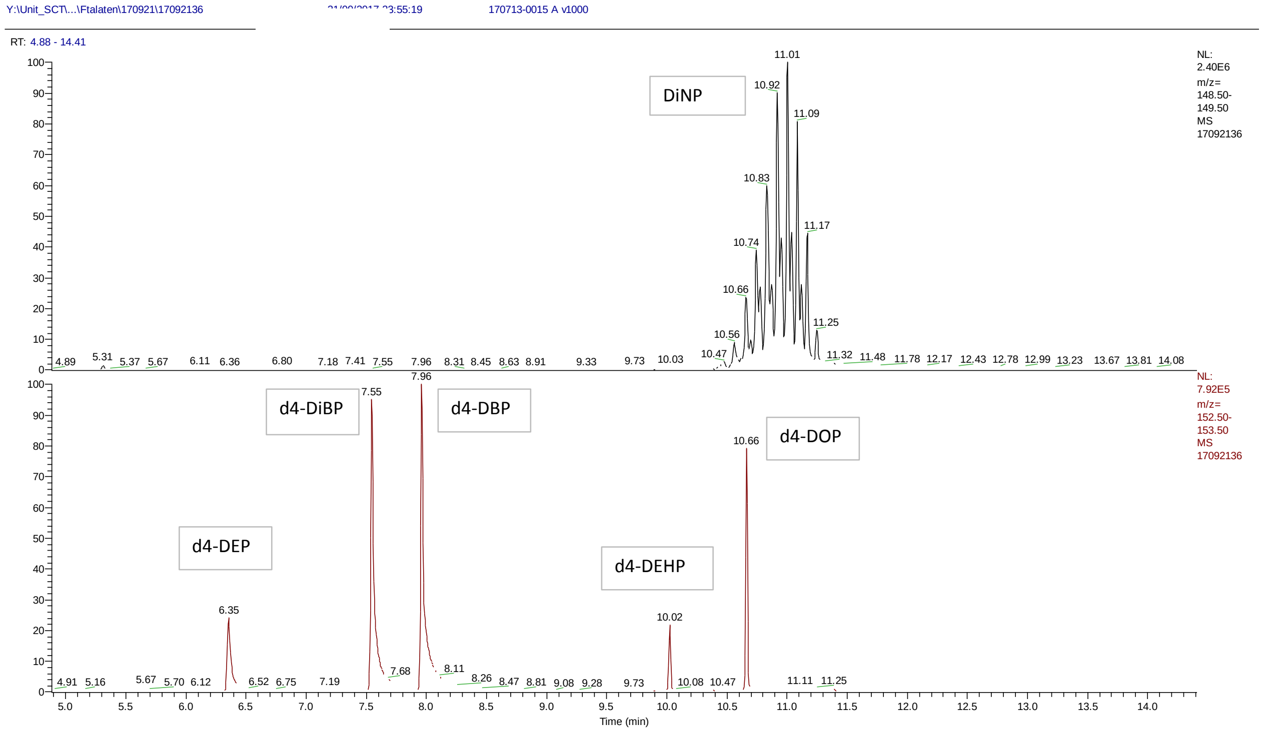


Figure 18: TIC chromatogram and ion chromatograms for phthalates in a polyacrylate sealant extract

5-10.5 min (undiluted)



1000 x diluted



CHAPTER 9 DETERMINATION OF THE CONTENT OF PENTACHLOROPHENOL IN CONSTRUCTION PRODUCTS

9.1. CEN/TR 14823 - DURABILITY OF WOOD AND WOOD-BASED PRODUCTS - QUANTITATIVE DETERMINATION OF PENTACHLOROPHENOL IN WOOD - GAS CHROMATOGRAPHIC METHOD

9.1.1. METHOD DESCRIPTION

A summary of CEN/TR 14823 and modifications done by VITO is given in Table 37. For the detection of PCP VITO uses GC-MS instead of GC-ECD. GC-MS is recommended because of higher selectivity and the possibility to correct for losses during extraction, derivatization and injection by using ^{13}C-labelled PCP as internal standard.

9.1.2. MEASUREMENT CONDITIONS

Hardware	GC-MS	Trace GC Ultra (Thermo) Trace DSQ (Thermo)
	GC-column	VF-17MS 30 m 0.25 mm 0.25 µm
Injector parameters	injection volume	1 µl
	injection modus	CT Splitless w/surge
	injection temperature	250 °C
	surge pressure	300 kPa
	surge duration	1 min
	split flow	25 ml/min
	splitless time	1 min
GC parameters	carrier gas	He - const flow 1 ml/min
	initial temperature	75°C
	initial time	1 min
	rate #1	25°C/min
	final temperature #1	300°C
	hold time #1	0 min
MS parameters	mode	Full scan
	scan 1	200-300
	scan rate 1	750
	source temperature	250 °C
	interface temperature	310 °C
	solvent delay	4 min

SIM ions	m/z 1 (Q)	m/z 2 (q)
Pentachlorophenol	266	268
13C-Pentachloorphenol	274	276
13C-1,2,3,4-tetrachlorobenzene	222	224

9.1.3. CALIBRATION DIAGRAM

PCP calibration standards undergo the same derivatisation procedure as the sample extracts (see below). A calibration diagram for PCP (internal standard method) is given in Figure 19. The diagram shows very good linearity in the range of 10 – 1000 µg/l extract. This corresponds to a working range of 0,01 – 1 mg/kg wood sample, based on 1 g intake and 1 mL final extract volume.

Figure 19: Calibration diagram for PCP

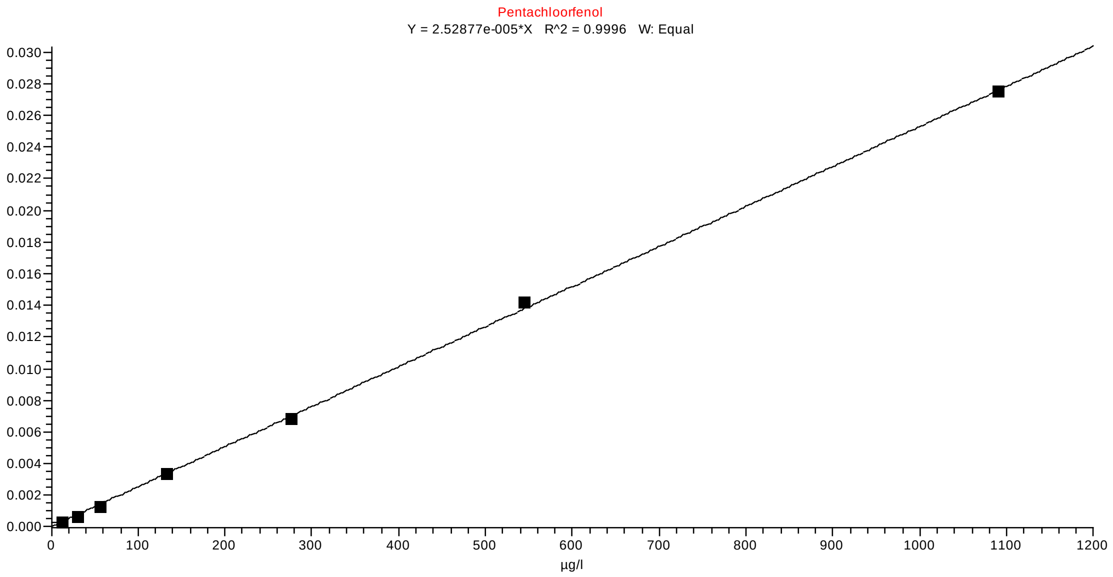


Table 37: Summary of CEN/TR 14823 and method applied by VITO

Samples Parameter list	Short Description of the method to be used	Departures from method by VITO and comments

Wood powder (CRM)
Pentachlorophenol
	- Matrix: wood
	- Intake: 1 – 5 g
	- IS: 2,4,6-tribromophenol
	- Extraction: USE with MeOH
	- Derivatization:
	  - addition of K_2CO_3 followed by acetylation with acetic anhydride
	  - extraction of acetate esters with n-hexane
	- Measurement: GC-ECD
	- LOQ: 100 µg/kg d.m.
		- IS: ^{13}C-PCP for more accurate correction of recovery during sample preparation
		- Washing of the hexane extract with water to remove interferences
		- Measurement: GC-MS

9.2. DETERMINATION OF PCP IN WOOD POWDER

9.2.1. SAMPLE

60 g of wood powder (beechwood, BCR-683) was received from JRC (Geel, Belgium). The sample was stored at -18°C in expectation of analysis. In addition to PCP the sample also contains considerable ammounts of PAH.

9.2.2. ANALYSIS

- 10 mL of methanol containing 10 µg ^{13}C-PCP was added to 1 g wood powder
- The mixture was sonicated during 1 h at 40°C.
- The mixture was allowed to settle and 1 mL of supernatant was taken for derivatization; 30ml 0.1M K2CO3-buffer was added, followed by the addition of 2 ml acetic anhydride and the mixture was shaken during 2 min.
- PCP-acetate was extracted by shaking with n-hexane during 10 min. The extraction was repeated once.
- The hexane layers were combined, washed with water, dried with Na_2SO_4 and evaporated to 1 mL.
- ^{13}C-tetrachlorobenzene was added to the final extract before injection into the GC-MS

9.2.3. COMMENTS

- As stated above we advice to include GC-MS as detection technique in the standard.
- ^{13}C-PCP should be used as internal standard (instead of tribromophenol) for correct quantification.
- Washing of the hexane extract with water is recommended to remove excess acetic anhydride and other polar constituents.

9.2.4. CHROMATOGRAM

A total ion chromatogram and chromatogram for m/z 266 is shown in Figure 20 for a beechwood extract.

9.2.5. RESULTS

→ Repeatability

The results of the replicate determinations of PCP in wood extracts are summarised in Table 38. The results show a very good repeatability of 5 %.

→ Recoveries

Recoveries were calculated relative to the certified value of 3.6 mg/kg. The average recovery was 104% (see Table 38).

→ Sensitivity

A LOD value was calculated on the basis of the signal-to-noise ratio for a wood extract. The LOD for 1 g intake and 1 ml final extract volume was <0,1 mg/kg and meets the LOD requirement of the umbrella standard.

Table 38: Measured concentrations of PCP in wood powder (BCR 683) and recoveries.

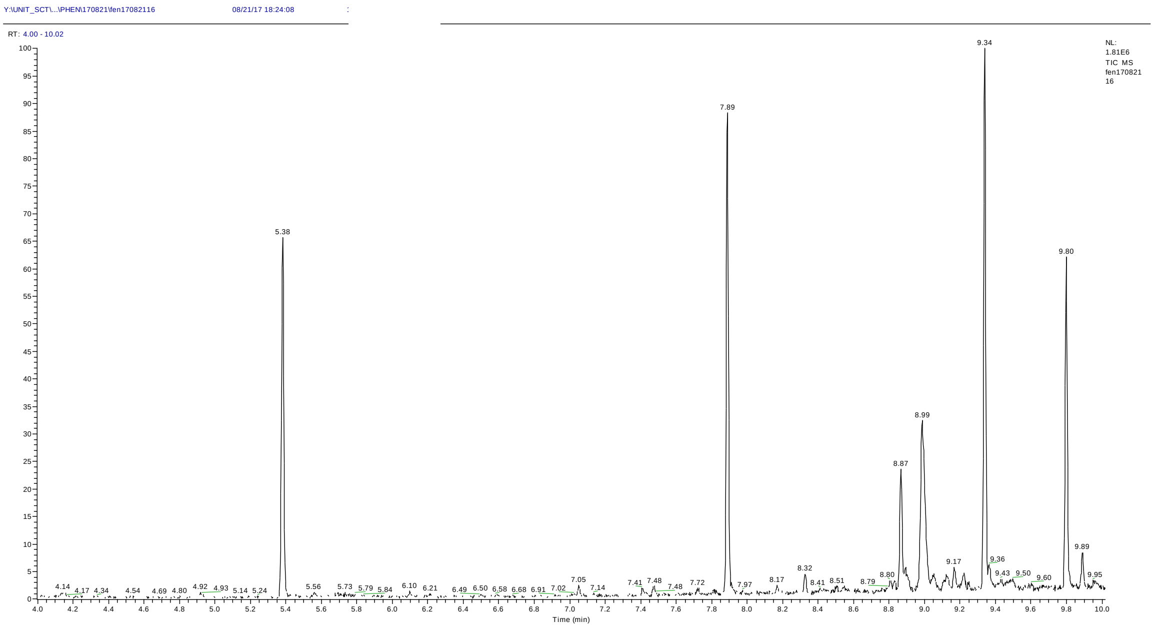
ID	***PCP*** mg/kg	***Recovery*** %
Wood powder 1	3,70	103
Wood powder 2	3,53	98
Wood powder 3	3,84	107
Wood powder 4	4,05	113
Wood powder 5	3,67	102
Average	3,76	104
Standdev	0,20	
CV_r%	5,2	

9.3. CONCLUSION

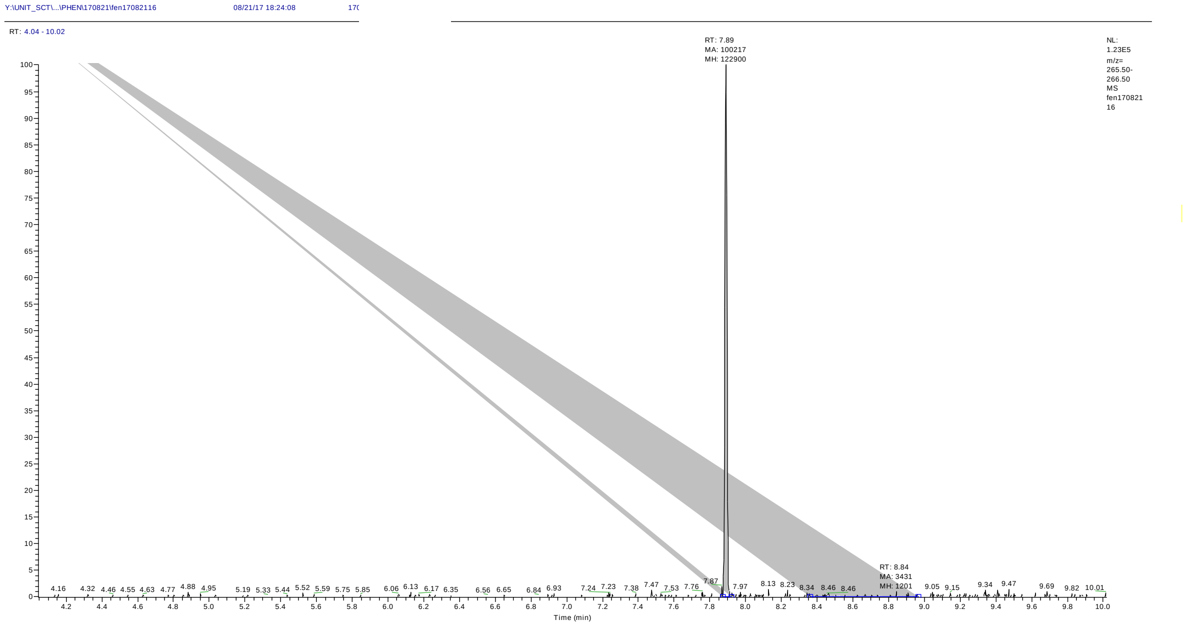
Method CEN/TR 14823 is suited for the analysis of PCP in wood.
Advised modifications are the inclusion of the more selective GC-MS as detection technique, the use of ^{13}C-PCP for a more reliable quantification and the washing of the hexane extract for the removal of interferences.

Figure 20: TIC and ion chromatogram (m/z 266) for PCP in wood powder extract

TIC



m/z 266



CHAPTER 10 DETERMINATION OF THE CONTENT OF SELECTED BIOCIDES IN CONSTRUCTION PRODUCTS

10.1. EN 15637 FOODS OF PLANT ORIGIN - DETERMINATION OF PESTICIDE RESIDUES USING LC-MS/MS FOLLOWING METHANOL EXTRACTION AND CLEAN-UP USING DIATOMACEOUS EARTH PESTICIDE

10.1.1. METHOD DESCRIPTION

A summary of EN 15637 and modifications done by VITO is given in Table 39.

The method was used for the determination of the following biocides:
- Diuron
- Terbutryn
- Methylisothiazolinone (MIT)
- Chloromethylisothiazolinone (CMIT)
- Benzisothiazolinone (BIT)
- Octylisothiazolinone (OIT)
- Propiconazole
- Tebuconazole
- Carbendazim

10.1.2. MEASUREMENT CONDITIONS APPLIED BY VITO

Instrument: Waters Acquity UPLC-Xevo TQ-S

LC-conditions
Injection: 10 uL
Column: BEH Shield RP 18 1.7µm, 2.1x100mm
Column temperature: 40°C
Mobile phase
A: Water + 0.1%FA + 4mM NH4AC
B: ACN + 0.1% FA

Time	A	B	flow
0	99	1	0,5
1	99	1	0,5
12	1	99	0,5
13	1	99	0,5
13,1	99	1	0,5
15	99	1	0,5

MS conditions
Ionisation: electrospray, positive mode

MRM transitions

Component	MRM	RT(min)
MIT	116>99	0,9
	116>101	
MIT-d3	119>102	0,91
	119>104	
CMIT	150>87	3,05
	150>115	
CMIT-d3	153>90	3,02
	153>118	
BIT	152>109	4,1
	152>134	
BIT C13	158>115	4,1
	158>140	
OIT	214>84	7,58
	214>102	
Diuron	233>72	6,91
	233>160	
Terbutryn	242>91	6,99
	242>186	
Terbutryn-d5	247>191	6,93
Terbuconazole	308>125	7,99
	308>151	
Triphenylphosphate	327>77	8,86
	327>152	
Propiconazole	342>123	8,25
	342>159	
Tris-(1,3-dichloroisopropyl)phosphate	431>99	8,64
	431>209	
Carbendazim	192>160	3,17
	192>132	

10.1.3. CALIBRATION DIAGRAMS

Calibration solutions were prepared in the concentration range of 0.1-150 µg/L. Calibration diagrams are given in Figure 21. Linearity is obtained for all compounds. The working ranges are:

- Diuron: 0.1-80 µg/L
- Terbutryn: 0.2-8 µg/L
- MIT: 0.1-80 µg/L
- CMIT: 0.1-80 µg/L
- BIT: 0.1-120 µg/L
- OIT: 0.1-170 µg/L

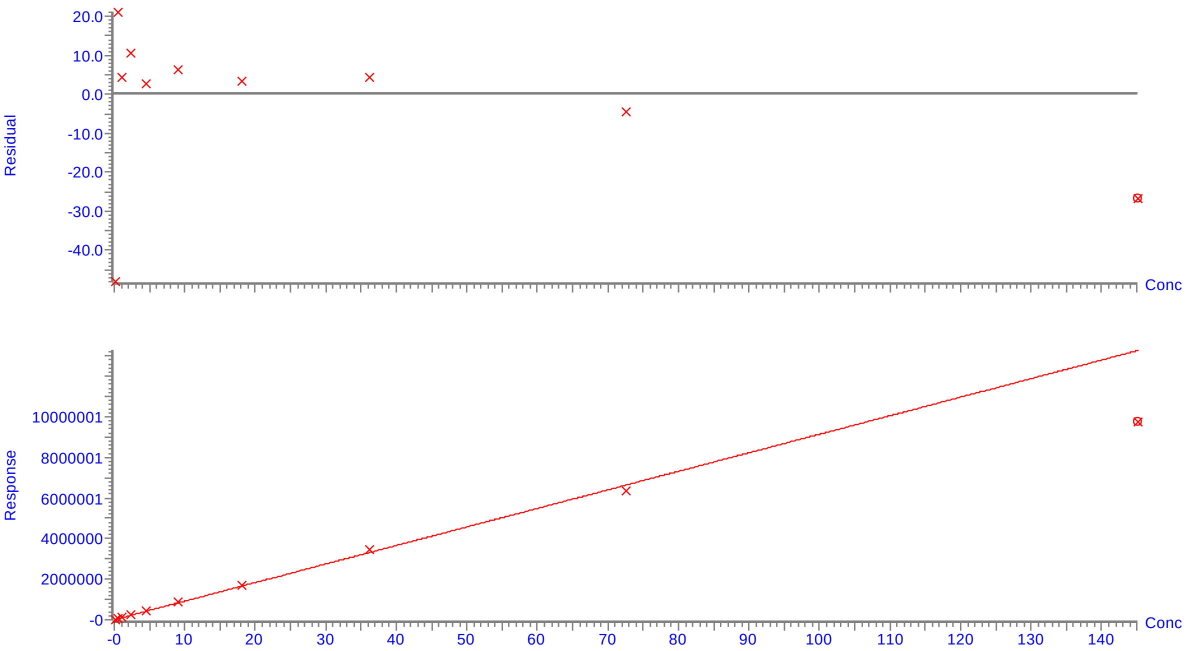
- Tebuconazole: 0.1-130 µg/L
- Propiconazole: 0.1-150 µg/L
- Carbendazim: 0.03-11 µg/L

Table 39: Summary of EN 15637 and method applied by VITO

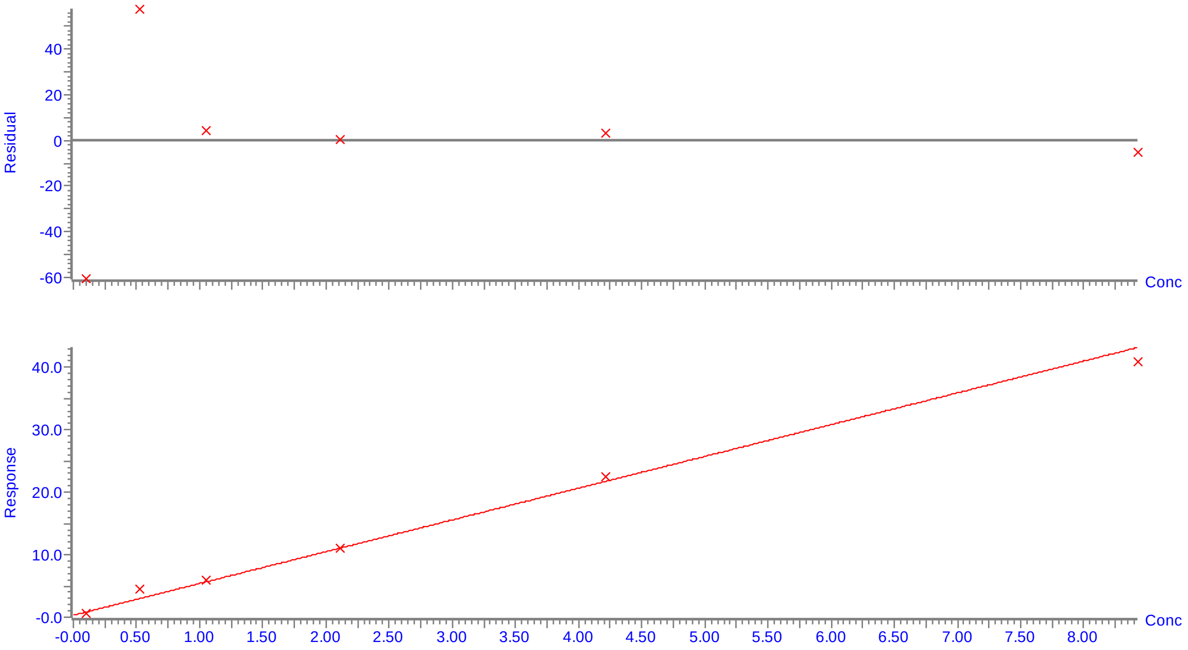
Samples Parameter list	Short Description of the method to be used	Departures from method by VITO and comments
Sealant Render Wood treated with biocide Diuron Terbutryn Methylisothiazolinone (MIT) Chloromethylisothiazolinone (CMIT) Benzisothiazolinone (BIT) Octylisothiazolinone (OIT) Propiconazole Tebuconazole Carbendazim	- Matrix: foods of plant origin - Intake: 5 – 10 g - IS: Triphenyl phosphate, tris-(1,3-dichlorisopropyl)-phosphate, bis-nitrophenyl urea (nicarbazin) – optional use of IS and QC - Extraction: methanol after addition of some water, high speed blender - Clean-up: diatomaceous earth (ChemElut CE1005) - Measurement: LC-MS/MS (SRM) - Calibration: matrix matched or IS method - LOQ: not given, biocide dependent	- IS: BIT-13C6, MIT-d3, CIT-d3, terbutryn-d5, Diuron-d6 - Clean-up: none - Calibration: external or internal standard method

Figure 21: Calibration diagrams for biocides

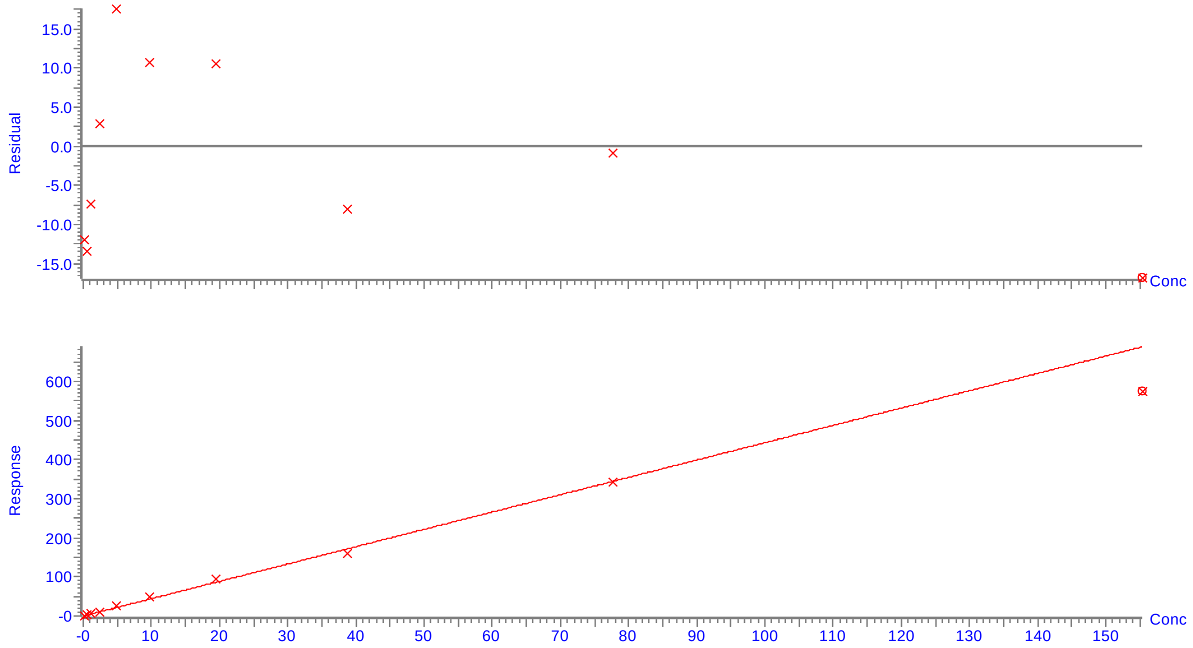
Compound name: diuron
Correlation coefficient: r = 0.998758, r^2 = 0.997518
Calibration curve: 91328.4 * x + 8031.9
Response type: External Std, Area
Curve type: Linear, Origin: Exclude, Weighting: 1/x, Axis trans: None



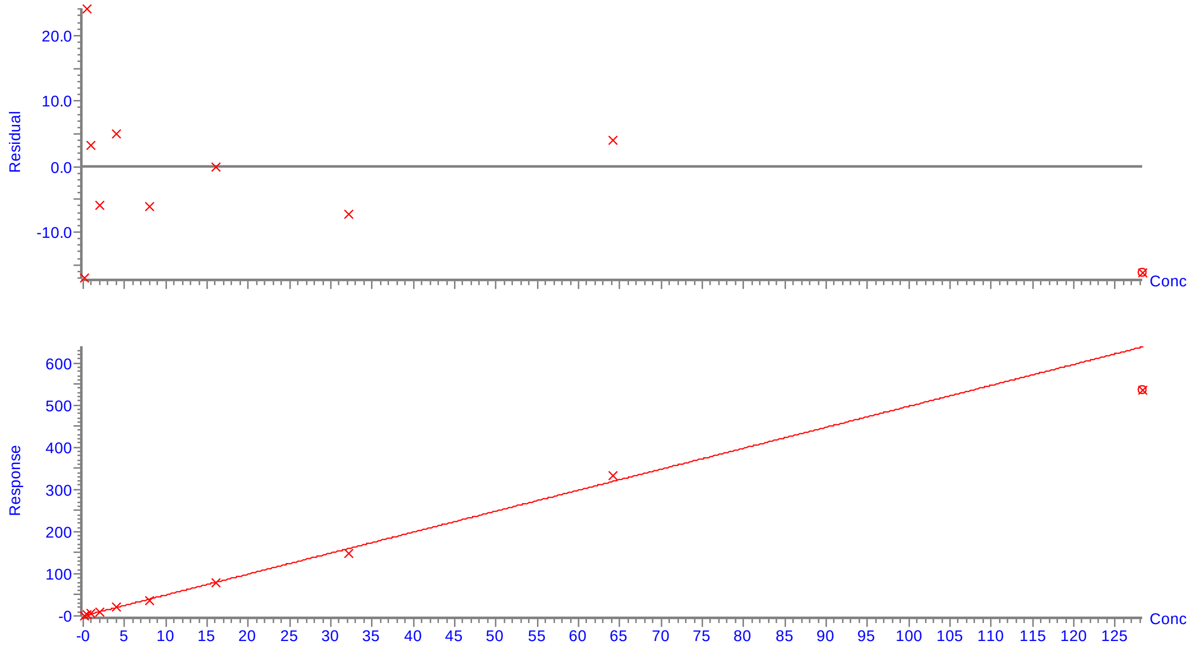
Compound name: terbutryn
Correlation coefficient: r = 0.991320, r^2 = 0.982715
Calibration curve: 5.08286 * x + 0.318612
Response type: Internal Std (Ref 10), Area * (IS Conc. / IS Area)
Curve type: Linear, Origin: Exclude, Weighting: 1/x, Axis trans: None



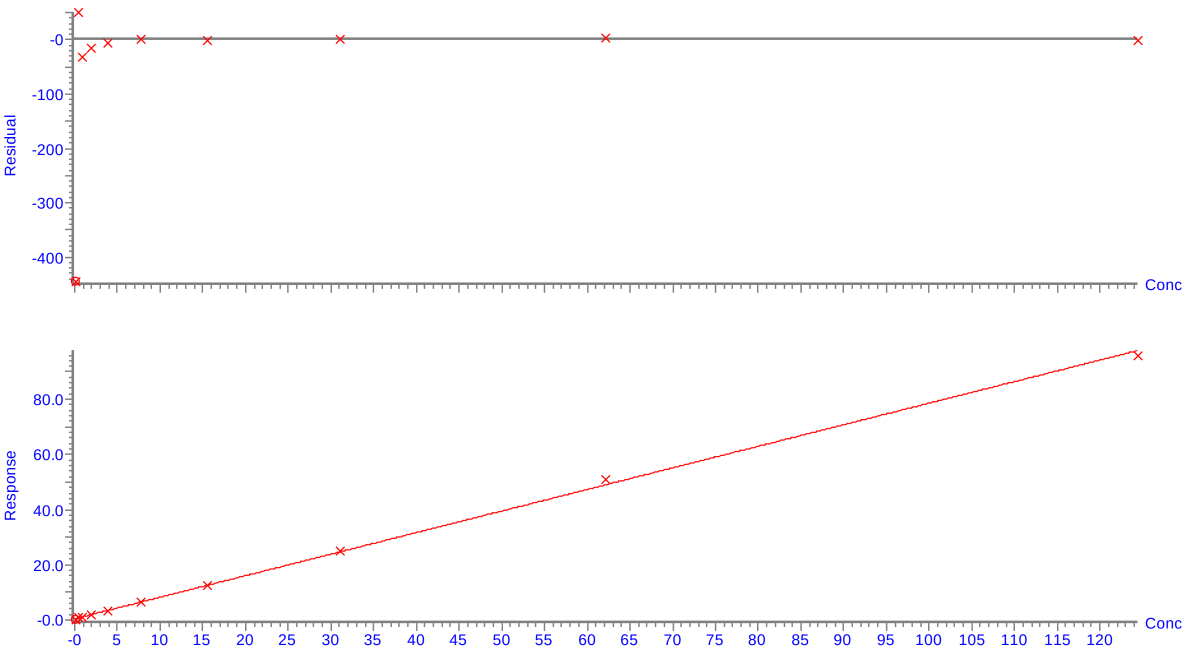
Compound name: MIT
Correlation coefficient: r = 0.997454, r^2 = 0.994915
Calibration curve: 4.43291 * x + -0.240429
Response type: Internal Std (Ref 4), Area * (IS Conc. / IS Area)
Curve type: Linear, Origin: Exclude, Weighting: 1/x, Axis trans: None



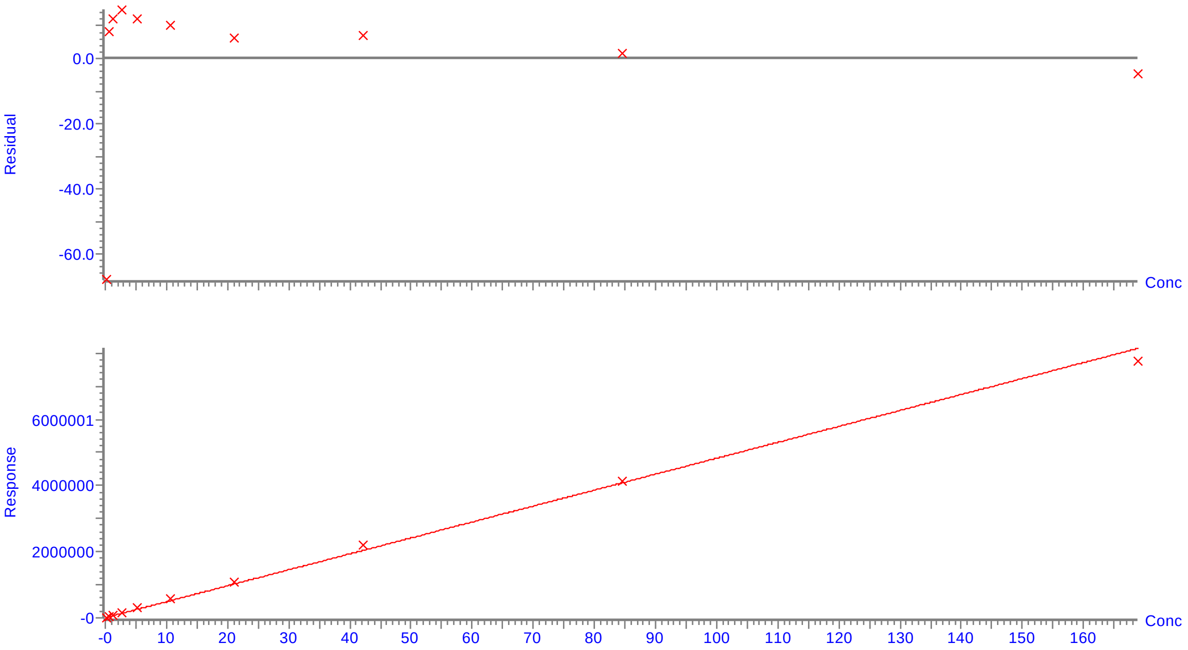
Compound name: CMIT
Correlation coefficient: r = 0.998527, r^2 = 0.997056
Calibration curve: 4.97121 * x + 0.00426928
Response type: Internal Std (Ref 7), Area * (IS Conc. / IS Area)
Curve type: Linear, Origin: Exclude, Weighting: 1/x, Axis trans: None



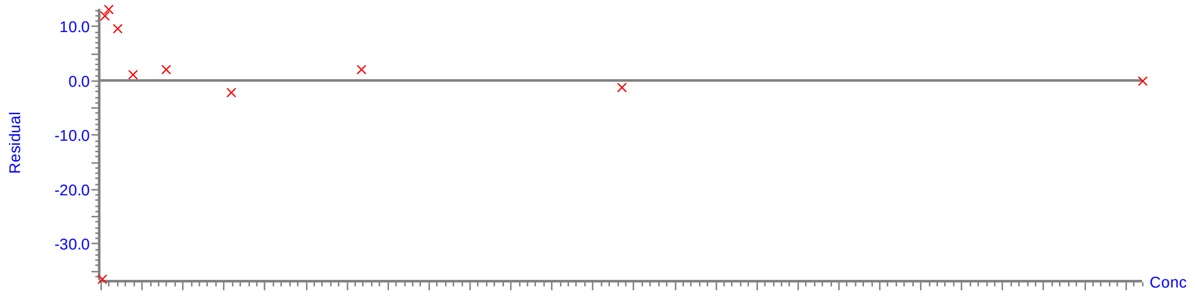
Compound name: BIT
Correlation coefficient: r = 0.999055, r^2 = 0.998110
Calibration curve: 0.781797 * x + 0.417615
Response type: Internal Std (Ref 8), Area * (IS Conc. / IS Area)
Curve type: Linear, Origin: Exclude, Weighting: 1/x, Axis trans: None

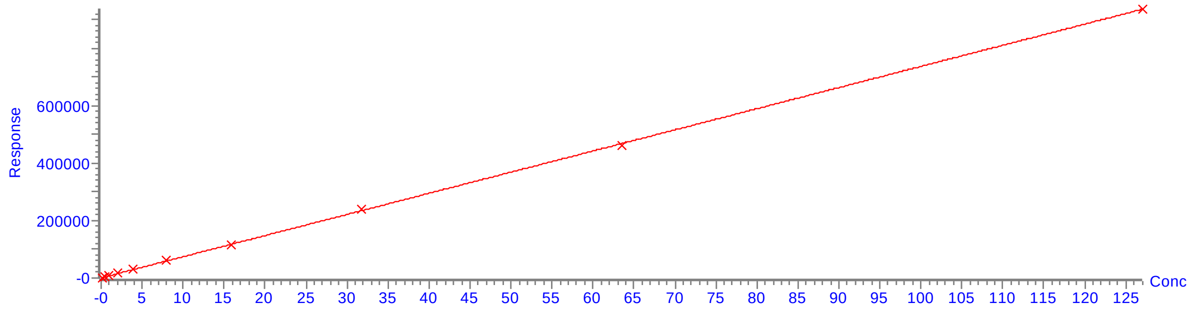


Compound name: OIT
Correlation coefficient: r = 0.998477, r^2 = 0.996956
Calibration curve: 48147.7 * x + 7984.48
Response type: External Std, Area
Curve type: Linear, Origin: Exclude, Weighting: 1/x, Axis trans: None

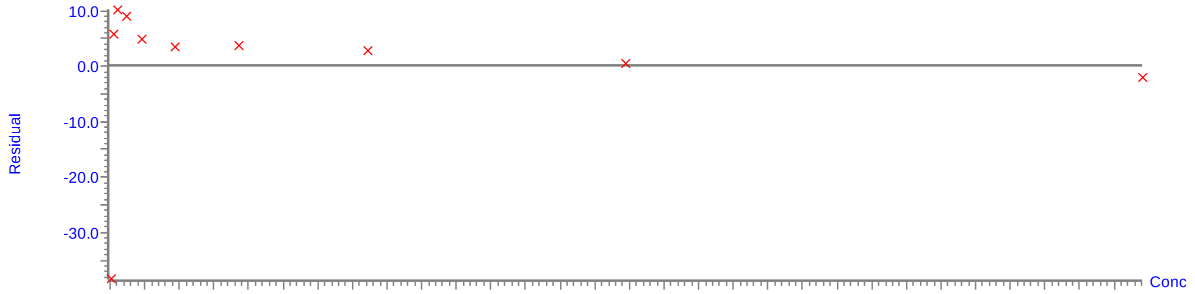


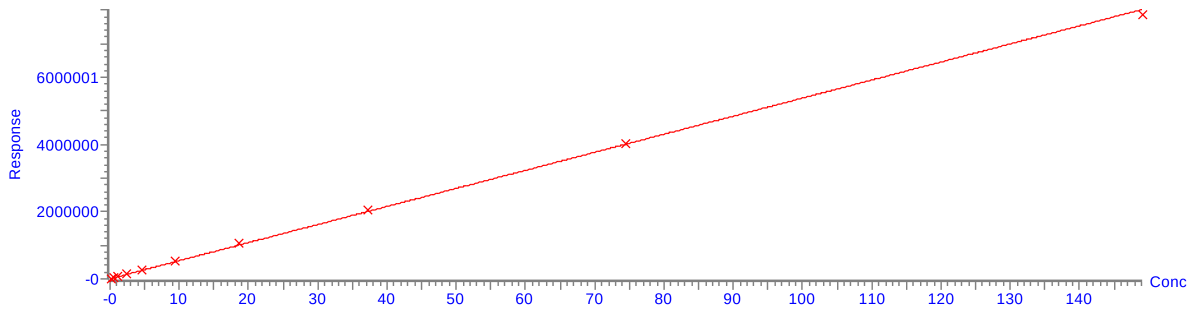
Compound name: Terbuconazole
Correlation coefficient: r = 0.999819, r^2 = 0.999637
Calibration curve: 7370.62 * x + 579.466
Response type: External Std, Area
Curve type: Linear, Origin: Exclude, Weighting: 1/x, Axis trans: None

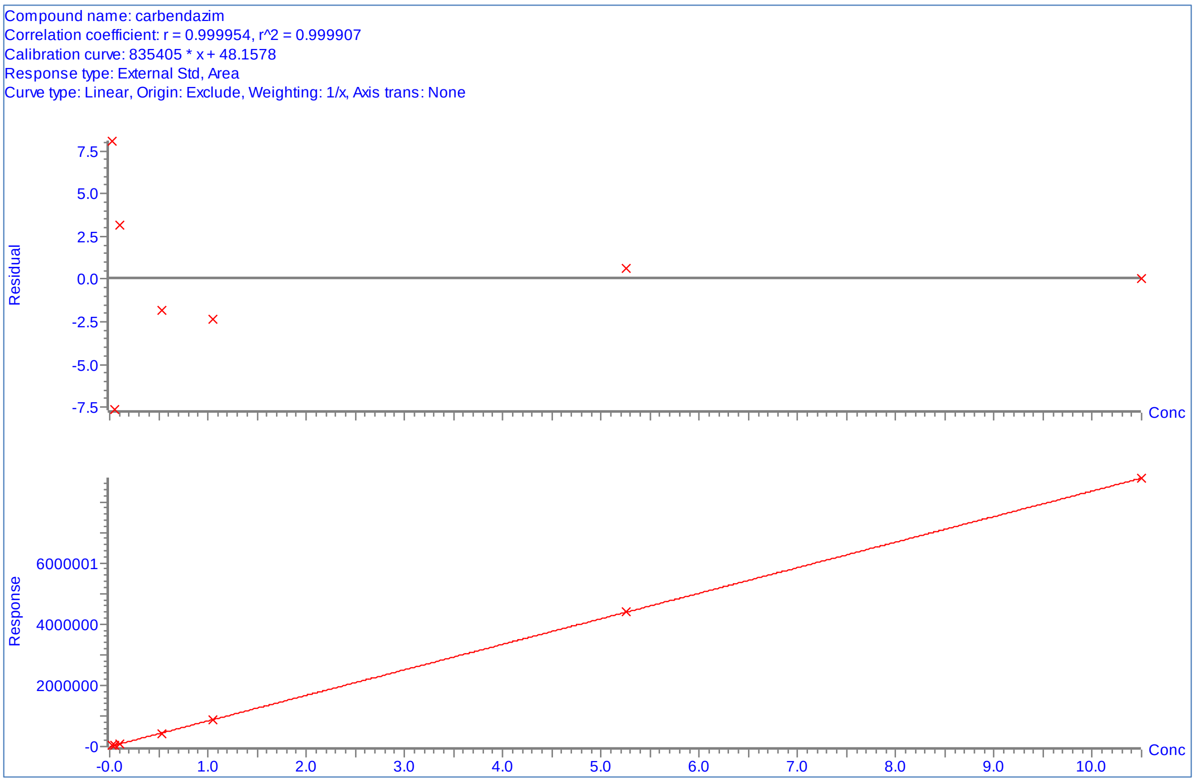




Compound name: Propiconazole
Correlation coefficient: r = 0.999675, r^2 = 0.999349
Calibration curve: 53758.7 * x + 6397.58
Response type: External Std, Area
Curve type: Linear, Origin: Exclude, Weighting: 1/x, Axis trans: None







10.2. DETERMINATION OF MIT, CMIT AND BIT IN SEALANT 2

10.2.1. SAMPLE

Sealant 2 was received from Fraunhofer. Sealant 2 is a polyacrylate containing MIT, CMIT and BIT. 5 kits were delivered. The contents of 2 kits were mixed. The paste was spread on a glass plate and after hardening the material was cut and grinded into pieces <1 mm.

10.2.2. ANALYSIS

- 5 test portions of 5 g were taken from the grinded material
- 10 g water was added and the mixture was allowed to stand for 10 min
- 20 g of methanol containing 200 ng of MIT-d3, CMIT-d3 and BIT-13C6 was added
- The mixture was homogenised during 2min using a high speed blender
- After settling at least 10 mL of supernatans was taken and centrifuged
- To 7.5mL supernatans 2.5mL NaCl 20% was added
- 1 mL of the mixture was transferred to an injection vial and analysed using LC-MS/MS according to the method given in 10.1.2.
- The concentrations of the target analytes were determined using the internal standard method
- A procedural blank as well as 2 matrix additions (100 ng) were analysed as well.

10.2.3. COMMENTS

- The chromatographic peaks of MIT and BIT were out of range. The extracts were diluted 200 times with methanol/water 1/1 with additional spiking of internal standards.
- The use of triphenylphosphate or tris-(1,3-dichlorisopropyl)-phosphate as internal standard is inappropriate because of:
    - high blank values
    - retention times and consequently matrix suppression/enhancement effects differing from the target analytes
- Bis-nitrophenyl urea (nicarbazin) is neither a suitable internal standard because this compound has to be analysed in negative mode
- The addition of water to a hydrophobic sample seems senseless
- Clean up on diatomaceous earth was not needed
- It is not clear why NaCl is added to the extract

10.2.4. CHROMATOGRAMS:

Chromatograms of MIT, CMIT and BIT in the sealant extract are given in Figure 22-Figure 24.

10.2.5. RESULTS

→ Repeatability

In Table 40 the concentrations which were determined for the different sealant test portions are given. For each compound the repeatability (CV_r) was calculated. For BIT the CV_r is 6%. MIT and CMIT show higher values due to a deviating result; in case of MIT the area of the IS for sample 2 was too low and in case of CMIT it was the signal of the native compound which was lower compared to the other test portions.

→ Recoveries

The results of the matrix additions are given in Table 41. The recoveries are between 100-120% for BIT and CMIT; for MIT a higher value of 130% is obtained. Note however that the added concentration (12.4 µg/L in the final extract) was lower than the original concentration (24.3 µg/L), which explains the overestimation.

→ Sensitivity

The lowest concentration of the linear range is 0.1 µg/L (using a UPLC-Xevo TQ-S). This corresponds to a concentration of 10 µg/kg in the sample (5g intake). A concentration of 10 µg/kg can be analysed with a good repeatability (see CMIT results).

Table 40: Measured concentrations of MIT, BIT and CMIT in sealant 2 (in mg/kg)

ID	**MIT**	**BIT**	**CMIT**
KIT 1	34,1	29,4	0,0103
KIT 2	52,1	35,0	0,0109
KIT 3	34,1	33,4	0,0074
KIT 4	33,1	32,4	0,0100
KIT 5	37,0	31,7	0,0100
Average	38,1	32,3	0,0097
St.dev	7,12	1,84	0,00121
CVr%	18,7	5,7	12,5
Outliers excluded			
Average	34,6	32,3	0,0103
St.dev	1,66	1,84	0,00039
CVr%	4,8	5,7	3,8

Table 41: Recoveries for matrix additions in %

ID	**MIT**	**CMIT**	**BIT**
KIT 6 ADD	124	104	115
KIT 7 ADD	133	119	107

Figure 22: MIT and MIT-d3 in a 200 times diluted sealant extract

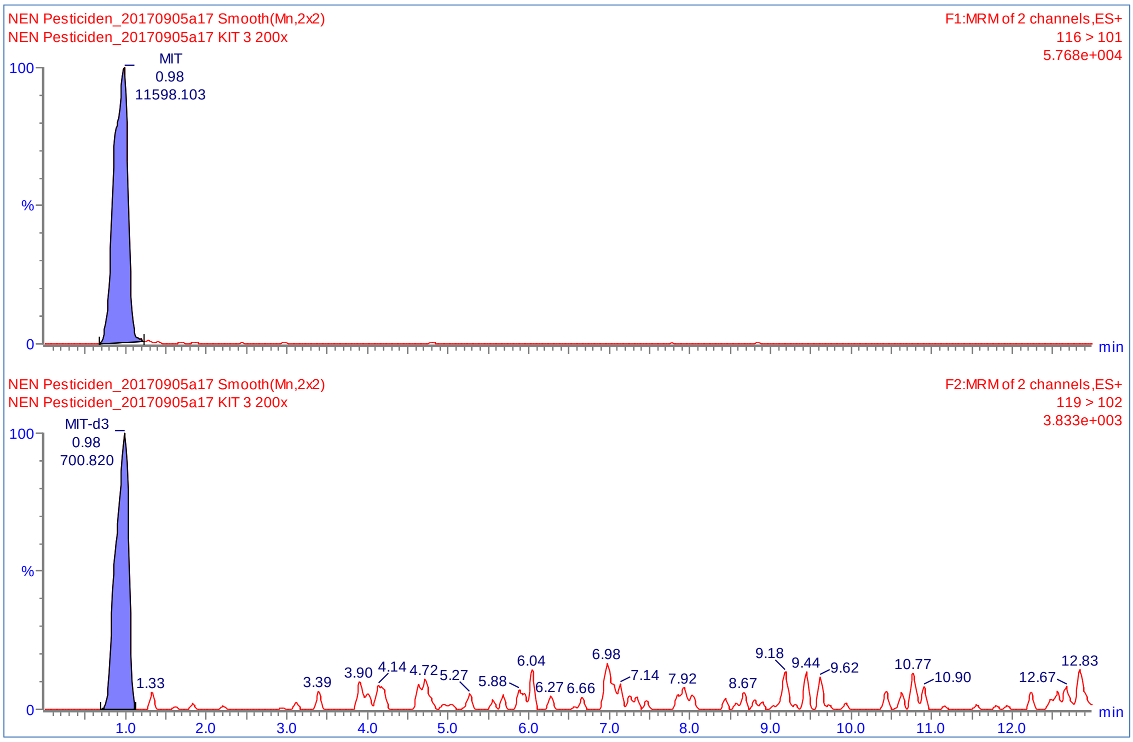


Figure 23: CMIT and CMIT-d3 in an undiluted sealant extract

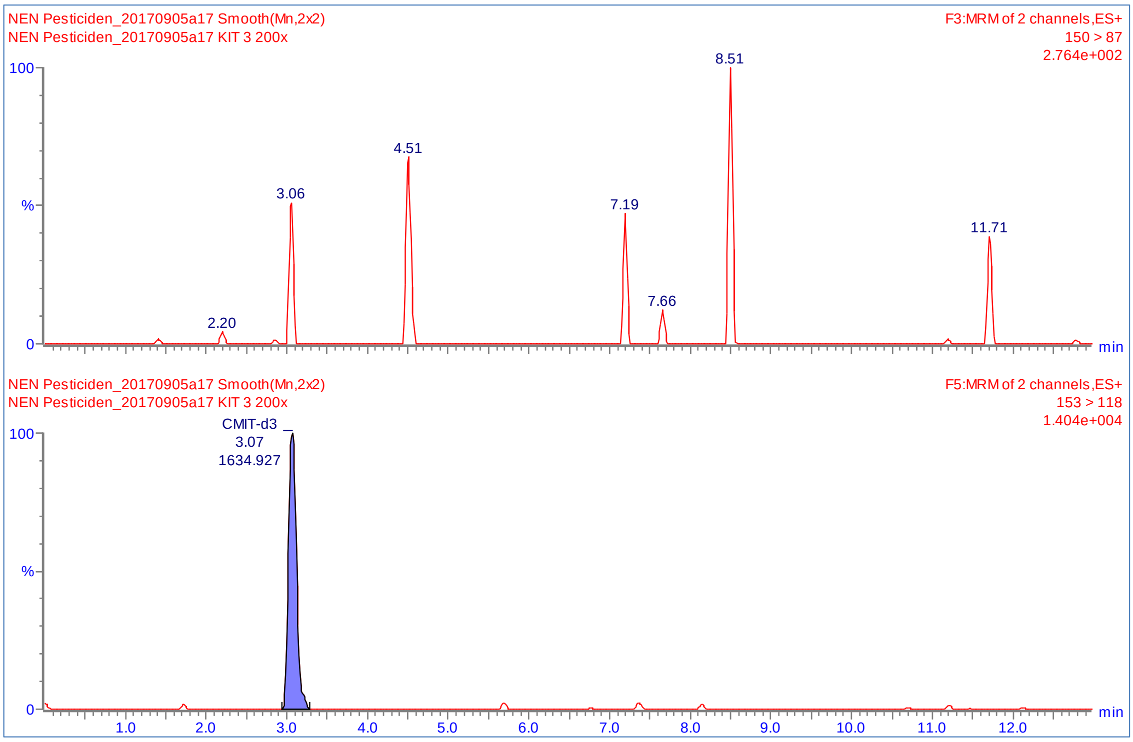
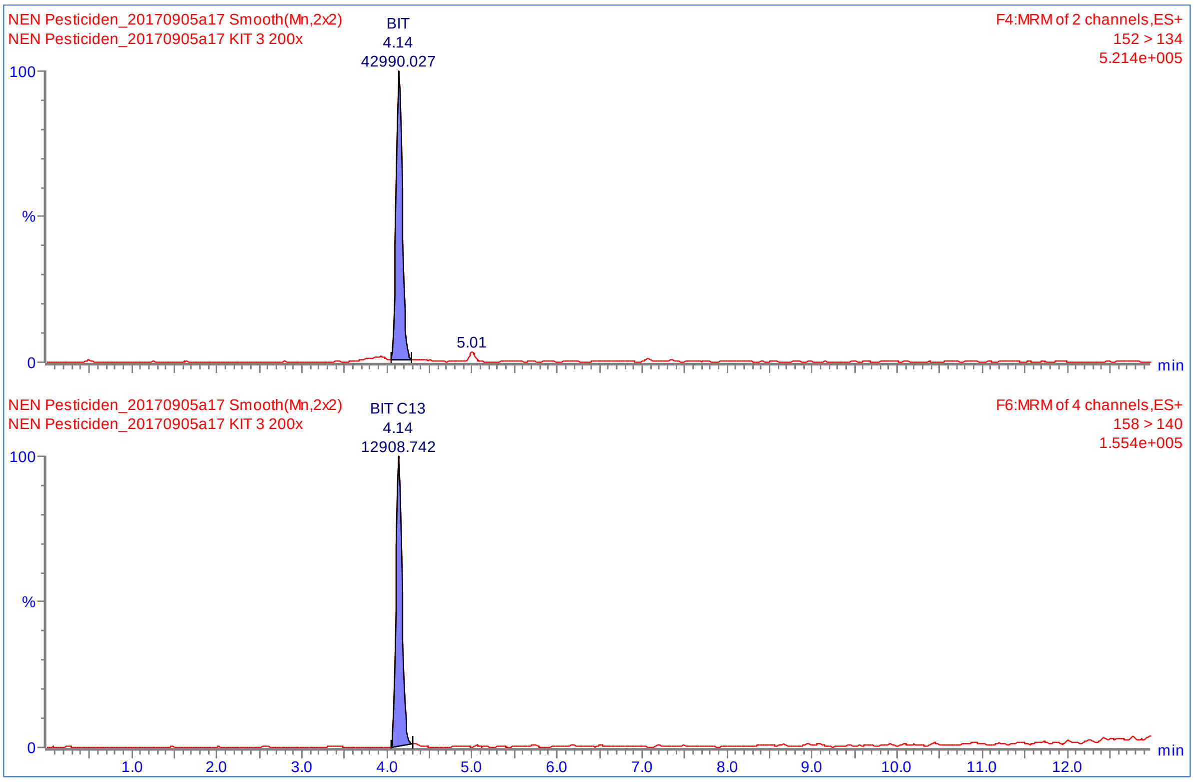


Figure 24: BIT and BIT-C13 in a 200 times diluted sealant extract



10.3. DETERMINATION OF PROPICONAZOLE AND TEBUCONAZOLE IN BIOCIDE TREATED WOOD

10.3.1. SAMPLE

A ground biocide treated wood was received from BAM.

10.3.2. ANALYSIS

- 5 test portions of 1 g were taken from the grinded material
- 10 g water was added and the mixture was allowed to stand for 10 min
- 20 g of methanol was added
- The mixture was homogenised during 2min using a high speed blender
- After settling at least 10 mL of supernatans was taken and centrifuged
- To 7.5mL supernatans 2.5mL NaCl 20% was added
- 1 mL of the mixture was transferred to an injection vial and analysed using LC-MS/MS according to the method given in 10.1.2.
- The concentrations of the target analytes were determined using the external standard method
- A procedural blank as well as 2 matrix additions (100 ng) were analysed as well.

10.3.3. COMMENTS

- The chromatographic peaks of propiconazole and tebuconazole were out of range. The extracts were diluted 50 times with 1/1 methanol/water.
- For other comments see 10.2.3.

10.3.4. CHROMATOGRAMS

Chromatograms of propiconazole and tebuconazole are given in Figure 25 for the wood extract

10.3.5. RESULTS

→ Repeatability

In Table 42 the concentrations which were determined for the different wood test portions are given. For each compound the repeatability (CVr) was calculated. For propiconazole the CV_r is 6%, for tebuconazole 7%.

→ Recovery

The results of the matrix additions are given in Table 43. The recoveries are 70% on average. The lower recovery is attributed to ionisation suppression caused by the matrix. Note that the results of the repeatability study have not been corrected for suppression (the objective is to check repeatability). The corrected average values are 103 mg/kg for both propiconazole and tebuconazole, which are closer to the concentrations determined by BAM (resp. 120 and 141 mg/kg)

→ **Sensitivity**

The lowest concentration of the linear range is 0.1 µg/L (using a UPLC-Xevo TQ-S), with signal-to-noise ratios of 35 and 10 for resp. propiconazole and tebuconazole. This corresponds to a concentration of 50 µg/kg in the sample (1 g intake).

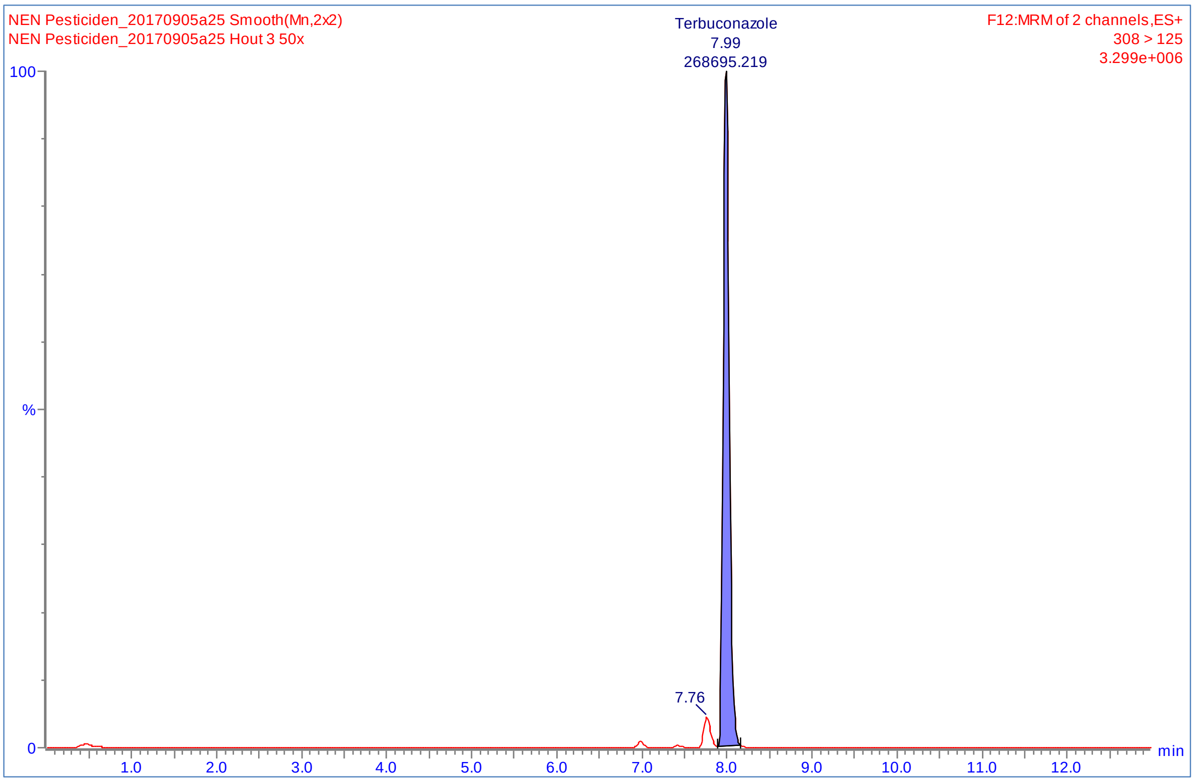
Table 42: Measured concentrations of propiconazole and tebuconazole in biocide treated wood (in mg/kg)

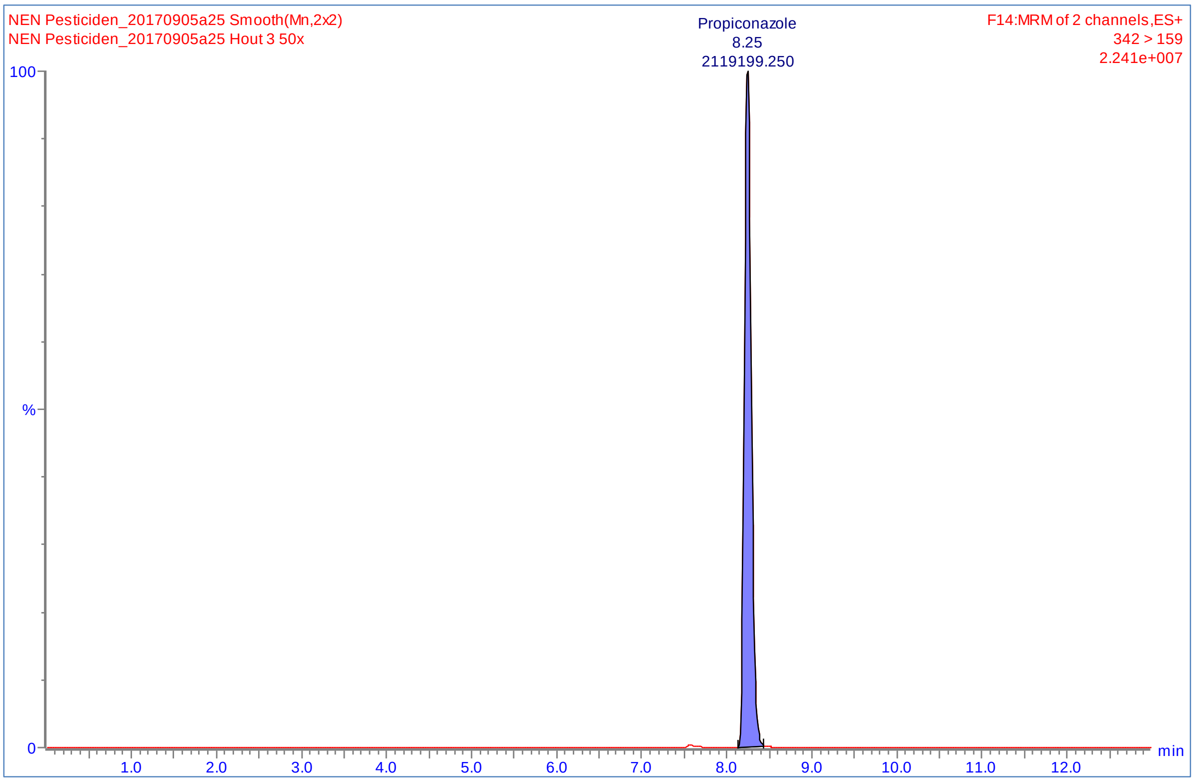
ID	**Tebuconazole**	**Propiconazole**
Treated wood 1	80,5	78,0
Treated wood 2	74,6	74,7
Treated wood 3	68,4	70,0
Treated wood 4	71,6	70,1
Treated wood 5	66,5	66,0
Average	72,3	71,8
St.dev	4,93	4,17
CV_r%	6,8	5,8

Table 43: Recoveries for matrix additions in %

ID	**Tebuconazole**	**Propiconazole**
Treated wood 6 ADD	79	75
Treated wood 7 ADD	63	65

Figure 25: Chromatograms of tebuconazole and propiconazole for a 50 times diluted wood extract





10.4. DETERMINATION OF DIURON, TERBUTRYN, CARBENDAZIM, MIT, BIT AND OIT IN RENDER 2.

10.4.1. SAMPLE

Render 2 was received from Dr. Robert-Murjahn-Institut GmbH (HDPE bucket containing a white pasty liquid). Render 2 was spread over a sheet of glass and hardened in the air during 24 h. The hardened render was grinded into pieces <1 mm.

10.4.2. ANALYSIS

- 5 test portions of 5 g were taken from the grinded material
- 10 g water was added and the mixture was allowed to stand for 10 min
- 20 g of methanol containing 200 ng of terbutryn-d5, MIT-d3 and BIT-13C6 was added
- The mixture was homogenised during 2min using a high speed blender
- After settling at least 10 mL of supernatans was taken and centrifuged
- To 7.5mL supernatans 2.5mL NaCl 20% was added
- 1 mL of the mixture was transferred to an injection vial and analysed using LC-MS/MS according to the method given in 10.1.2.
- The concentrations of the target analytes were determined using the internal resp. external standard method
- A procedural blank as well as 2 matrix additions (100 ng) were analysed as well

10.4.3. COMMENTS

- The chromatographic peaks of diuron, terbutryn, carbendazim, MIT, BIT and OIT were out of range. The extracts were diluted 10.000 times with methanol/water 1/1 with additional spiking of internal standards.
- For other comments see 10.2.3.

10.4.4. CHROMATOGRAMS:

Chromatograms of diuron, terbutryn, carbendazim, MIT, BIT and OIT are given in Figure 26 for the render extract (10.000 dilution). For MIT, which shows only minor retention on the C18 column, a chromatographic interference can be noticed; the peak is broad and split.

10.4.5. RESULTS

→ Repeatability

In Table 44 the concentrations which were determined for the different render test portions are given. For each compound the repeatability (CV_r) was calculated. The measurements appear to be less repeatable, with CV_r values ranging from 9 to 19% (with exclusion of the render 2-3 values which are clearly outliers). The higher %RSD can be attributed to the more heterogeneous nature of the material.

→ **Recoveries**

The results of the matrix additions (corresponding to ca 800 mg/kg) are given in Table 45. The recoveries are between 70-130%, except for terbutryn for which somewhat lower values are observed. Carbendazim was not present in the matrix addition solution.

→ **Sensitivity**

The lowest concentration of the linear range is 0.1 µg/L (using a UPLC-Xevo TQ-S). This corresponds to a concentration of 10 µg/kg in the sample (5 g intake).

Table 44: Measured concentrations of pesticides in render 2 (in mg/kg)

ID	diuron	terbutryn	MIT	BIT	OIT	carbendazim
Render 2-1	399	364	469	764	504	245
Render 2-2	567	523	643	815	670	369
Render 2-3	~~871~~	~~670~~	~~971~~	~~1340~~	~~961~~	~~522~~
Render 2-4	501	442	572	679	469	294
Render 2-5	524	491	452	827	577	365
Average	498	455	534	771	555	318
St.Dev.	71	69	90	67	89	60
CV_r	14%	15%	17%	9%	16%	19%

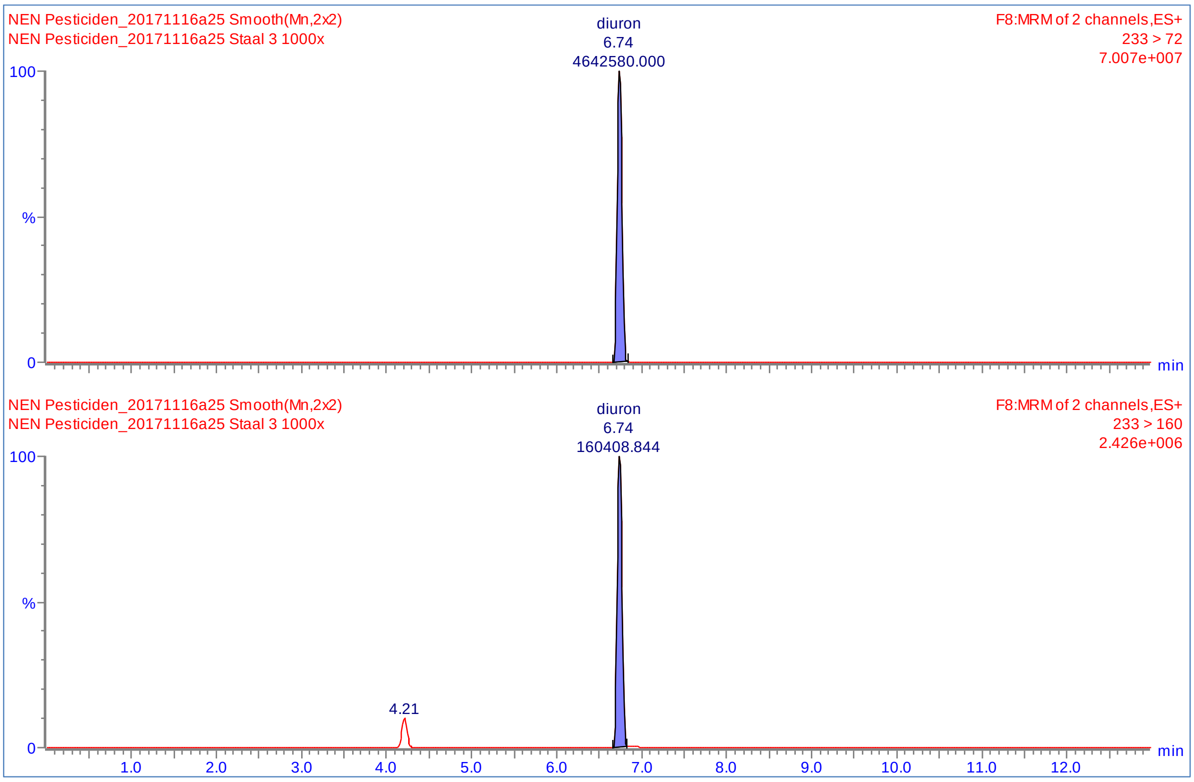
Table 45: Recoveries for matrix additions in %

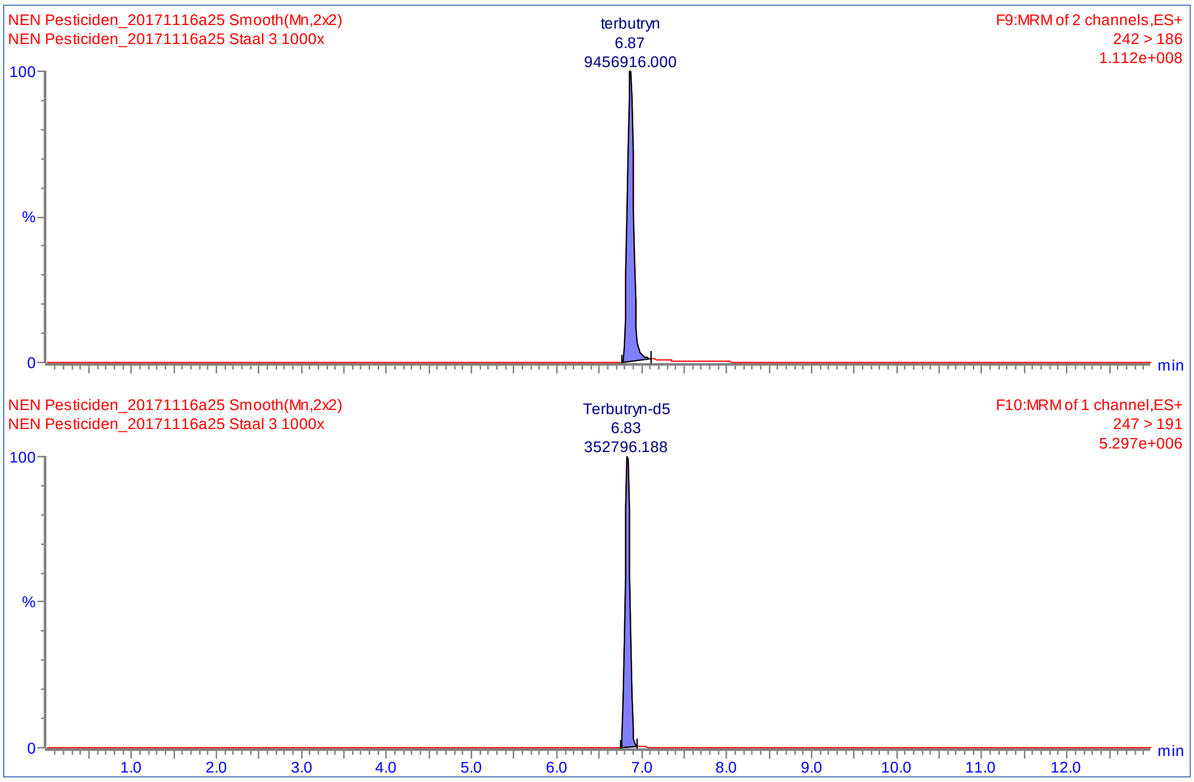
ID	diuron	Terbutryn	MIT	BIT	OIT
Render 2-2 ADD	96	61	122	105	134
Render 2-1 ADD	92	70	78	76	123

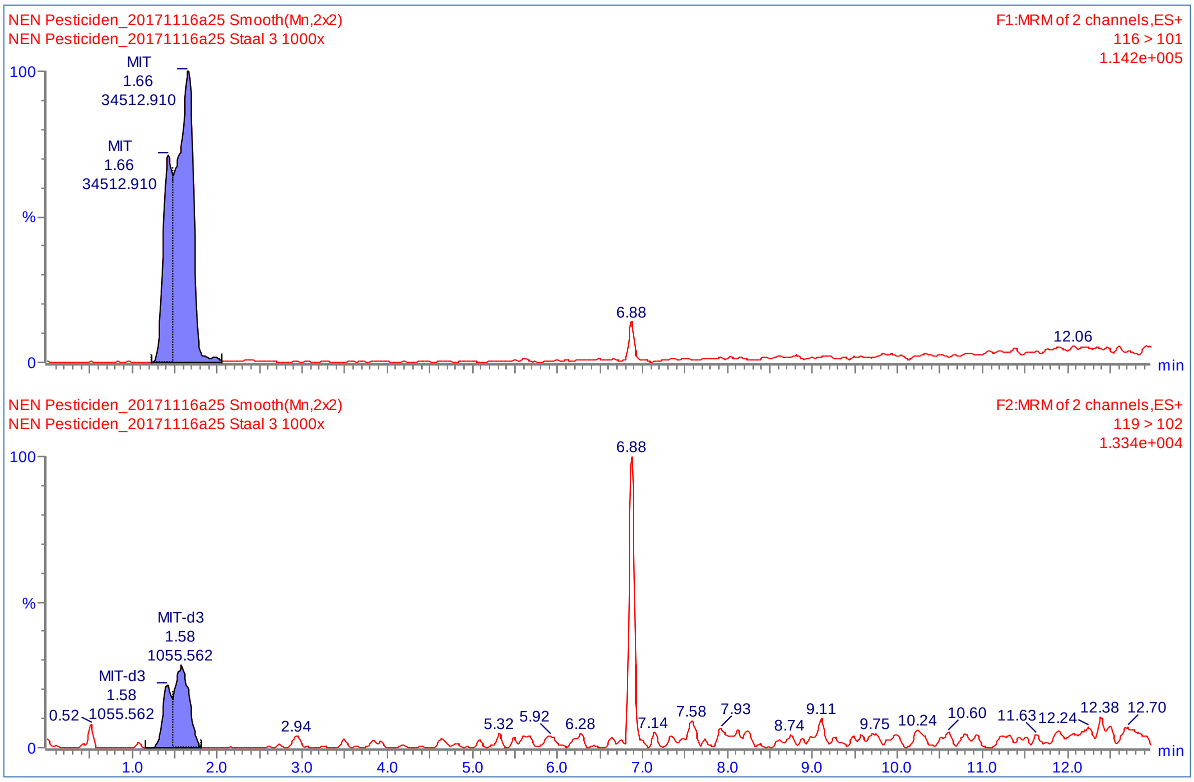
10.5. CONCLUSION

On the basis of the replicate determinations it can be concluded that EN 15637 can be used for the determination of biocides in construction materials. Nevertheless adaptations should be made to this standard to make it more appropriate for the analysis of construction materials (see CHAPTER 21).

Figure 26: Chromatograms of diuron, terbutryn, MIT, BIT, OIT and carbendazim in render extract



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NEN Pesticiden_20171116a25 Staal 3 1000x
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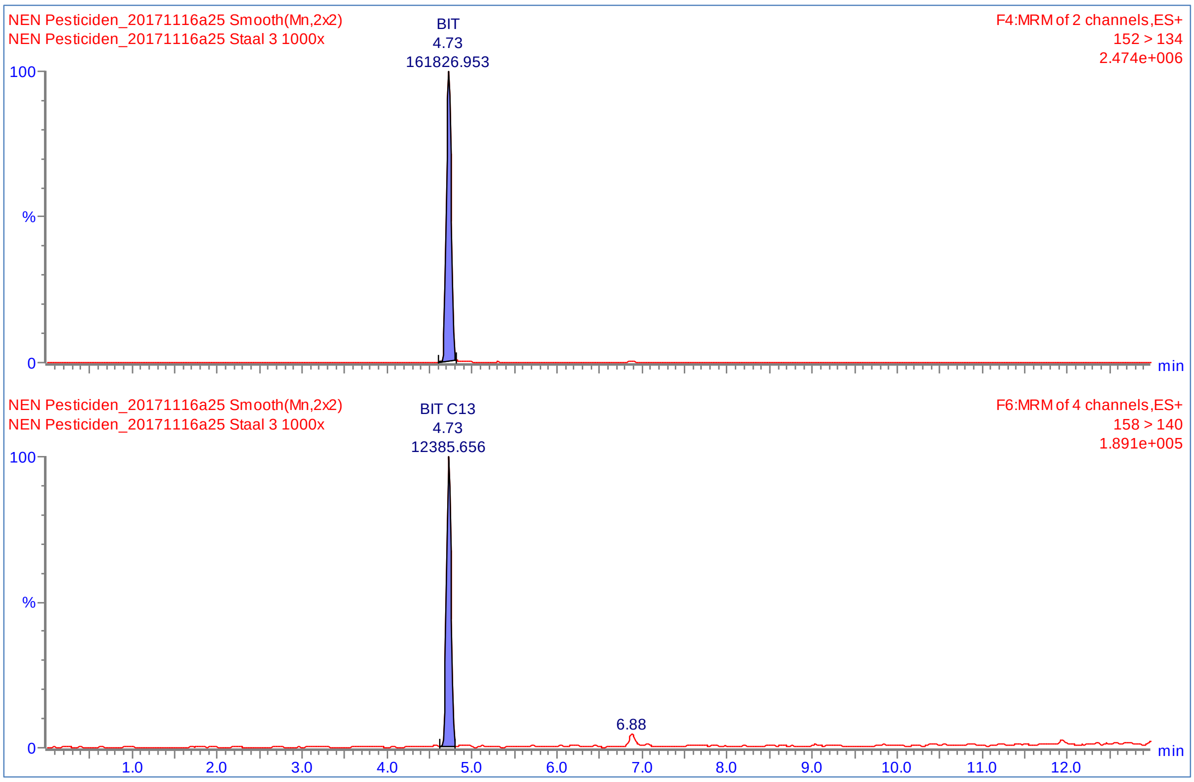
116 > 101
1.142e+005
MIT
1.66
34512.910
MIT
1.66
34512.910
6.88
12.06
100
%
0
min
NEN Pesticiden_20171116a25 Smooth(Mn,2x2)
NEN Pesticiden_20171116a25 Staal 3 1000x
F2:MRM of 2 channels,ES+
119 > 102
1.334e+004
6.88
MIT-d3
1.58
1055.562
MIT-d3
1.58
1055.562
0.52
2.94
5.32
5.92
6.28
7.14
7.58
7.93
8.74
9.11
9.75
10.24
10.60
11.63
12.24
12.38
12.70
100
%
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
min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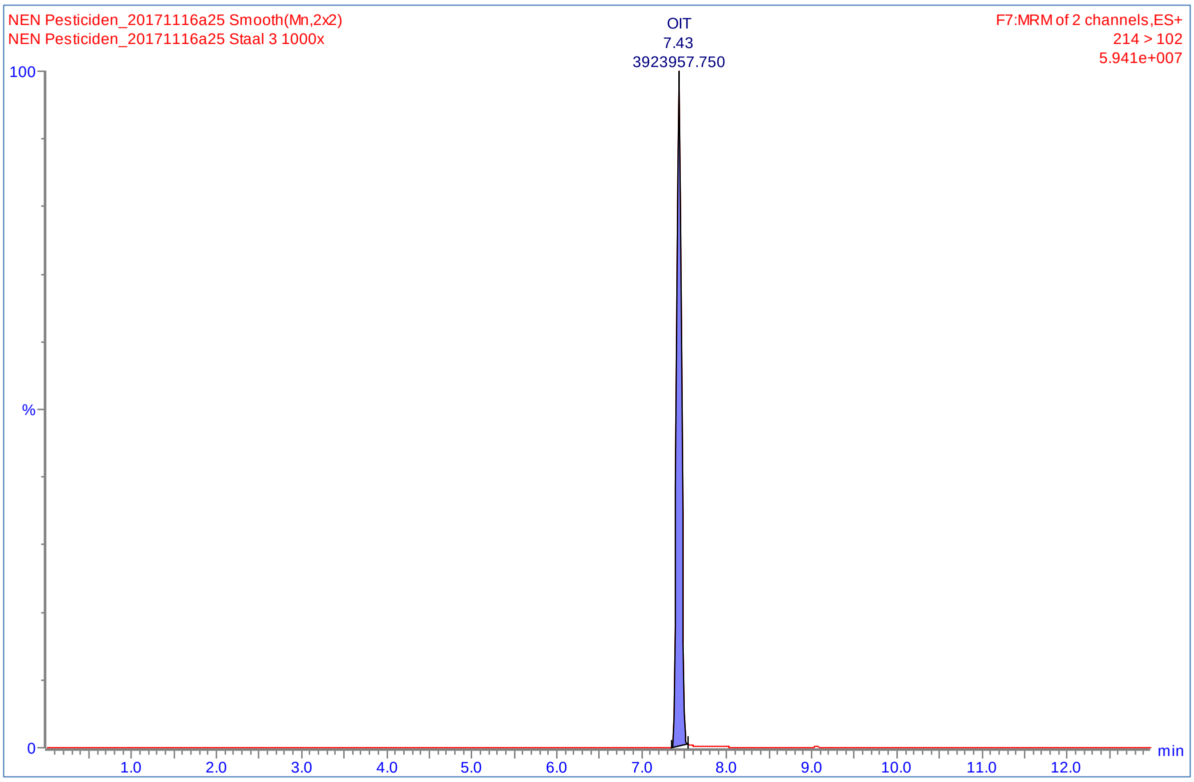
NEN Pesticiden_20171116a25 Staal 3 1000x
BIT
4.73
161826.953
F4:MRM of 2 channels,ES+
152 > 134
2.474e+006
100
%
0
min
NEN Pesticiden_20171116a25 Smooth(Mn,2x2)
NEN Pesticiden_20171116a25 Staal 3 1000x
BIT C13
4.73
12385.656
F6:MRM of 4 channels,ES+
158 > 140
1.891e+005
6.88
100
%
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
min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214 > 102
5.941e+007
100
%
0
1.0
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3.0
4.0
5.0
6.0
7.0
8.0
9.0
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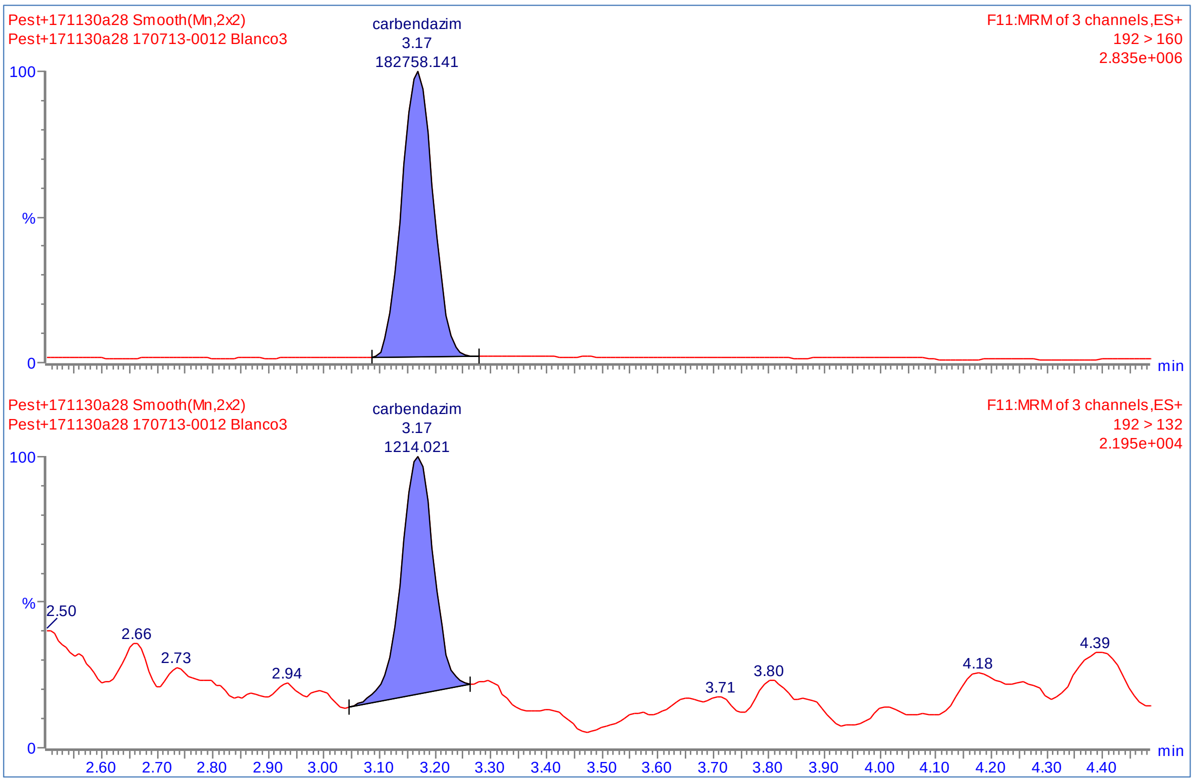
11.0
12.0
min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Pest+171130a28 170713-0012 Blanco3
carbendazim
3.17
182758.141
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192 > 160
2.835e+006
100
%
0
min
Pest+171130a28 Smooth(Mn,2x2)
Pest+171130a28 170713-0012 Blanco3
carbendazim
3.17
1214.021
F11:MRM of 3 channels,ES+
192 > 132
2.195e+004
100
%
0
2.50
2.66
2.73
2.94
3.71
3.80
4.18
4.39
2.60
2.70
2.80
2.90
3.00
3.10
3.20
3.30
3.40
3.50
3.60
3.70
3.80
3.90
4.00
4.10
4.20
4.30
4.40
min

CHAPTER 11 DETERMINATION OF THE CONTENT OF PHENOLS IN CONSTRUCTION PRODUCTS

11.1. 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)

11.1.1. METHOD DESCRIPTION

A summary of CEN/TS 16182 and modifications done by VITO is given in Table 46. The method was applied to render. The method was used for the determination of the following compounds:

- 4-nonylphenol (isomeric mixture)(NP)
- 4-nonylphenol monoethoxylate (isomeric mixture) (NP1EO)
- 4-nonylphenol diethoxylate (isomeric mixture) (NP2EO)

11.1.2. MEASUREMENT CONDITIONS

Instrument settings

Hardware	Gaschromatograaf Massaspectrometer Autosampler GC-kolom	Trace GC (Thermo) Trace DSQ (Thermo) CTC-PAL VF-17-MS 30 m 0.25 mm 0.25 µm
Injector parameters	Injectievolume Injectiemodus injectie temperatuur surge pressure surge duration split flow splitless time solvent valve temperature	1 µl CT Splitless w/surge 250 °C 300 kPa 1 min 25 ml/min 1 min off
GC parameters	carrier gas initial temperature initial time rate #1 final temperature #1 hold time #1	He - const flow 1 ml/min 70°C 1 min 10°C/min 300°C 0 min
MS parameters	mode scan 1 scan rate 1 detector gain source temperature	Full scan 50-400 500 100000 250 °C

	interface temperature solvent delay	310 °C 7 min

Internal standards and ions used for quantitation

component	**m/z**	**RT**
nonylphenol	207	13.02-13.9
nonylphenol monoethoxylate	265	16,75
nonylphenol diethoxylate	309	19,54
^{13}C-nonylphenol	227	13,08
^{13}C-nonylphenol monoethoxylate	271	16,75
^{13}C-nonylphenol diethoxylate	315	19,54
^{13}C-1,2,4,5-tetrachlorobenzene (injection standard)	222	9,84

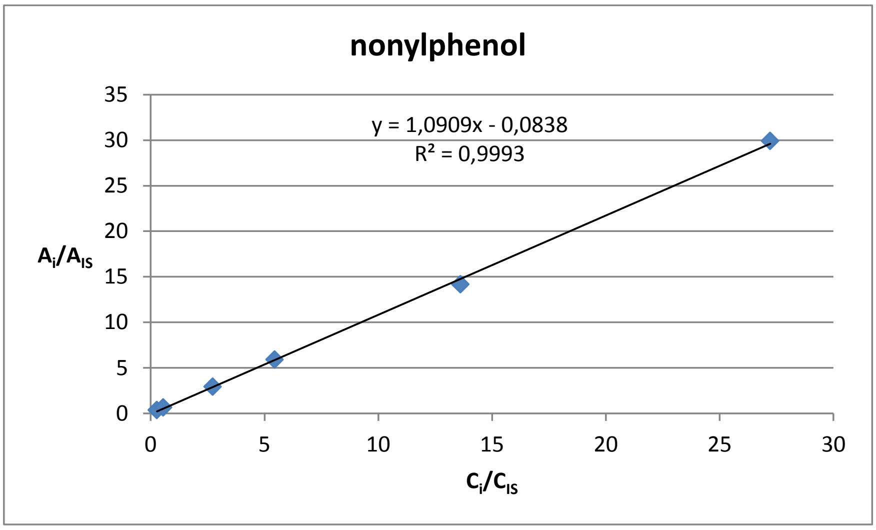
11.1.3. CALIBRATION DIAGRAMS

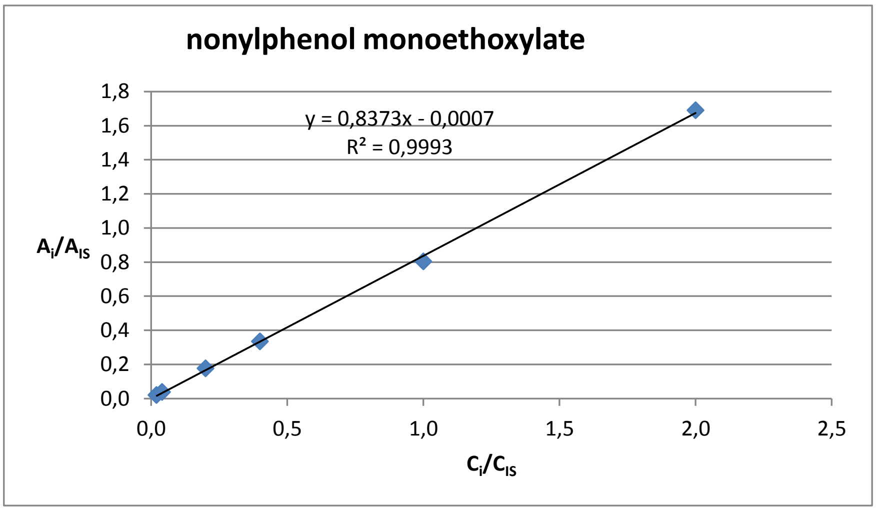
Calibration diagrams (internal standard method) are shown in Figure 27. The calibration solutions were derivatised in the same way as the samples. The native compounds were isomeric mixtures purchased from Sigma-Aldrich. The internal standards ($^{13}C_{ring}$-4-(3,6-dimethyl-3-heptyl)phenol and corresponding mono- and diethoxylates) were added in a concentration of 500 ng/mL. Linearity was obtained for the concentration range of 0.1-14 µg/mL for nonylphenol and 0.01-1 µg/mL for the ethoxylate derivatives.

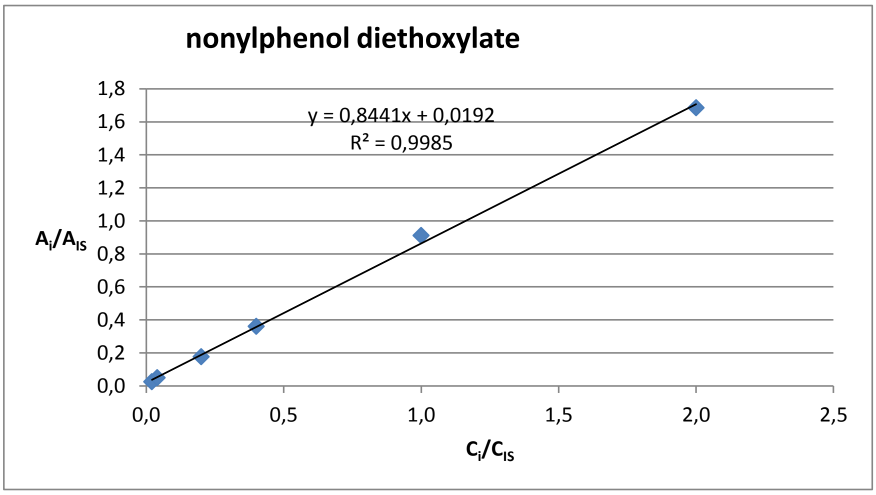
Table 46: Summary of CEN/TS 16182 and modifications by VITO

Sample Parameter list	Short description of the method	Departures from method by VITO and comments
Render 1 Nonylphenol Nonylphenol monoethoxylate Nonylphenol diethoxylate	- Matrix: Sludge, treated biowaste, soil - Intake: sludge 2-3 g d.m., soil and biowaste 10-20 g dm - IS: ^{13}C-4-n-nonylphenol and ^{13}C-n-nonylphenol diethoxylate - Extraction: agitation with acetone and hexane; wash with water - Clean-up (optional): silica, alumina or florisil - Derivatization: MSTFA 5% - Measurement: GC-MS - LOQ: 0.02 – 0.1 mg/kg d.m.	- IS: VITO uses a branched ^{13}C-labeled nonylphenol as internal standard as well as branched ^{13}C-labelled nonylphenol mono- and diethoxylates

Figure 27: Calibration diagrams for nonylphenol and nonylphenol ethoxylates







11.2. DETERMINATION OF NONYLPHENOL AND NONYLPHENOL ETHOXYLATES IN RENDER 1

11.2.1. SAMPLE

Render 1 was received from Dr. Robert-Murjahn-Institut GmbH (HDPE bucket containing a white pasty liquid). The render was spiked with a styrene-acrylate binder (14%) containing nonylphenol ethoxylate (NP30EO). The concentration of the polyethoxylate in the render was 2000 mg/kg. The render was spread over a sheet of glass and hardened in the air during 24 h. The hardened render was grinded into pieces <1 mm.

11.2.2. ANALYSIS

- 20 g of grinded render was brought into a flask and shaked thoroughly with 10 mL of water, then 30 mL of acetone
- 30 mL of hexane was added and the mixture was shaken for 2 h on a reciprocating shaker
- the white suspension was centrifuged and the supernatant was washed with 150 mL of water to remove the acetone and centrifuged
- the supernatant hexane was dried with Na_2SO_4
- 1 mL of the dried extract was transferred to an injection vial, internal standards were added (500 ng) and the mixture was evaporated to dryness using a gentle stream of nitrogen
- 0.5 mL hexane containing 5% MSTFA was added and the mixture was allowed to react for 15 min
- ^{13}C-tetrachlorobenzene was added as injection standard and the solution was injected into the GC-MS

11.2.3. COMMENTS

Because of the high organic load of the sample (styrene-acrylate binder) only 1 mL of the extract was taken for further analysis in order to maintain chromatographic performance. Internal standards were added to the extract and not to the sample.

11.2.4. CHROMATOGRAMS

Chromatograms of nonylphenol and ethoxylates in render 1 extract can be found in Figure 28. The isomeric profiles of nonylphenol and nonylphenol monoethoxylate correspond to that of the standard. For nonylphenol diethoxylate the signal is to small for pattern recognition.

11.2.5. RESULTS

→ Repeatabilities

The results of the replicate determinations of nonylphenol derivatives in render are given Table 47. Nonylphenol was present in an average concentration of 0.75 mg/kg; it was determined with a repeatabality of 11%. The concentrations of NP1EO and NP2EO were much lower, resp. 0.03 and 0.06 mg/kg. For NP1EO the %RSD is acceptable (16%), for NP2EO it is much too high (53%). Note however that the concentration is low and that the blank contribution is relatively high (blank value of 0.027 mg/kg). Better repeatabilities will be obtained in case of higher concentration factors.

→ Recoveries

A recovery test was carried out by spiking 5 test portions of 1 g of render with native nonylphenol derivatives (concentrations: NP 7 mg/kg, NP1EO and NP2EO 0.5 mg/kg), followed by spiking with internal standards and extraction and derivatisation according to the procedure described above. The results of the replicate determinations are given in Table 48. For all compounds very good recoveries (90-100%) and repeatabilities (2-10%) were obtained.

→ Sensitivities

Based on the lowest calibration solution of the linear range and for a concentration factor of 1 (0.5 g sample in 0.5 mL final extract) the detection limits are <0.1 mg/kg for nonylphenol and <0.01 mg/kg for the ethoxylates which is in compliance with the LOD's set in the standard. Blanks however determine the limits of quantification. With higher concentration factors lower LOQ's are achievable depending on the degree of matrix interferences.

11.3. CONCLUSION

CEN/TS 16182 can be sonsidered to be appropriate for the determination of nonylphenol and nonylphenol mono- and diethoxylate in construction products. Repeatabilities are acceptable, recoveries are quantitative and LOD's are sufficiently low. Care should be taken with regard to possible contamination by the laboratory environment in order to meet the LOQ requirement.

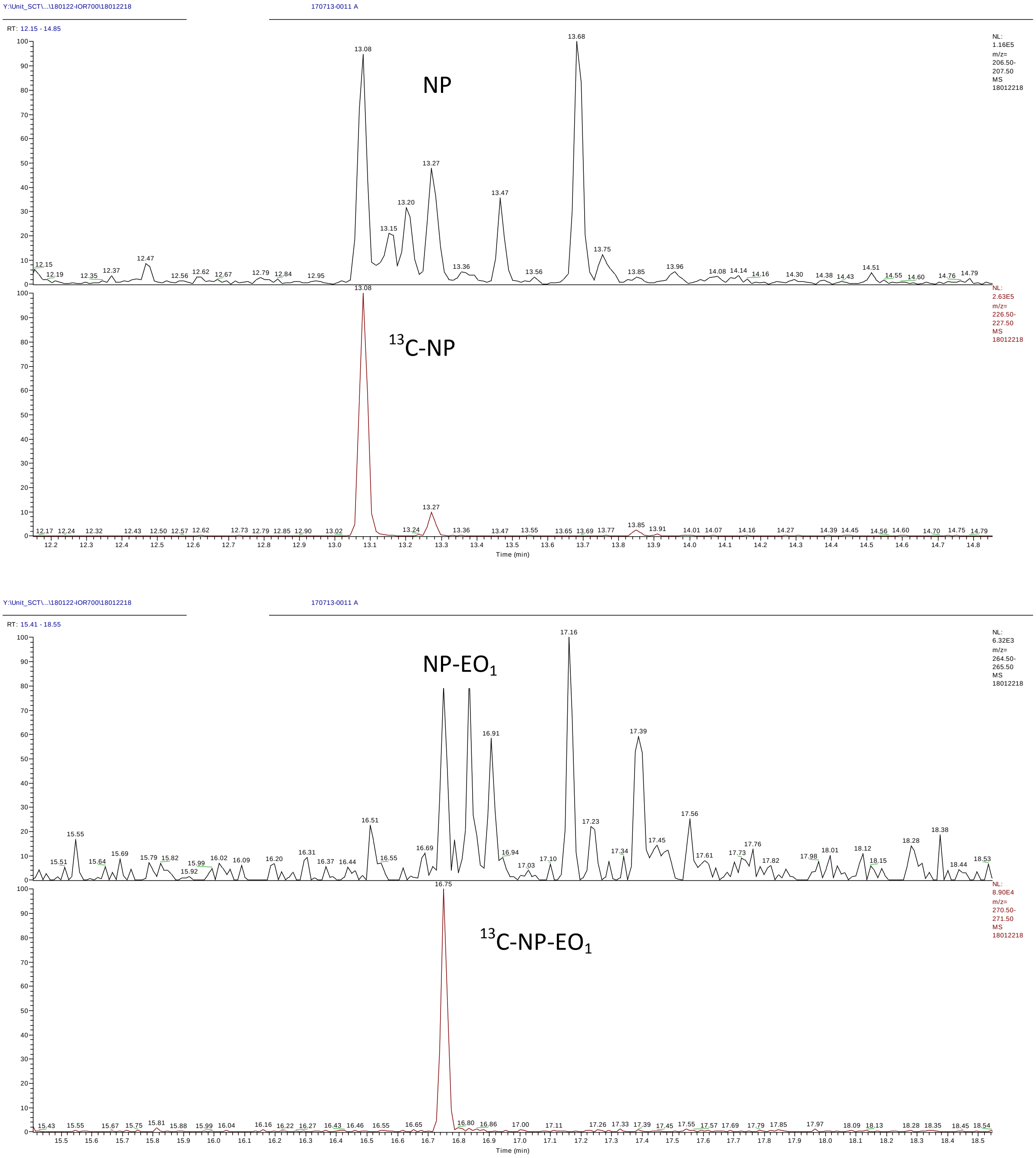
Table 47: Measured concentrations of nonylphenol and nonylphenol ethoxylates in render

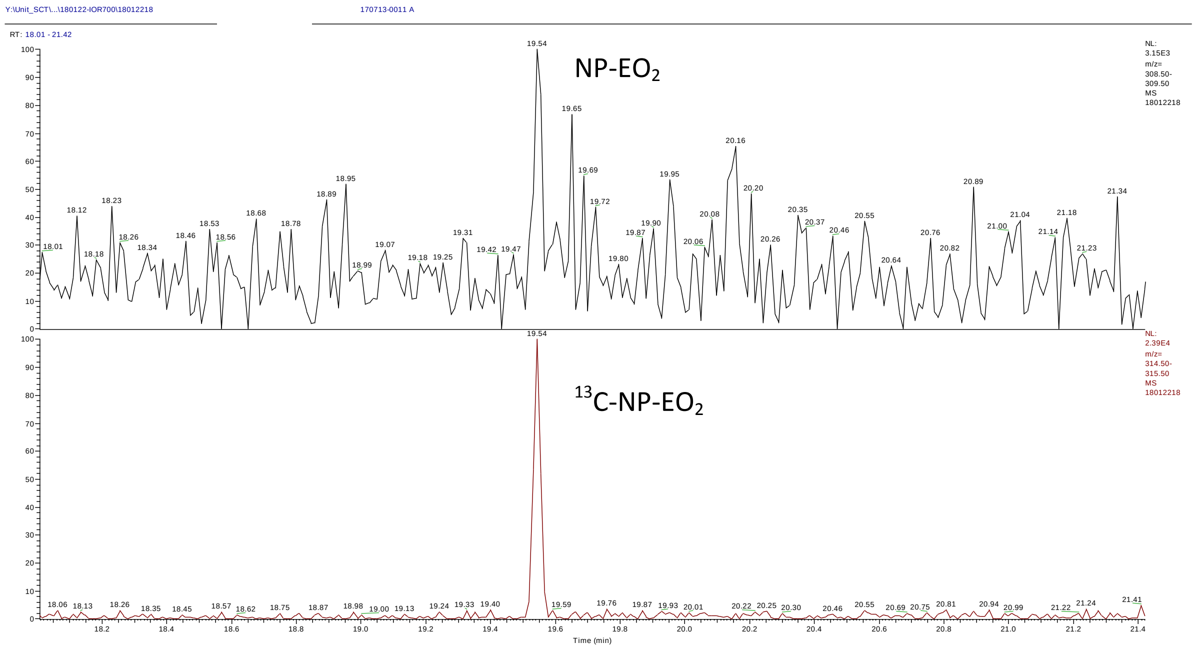
Sample	**Proc.blank** mg/kg	***1*** mg/kg	***2*** mg/kg	***3*** mg/kg	***4*** mg/kg	***5*** mg/kg	***Average*** mg/kg	***St.Dev.*** mg/kg	***CV_r*** %
NP	0,099	0,752	0,645	0,701	0,833	0,835	0,753	0,083	11%
NP1EO	0,013	0,031	0,027	0,030	0,040	0,030	0,032	0,005	16%
NP2EO	0,027	0,068	0,028	0,067	0,103	0,029	0,059	0,031	53%

Table 48: Measured concentrations and recoveries of nonylphenol and nonylphenol ethoxylates for spiked render samples

Sample	***1*** mg/kg	***2*** mg/kg	***3*** mg/kg	***4*** mg/kg	***5*** mg/kg	***Average*** mg/kg	***St.Dev.*** mg/kg	***CV_r***	***Addition*** mg/kg	***Recovery***
NP	7,48	7,41	7,65	7,36	7,56	7,49	0,115	2%	6,806	99%
NP1EO	0,492	0,463	0,511	0,538	0,531	0,51	0,031	6%	0,500	95%
NP2EO	0,510	0,421	0,501	0,559	0,523	0,50	0,051	10%	0,500	89%

Figure 28: Ion chromatograms of silylated nonylphenol, nonylphenol monoethoxylate, nonylphenol diethoxylate and corresponding ^{13}C-labelled internal standards for a render 1 extract

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19.69
19.72
19.95
18.95
18.89
20.20
18.23
18.12
20.89
21.34
20.35
21.18
21.04
20.08
20.55
18.68
18.78
18.53
19.90
20.37
21.00
20.46
21.14
18.46
18.56
18.26
19.31
19.87
20.76
20.26
18.01
18.34
19.07
20.06
19.42
19.47
20.82
21.23
18.18
19.18
19.25
19.80
20.64
18.99
^{13}C-NP-EO$_2$
NL:
2.39E4
m/z=
314.50-
315.50
MS
18012218
18.06
18.13
18.26
18.35
18.45
18.57
18.62
18.75
18.87
18.98
19.00
19.13
19.24
19.33
19.40
19.59
19.76
19.87
19.93
20.01
20.22
20.25
20.30
20.46
20.55
20.69
20.75
20.81
20.94
20.99
21.22
21.24
21.41
0
10
20
30
40
50
60
70
80
90
100
18.2
18.4
18.6
18.8
19.0
19.2
19.4
19.6
19.8
20.0
20.2
20.4
20.6
20.8
21.0
21.2
21.4
Time (min)

11.4. EN ISO 14154 – REPLACED BY METHOD 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)

11.4.1. METHOD DESCRIPTION

Remark: the scope of method EN ISO 14154 is limited to chlorophenols and is not suited for the analysis of nonylphenols. Therefore it was decided to replace the method by method CEN/TS 16182. The latter method is suited for the analysis of nonylphenols and nonylphenol ethoxylates, and possibly also for other phenols. Method CEN/TS 16182 was applied for water proofing sheets (PVC) and was used for the determination of the following phenols:

- 4-nonylphenol (isomeric mixture)(NP)
- 4-nonylphenol monoethoxylate (isomeric mixture) (NP1EO)
- 4-nonylphenol diethoxylate (isomeric mixture) (NP2EO)
- 4-tert.-octylphenol (OP)
- Bisphenol A (BPA)
- Phenol
- Chlorophenols (mono- to penta-)

A summary of method CEN/TS 16182 and modifications done by VITO is given in Table 49.

11.4.2. MEASUREMENT CONDITIONS APPLIED BY VITO

Instrument settings:

Hardware	Instrument GC-column	Thermo Quest Trace GC Thermo DSQ MS Agilent VF-17MS 30 m lenght, 0.25 mm ID, 0.25 um FT
Injector parameters	Injection volume Injection modus Injection temperature Pulse pressure Pulse time Purge flow Purge time	1 µl Pulsed splitless 250 °C 300 kPa 1.0 min 25 ml/min 1.0 min
GC parameters	Carrier gas Initial temperature Initial time Rate #1 Final temperature #1 Hold time #1 Rate #2 Final temperature #2 Hold time #2	Helium - const flow 1 ml/min 55 °C 1.0 min 6 °C/min 205 °C 0 min 25.0 °C/min 305 °C 5 min
MS parameters	Mode Source temperature	Full scan (120 – 400 amu) 250 °C

	Interface temperature Solvent delay	310 °C 6.5 min

Internal standards and ions used for quantitation:

Component	**m/z**	**Internal standard**	**m/z**
fenol	151	13C fenol	157
2-Chloorfenol	185	13C 4-Cl-fenol	191
3-Chloorfenol	185	13C 4-Cl-fenol	191
4-Chloorfenol	185	13C 4-Cl-fenol	191
2,3-Dichloorfenol	219	13C 2,4-diClfenol	225
2,4-Dichloorfenol	219	13C 2,4-diClfenol	225
2,5-Dichloorfenol	219	13C 2,4-diClfenol	225
2,6-Dichloorfenol	219	13C 2,4-diClfenol	225
3,4-Dichloorfenol	219	13C 2,4-diClfenol	225
3,5-Dichloorfenol	219	13C 2,4-diClfenol	225
2,3,4-Trichloorfenol	253	13C 2,4,5-triClfenol	259
2,3,5-Trichloorfenol	253	13C 2,4,5-triClfenol	259
2,3,6-Trichloorfenol	253	13C 2,4,5-triClfenol	259
2,4,5-Trichloorfenol	253	13C 2,4,5-triClfenol	259
2,4,6-Trichloorfenol	253	13C 2,4,5-triClfenol	259
3,4,5-Trichloorfenol	253	13C 2,4,5-triClfenol	259
2,3,4,5-Tetrachloorfenol	289	13C 2,3,4,5-tetraClfenol	295
2,3,4,6-Tetrachloorfenol	289	13C 2,3,4,5-tetraClfenol	295
2,3,5,6-Tetrachloorfenol	289	13C 2,3,4,5-tetraClfenol	295
Pentachloorfenol	323	13C pentaClfenol	329
4 tert-octylphenol	207	13C-OP	213
Bisfenol A	357	D16-bisphenol A	372
Nonylfenol	207	13C-NP	227
NP mono ethox	265	13C-NP mono ethox	271
NP di ethox	309	13C-NP di ethox	315

11.4.3. CALIBRATION DIAGRAMS

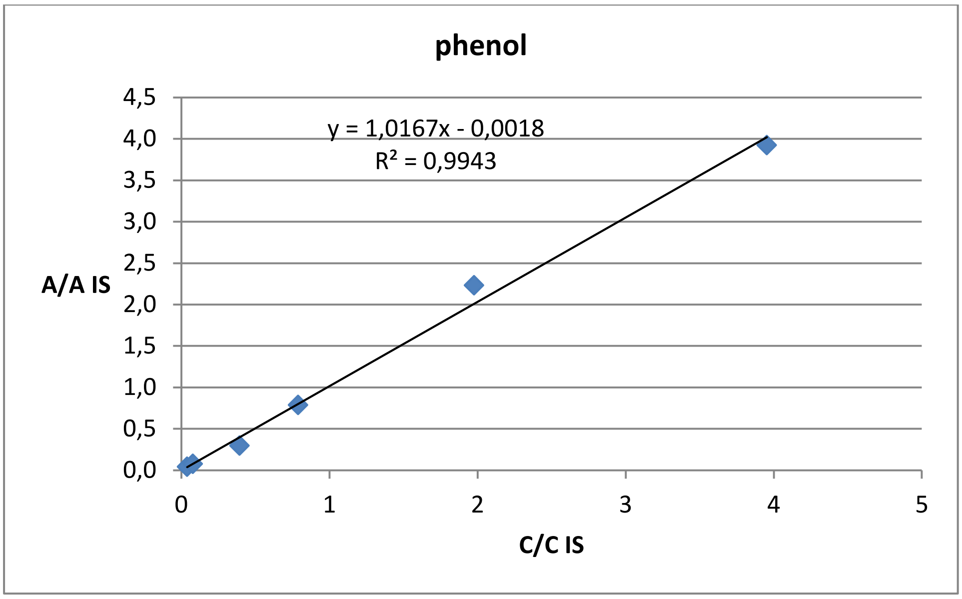
Six calibration solutions were prepared in a concentration range of 0.02 µg/ml to 2 µg/ml (except nonylphenol ethoxylates: 0.01 – 1 µg/l and nonylphenol 0.13 – 13 µg/ml). The internal standards and the injection standard (13C-1,2,4,5-tetrachlorobenzene) were added in a fixed concentration of 0.5 µg/ml. The calibration solutions were derivatised with MSTFA in the same way as the sample extracts. Calibration diagrams are given in Figure 29. Good linearity is obtained for phenol, monochlorophenols, octylphenol, nonylphenol and ethoxylates and bisphenol A. The quality of the calibration is worse for the polychlorinated phenols, which might be a consequence of reduced reactivity or solubility in hexane.

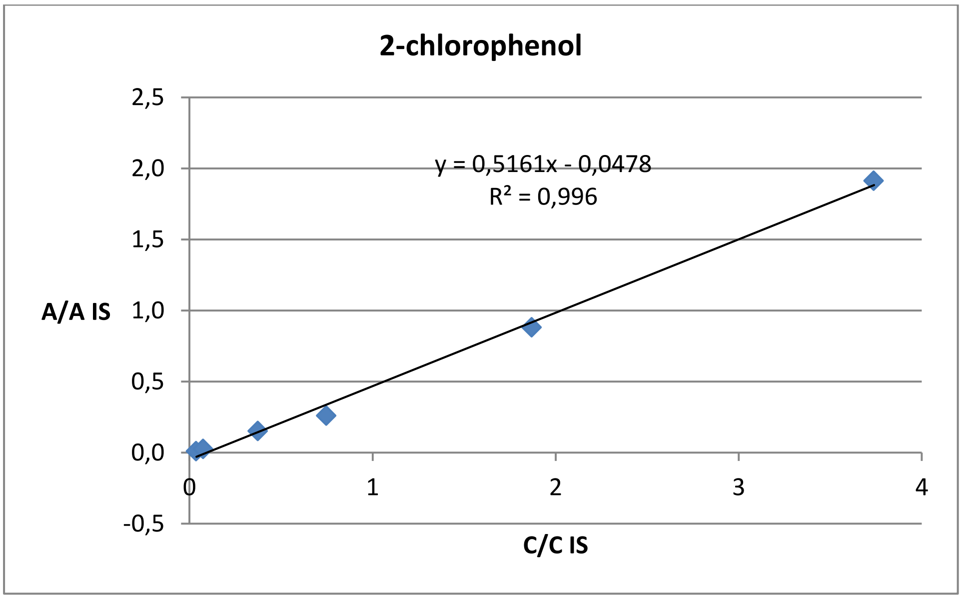
In case of an intake of 2 g and a final volume of 1 ml, the concentration range of the calibrations solutions correspond to a sample concentrations range of 0.01 – 1 mg/kg per phenol (except nonyl ethoxylates 0.005 – 0.5 mg/kg and nonylphenol 0.06 – 6 mg/kg).

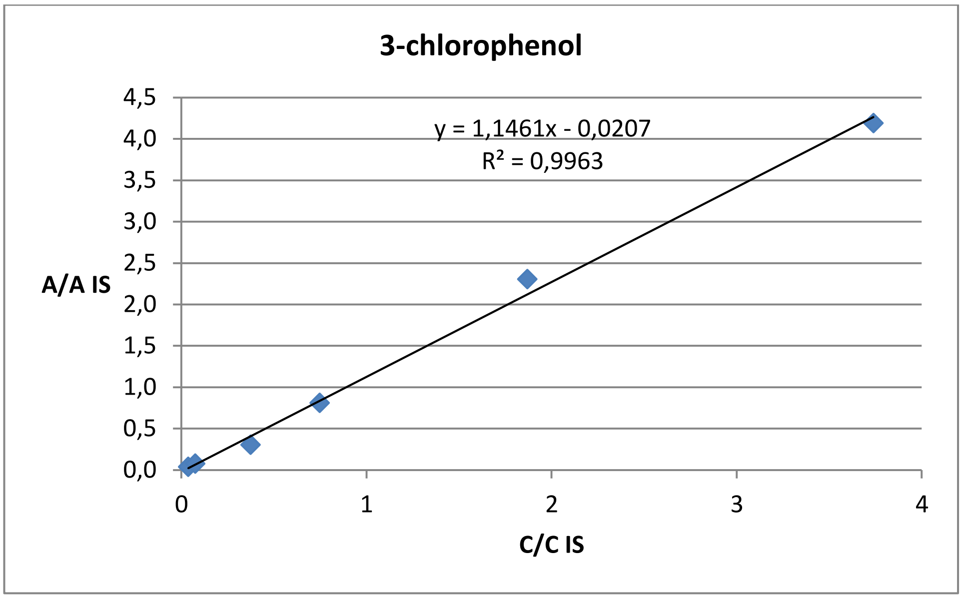
Table 49: Summary of CEN/TS 16182 and modifications by VITO

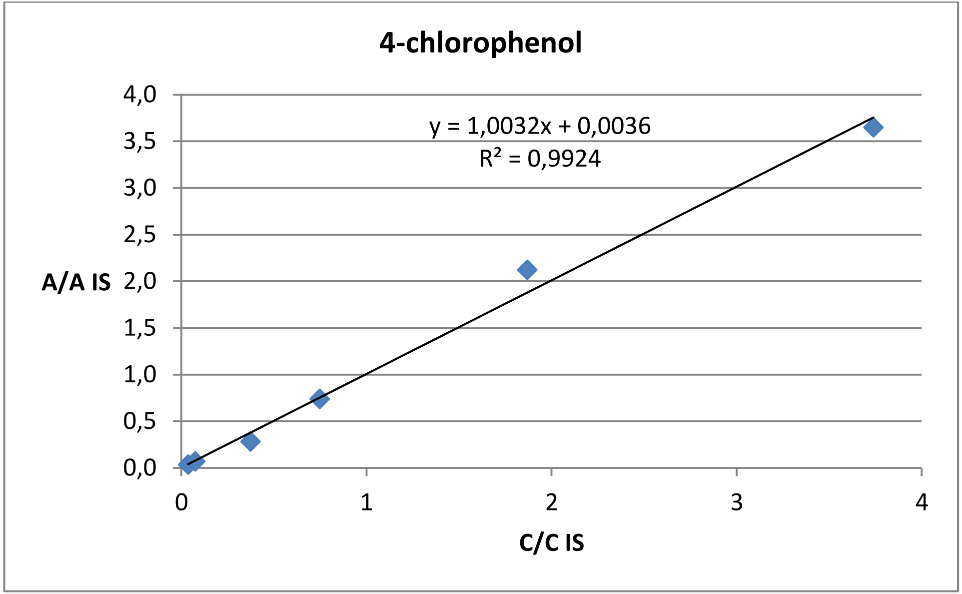
Sample Parameter list Method to be used	Short Description of the method to be used	Short description of the VITO Method	Method differences	Comment
Water proofing sheets (PVC) Phenols CEN/TS 16182	- Matrix: Sludge, treated biowaste, soil - Intake: 10-50g (2-3 g dm) - IS: 13C-4-n-nonylphenol and 13C-n-nonylphenol diethoxylate - Extraction: agitation with acetone and hexane; wash with water - Clean-up (optional): silica, alumina or florisil - Derivatization: MSTFA 5% - Measurement: GC-MS - LOQ: 0.02 – 0.1 mg/kg d.m.	- Matrix: PVC - Intake: 2 g PVC - IS: branched 13C-nonylphenol, branched 13C-nonylphenol mono- and diethoxylates; 13C-octylphenol, 13C-chlorophenols -Ultrasonic extraction with acetone; dissolved PVC is precipitated by addition of hexane. After centrifugation the upper layer is concentrated and dissolved in 1 ml hexane. No clean-up is applied. - Derivatisation: MSTFA 10% - Measurement: GC-MS	- VITO applied the method also for chlorophenols, octylphenol, bisphenol A - IS: VITO uses a branched 13C-labeled nonylphenol and -mono- and diethoxylates instead of linear; 13C-octylphenol and 13C-(chloro)phenols are also added - Sample extraction and pretratment was modified because PVC had to be eliminated from the final extract, otherwise the GC injection system would be damaged - More MSTFA was added because phthalates were present in a high concentration and these components also consume MSTFA	- Method was evaluated for phenols (including chlorophenol, octylphenol and bisphenol A) - Nonylphenol mixtures in real samples are branched, so a branched IS is more suited; extra IS for determination of octylphenol and (chloro)phenols

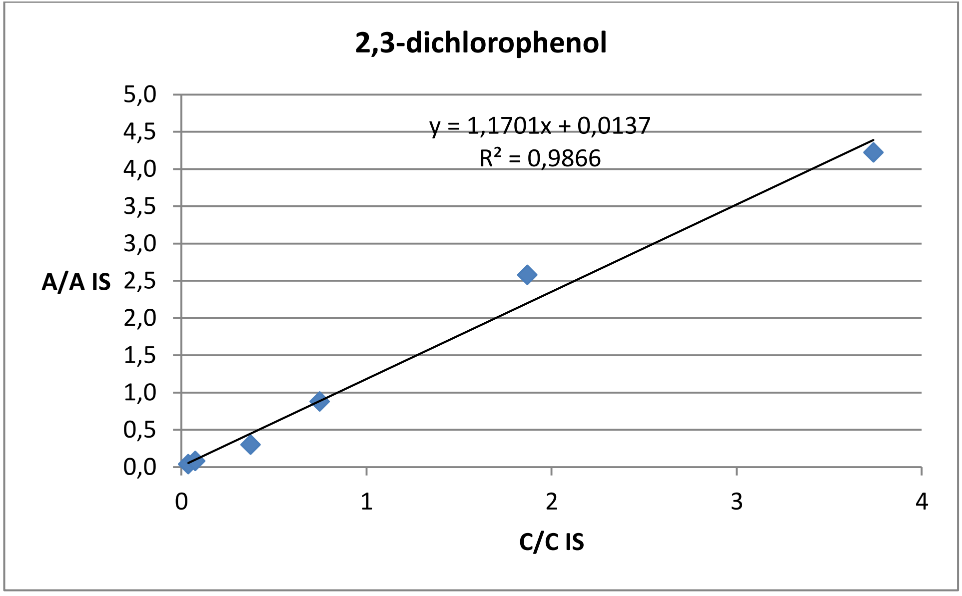
Figure 29 : Calibration diagrams of the phenols (method CEN/TS16182)

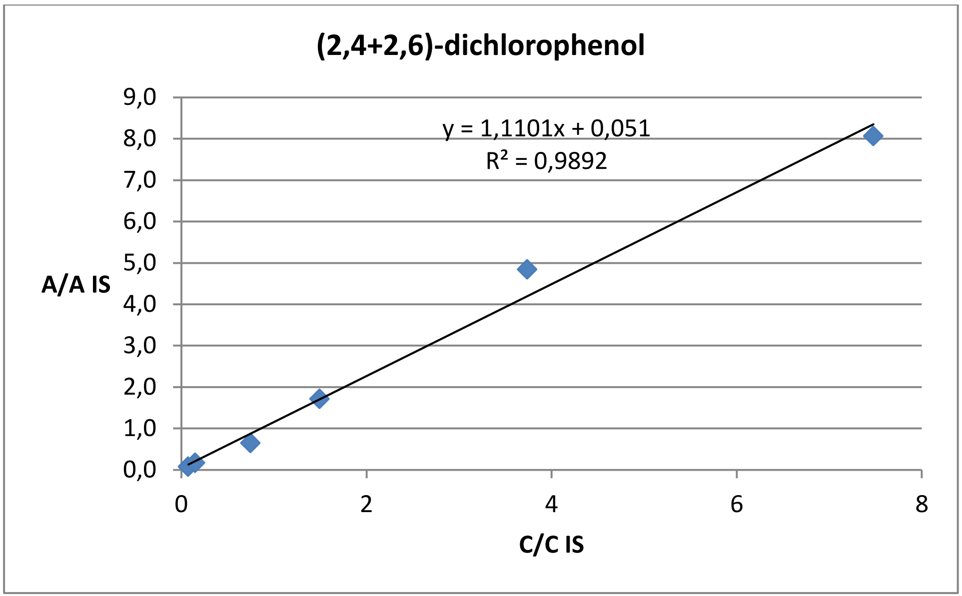


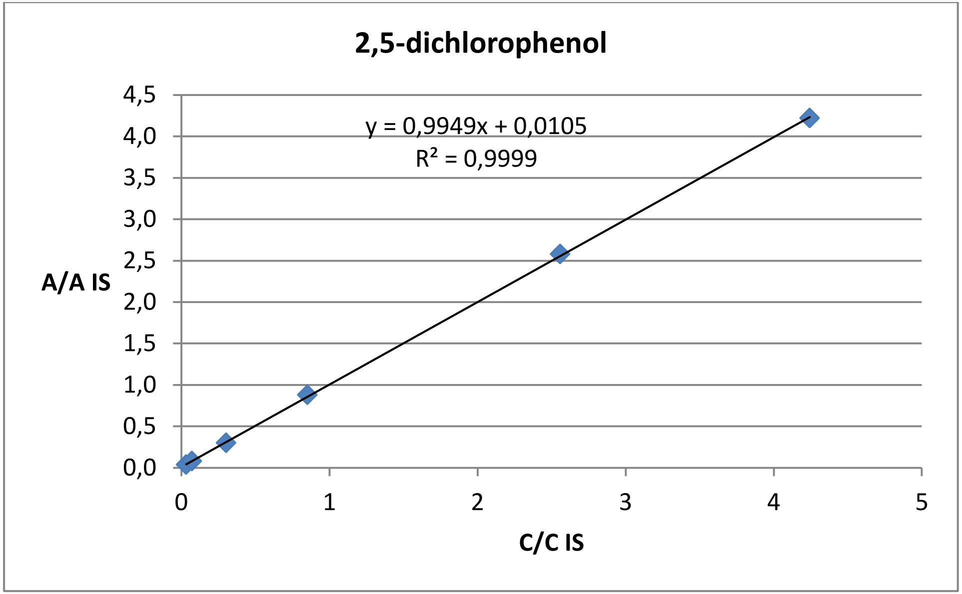


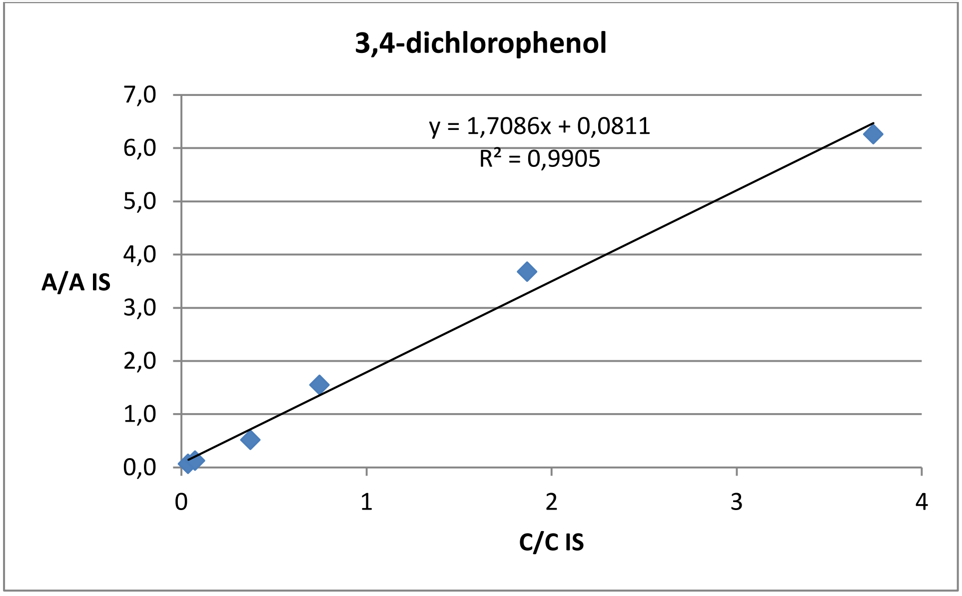

3-chlorophenol
y = 1,1461x - 0,0207
R² = 0,9963
A/A IS
4,5
4,0
3,5
3,0
2,5
2,0
1,5
1,0
0,5
0,0
0
1
2
3
4
C/C IS

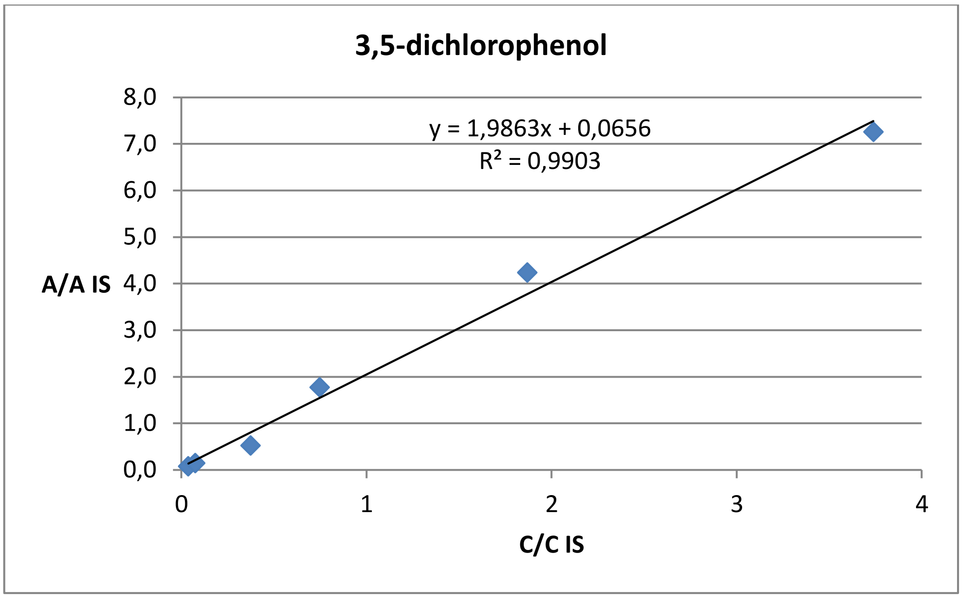

4-chlorophenol
y = 1,0032x + 0,0036
R² = 0,9924
A/A IS
4,0
3,5
3,0
2,5
2,0
1,5
1,0
0,5
0,0
0
1
2
3
4
C/C IS

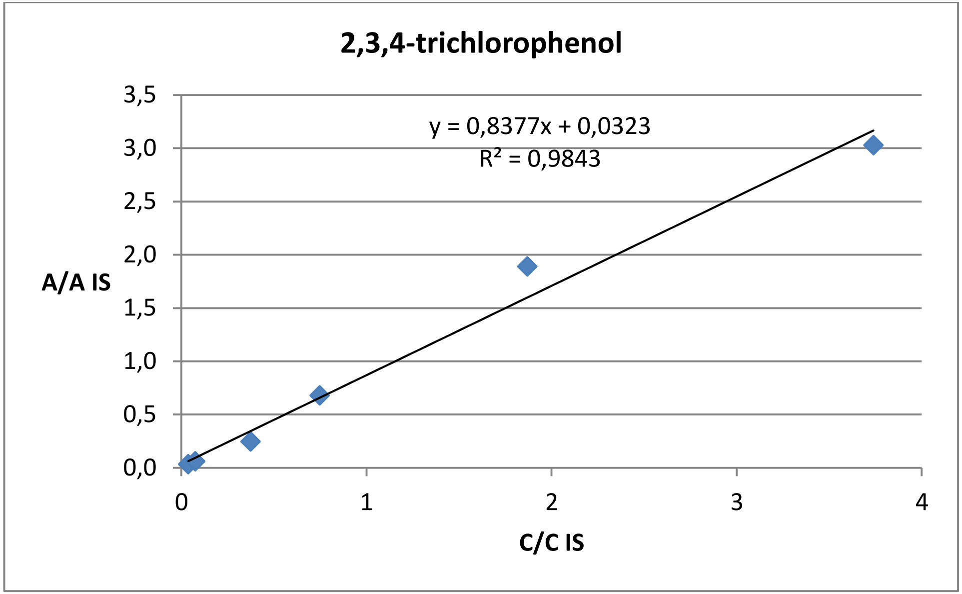

2,3-dichlorophenol
y = 1,1701x + 0,0137
R² = 0,9866
A/A IS
5,0
4,5
4,0
3,5
3,0
2,5
2,0
1,5
1,0
0,5
0,0
0
1
2
3
4
C/C IS

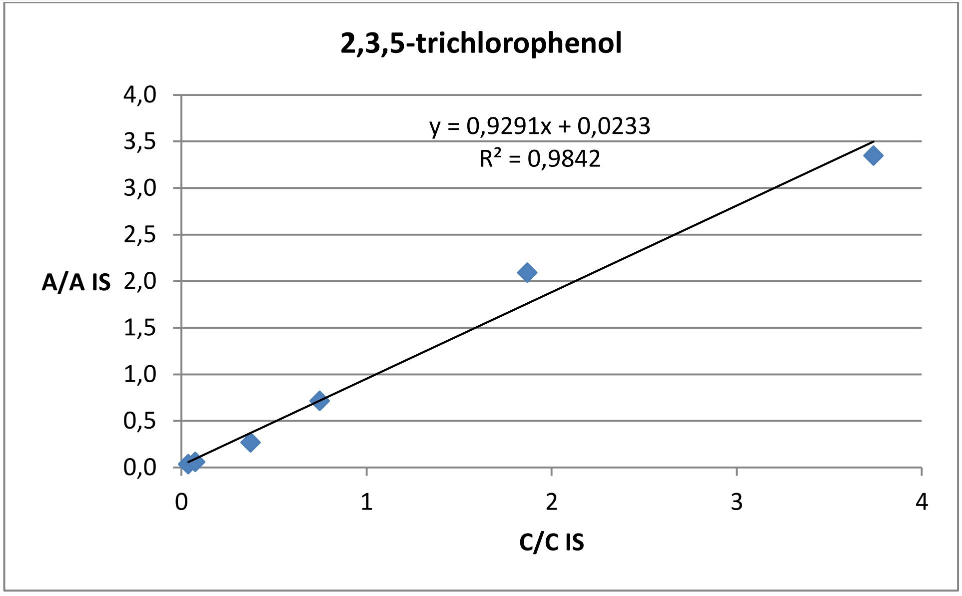

(2,4+2,6)-dichlorophenol
y = 1,1101x + 0,051
R² = 0,9892
A/A IS
9,0
8,0
7,0
6,0
5,0
4,0
3,0
2,0
1,0
0,0
0
2
4
6
8
C/C IS

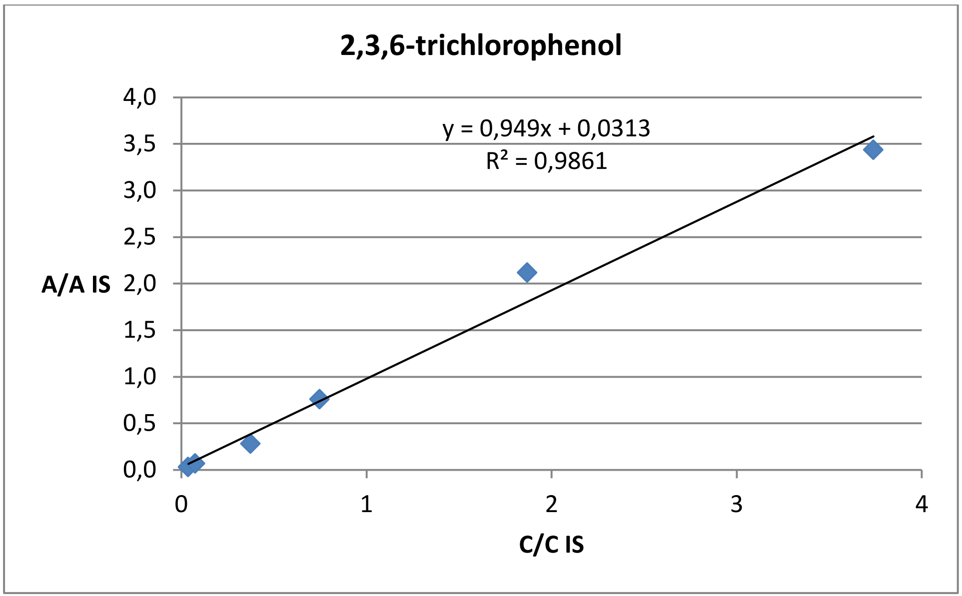

2,5-dichlorophenol
y = 0,9949x + 0,0105
R² = 0,9999
A/A IS
4,5
4,0
3,5
3,0
2,5
2,0
1,5
1,0
0,5
0,0
0
1
2
3
4
5
C/C IS

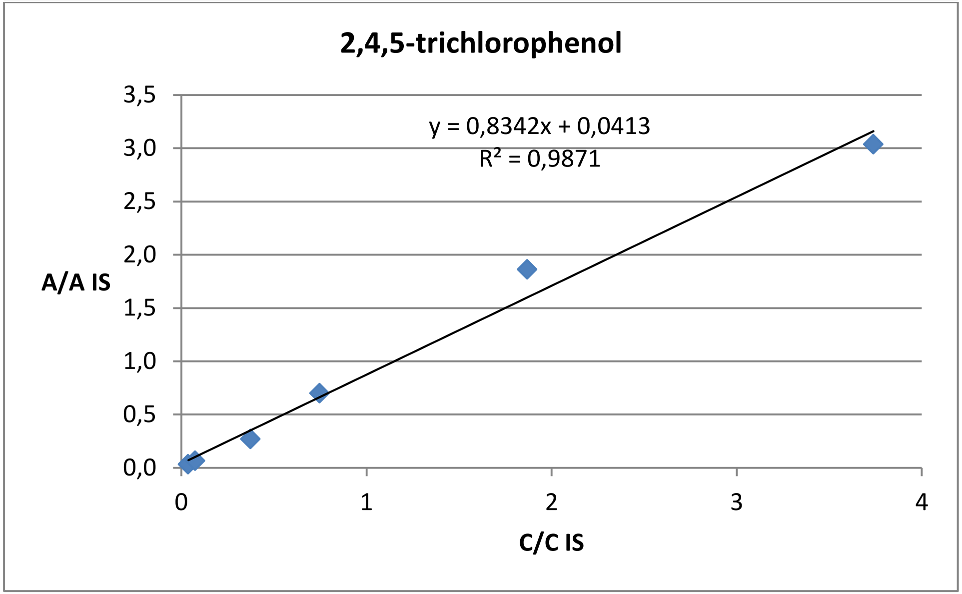

3,4-dichlorophenol
y = 1,7086x + 0,0811
R² = 0,9905
A/A IS
7,0
6,0
5,0
4,0
3,0
2,0
1,0
0,0
0
1
2
3
4
C/C IS

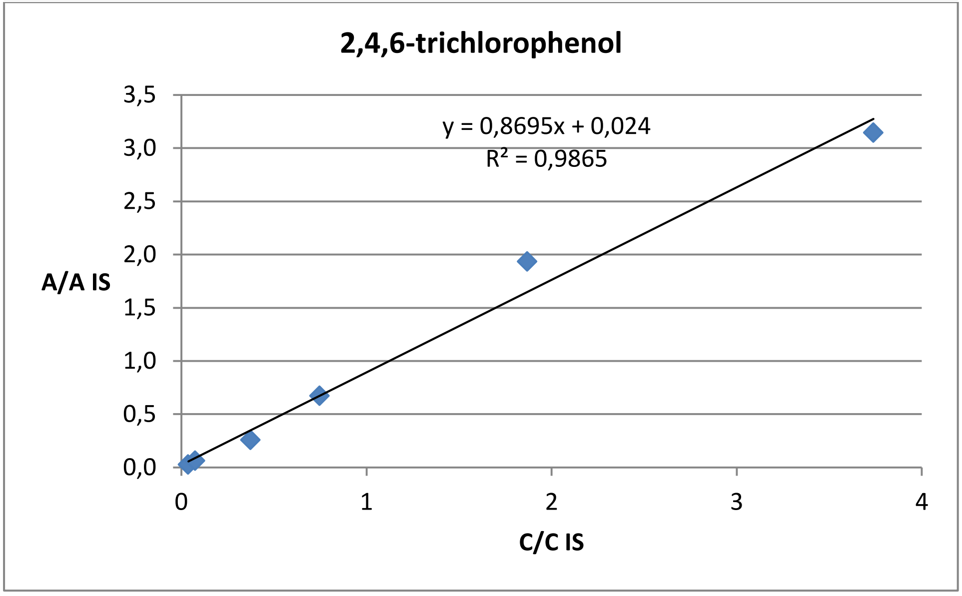

3,5-dichlorophenol
y = 1,9863x + 0,0656
R² = 0,9903
A/A IS
8,0
7,0
6,0
5,0
4,0
3,0
2,0
1,0
0,0
0
1
2
3
4
C/C IS

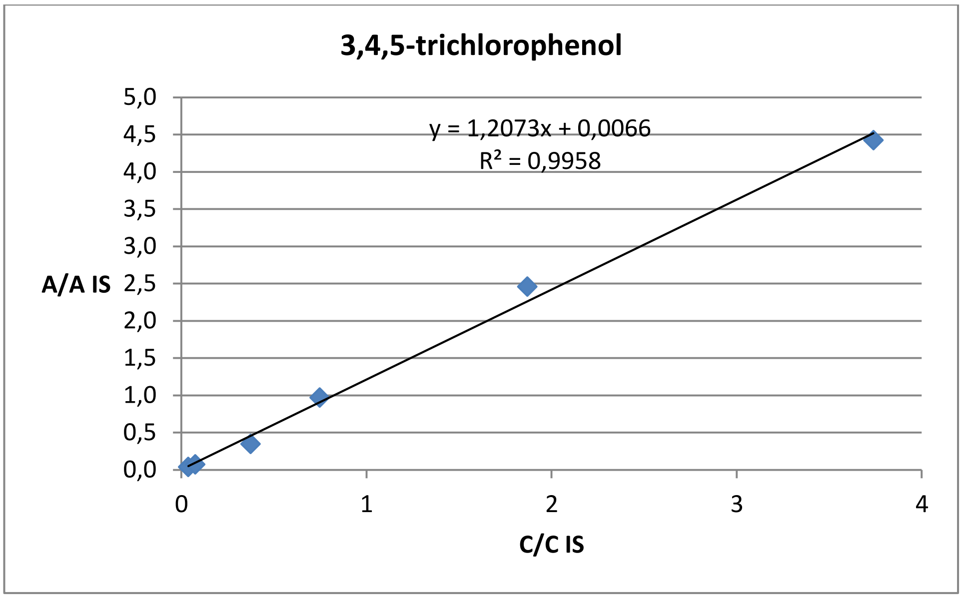

2,3,4-trichlorophenol
y = 0,8377x + 0,0323
R² = 0,9843
A/A IS
3,5
3,0
2,5
2,0
1,5
1,0
0,5
0,0
0
1
2
3
4
C/C IS

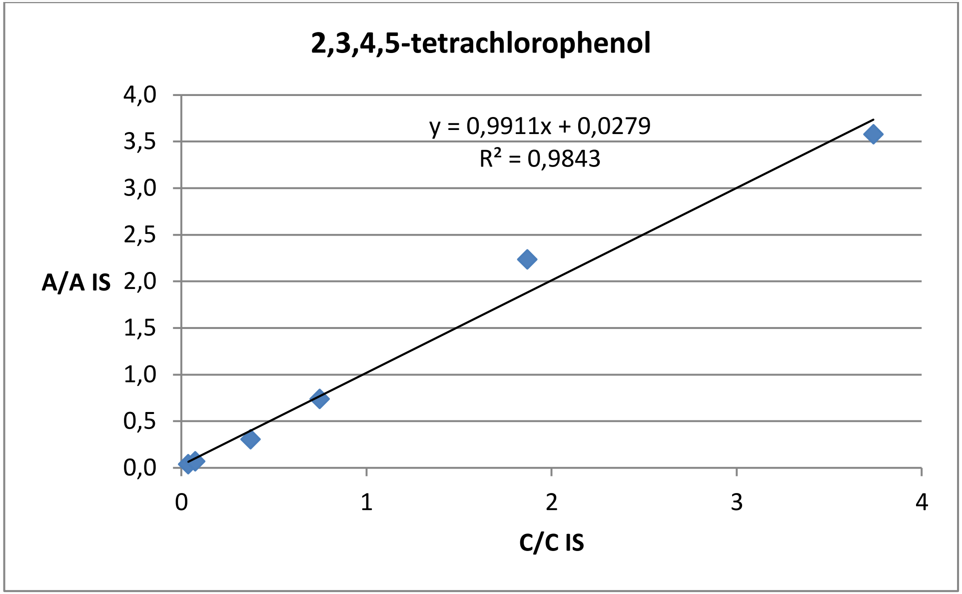

2,3,5-trichlorophenol
y = 0,9291x + 0,0233
R² = 0,9842
A/A IS
4,0
3,5
3,0
2,5
2,0
1,5
1,0
0,5
0,0
0
1
2
3
4
C/C IS

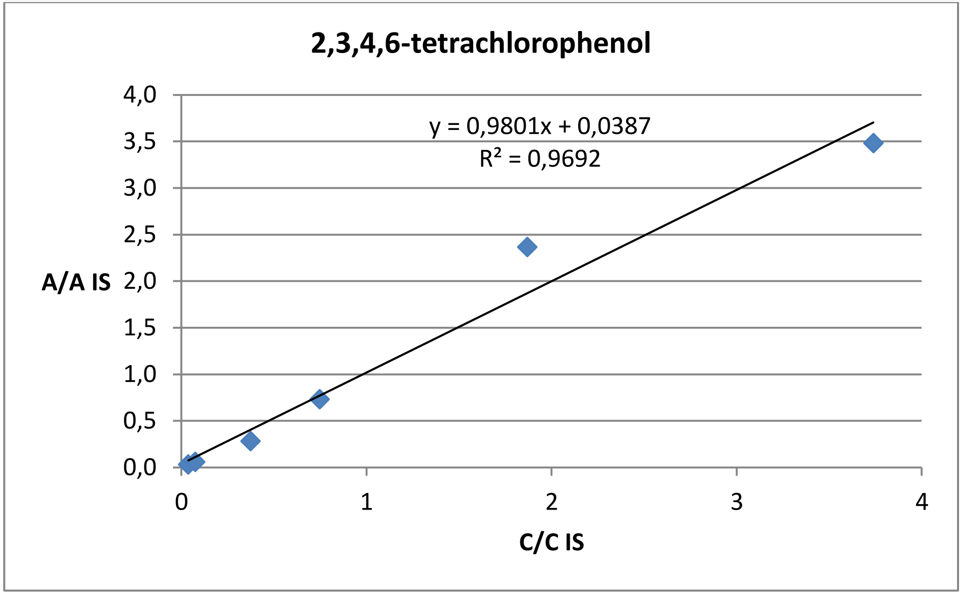

2,3,6-trichlorophenol
y = 0,949x + 0,0313
R² = 0,9861
A/A IS
4,0
3,5
3,0
2,5
2,0
1,5
1,0
0,5
0,0
0
1
2
3
4
C/C IS

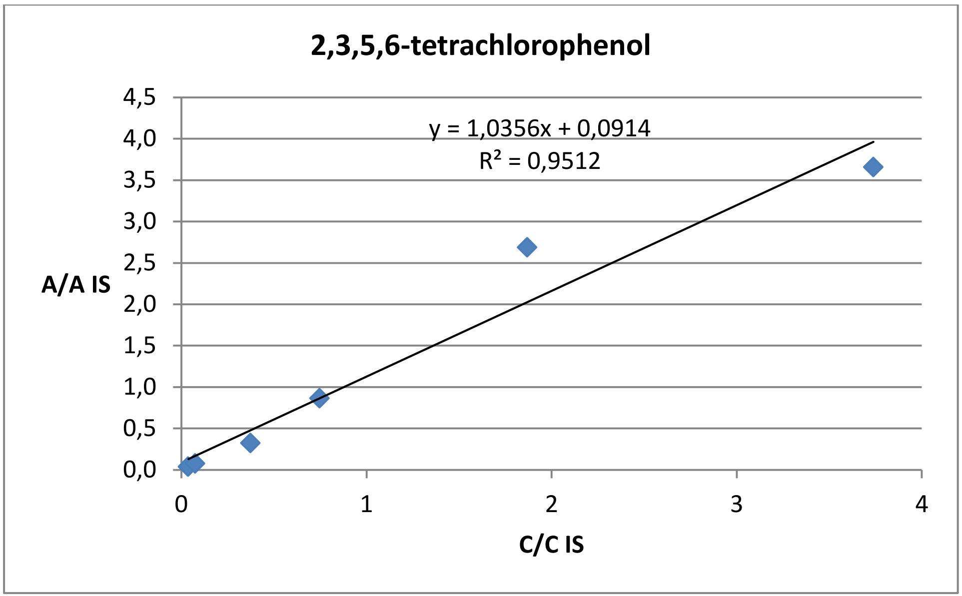

2,4,5-trichlorophenol
y = 0,8342x + 0,0413
R² = 0,9871
A/A IS
3,5
3,0
2,5
2,0
1,5
1,0
0,5
0,0
0
1
2
3
4
C/C IS

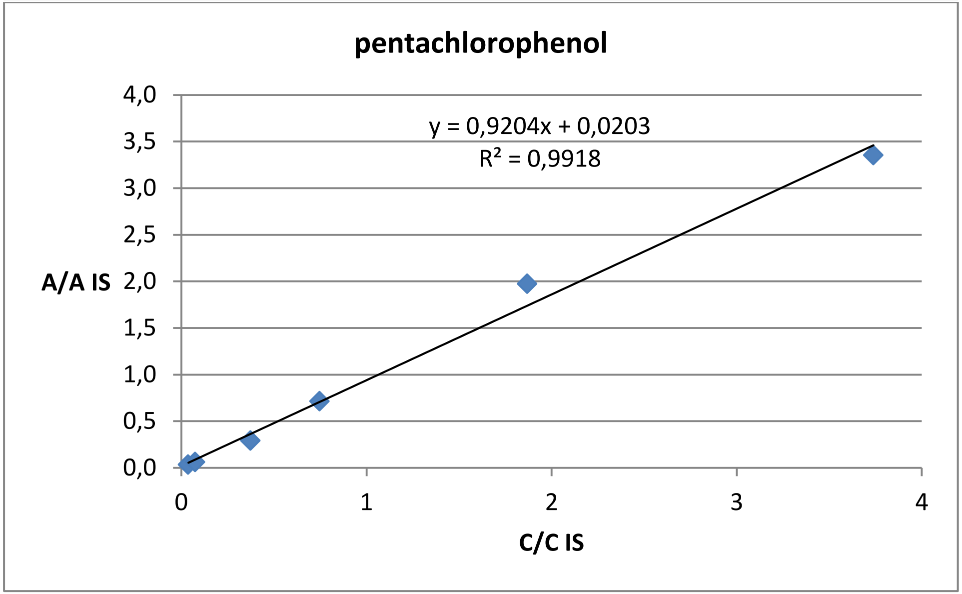

2,4,6-trichlorophenol
y = 0,8695x + 0,024
R² = 0,9865
A/A IS
3,5
3,0
2,5
2,0
1,5
1,0
0,5
0,0
0
1
2
3
4
C/C IS

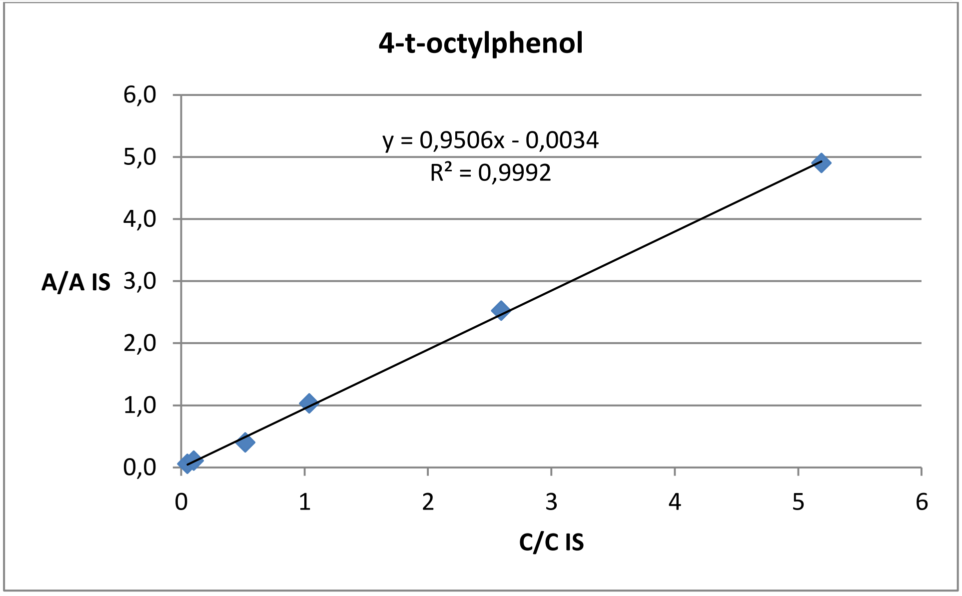

3,4,5-trichlorophenol
y = 1,2073x + 0,0066
R² = 0,9958
A/A IS
5,0
4,5
4,0
3,5
3,0
2,5
2,0
1,5
1,0
0,5
0,0
0
1
2
3
4
C/C IS

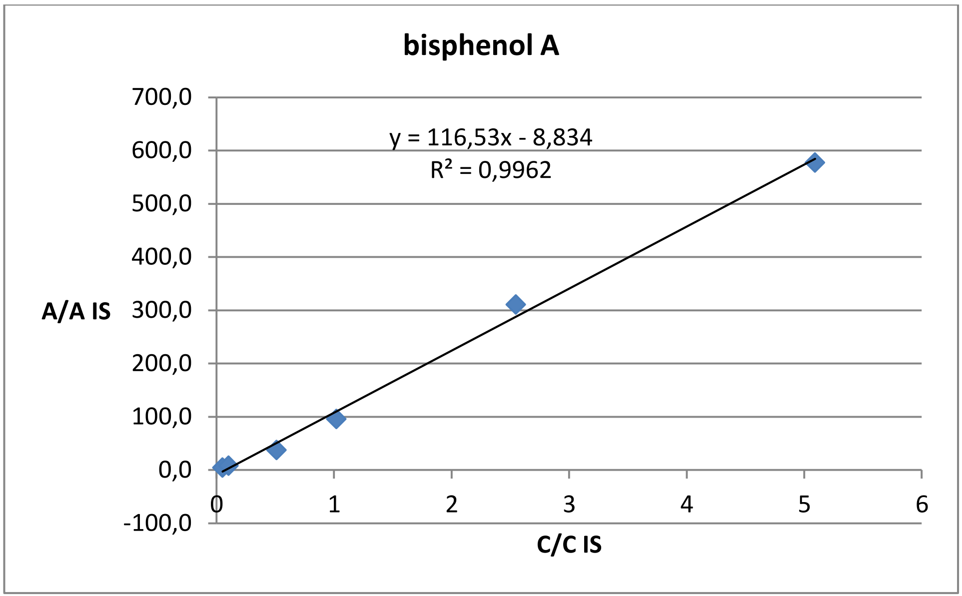

2,3,4,5-tetrachlorophenol
y = 0,9911x + 0,0279
R² = 0,9843
A/A IS
4,0
3,5
3,0
2,5
2,0
1,5
1,0
0,5
0,0
0
1
2
3
4
C/C IS

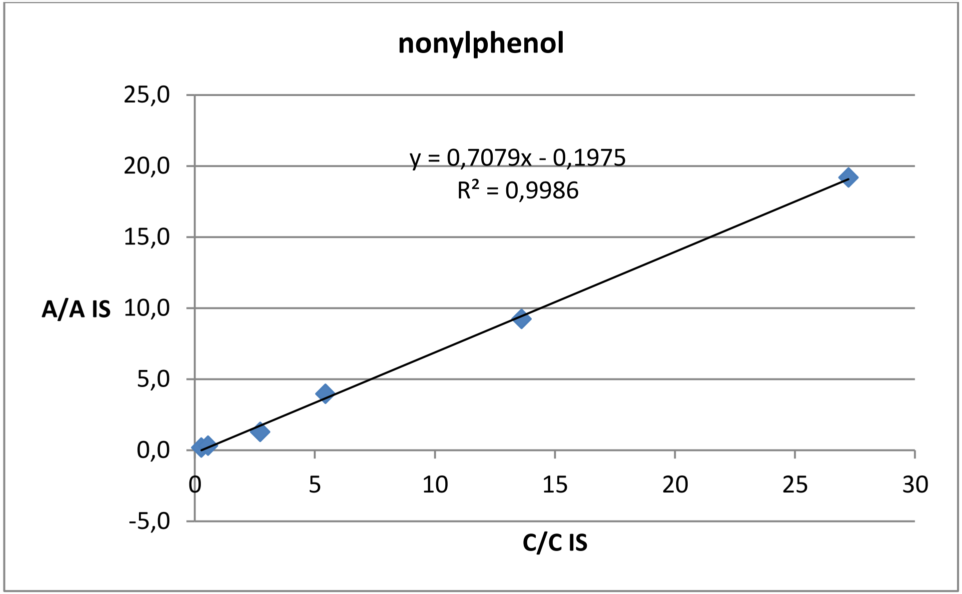

2,3,4,6-tetrachlorophenol
y = 0,9801x + 0,0387
R² = 0,9692
A/A IS
4,0
3,5
3,0
2,5
2,0
1,5
1,0
0,5
0,0
0
1
2
3
4
C/C IS

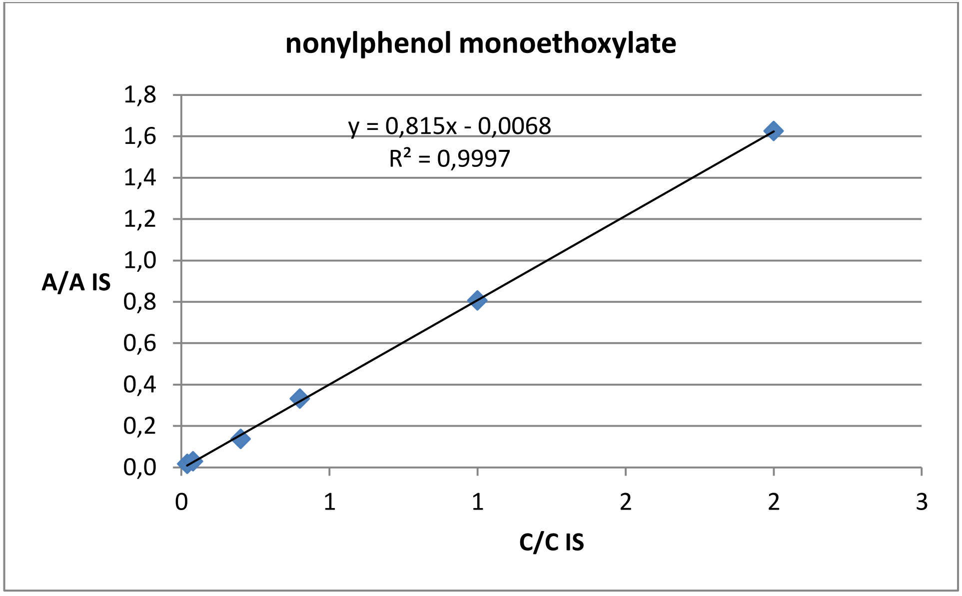

2,3,5,6-tetrachlorophenol
y = 1,0356x + 0,0914
R² = 0,9512
A/A IS
4,5
4,0
3,5
3,0
2,5
2,0
1,5
1,0
0,5
0,0
0
1
2
3
4
C/C IS

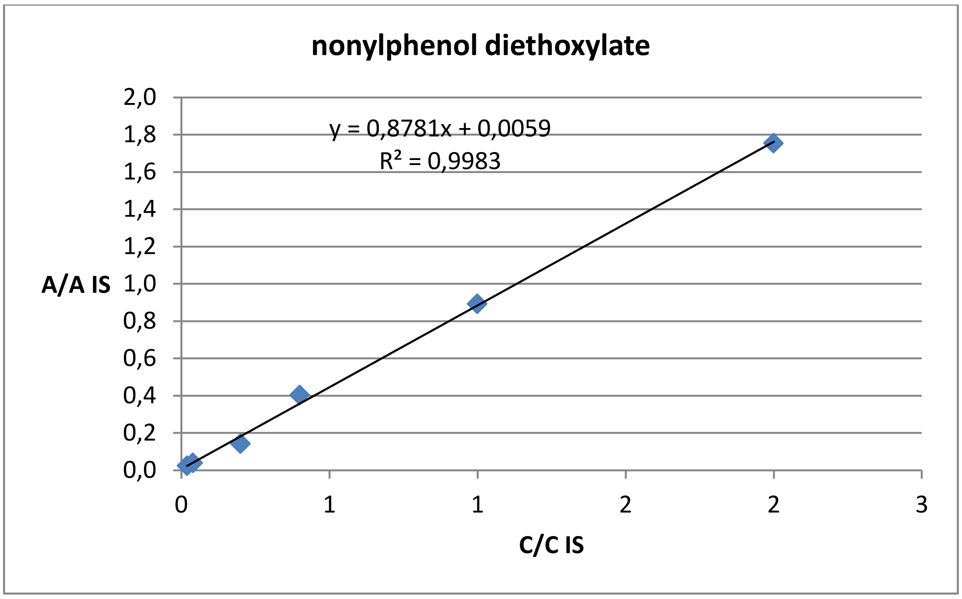

pentachlorophenol
y = 0,9204x + 0,0203
R² = 0,9918
A/A IS
4,0
3,5
3,0
2,5
2,0
1,5
1,0
0,5
0,0
0
1
2
3
4
C/C IS


4-t-octylphenol
y = 0,9506x - 0,0034
R² = 0,9992
A/A IS
6,0
5,0
4,0
3,0
2,0
1,0
0,0
0
1
2
3
4
5
6
C/C IS


bisphenol A
y = 116,53x - 8,834
R² = 0,9962
A/A IS
700,0
600,0
500,0
400,0
300,0
200,0
100,0
0,0
-100,0
0
1
2
3
4
5
6
C/C IS


nonylphenol
y = 0,7079x - 0,1975
R² = 0,9986
A/A IS
25,0
20,0
15,0
10,0
5,0
0,0
-5,0
0
5
10
15
20
25
30
C/C IS


nonylphenol monoethoxylate
y = 0,815x - 0,0068
R² = 0,9997
A/A IS
1,8
1,6
1,4
1,2
1,0
0,8
0,6
0,4
0,2
0,0
0
1
1
2
2
3
C/C IS



11.5. DETERMINATION OF PHENOLS IN WATER PROOFING SHEETS (PVC) WITH METHOD CEN/TS 16182

11.5.1. SAMPLE

Water proofing sheets (PVC) were obtained from Dakgroothandel. A particule size reduction to 1 cm was carried out by SGS Intron.

11.5.2. ANALYSIS

- 15 ml acetone was added to 2 g of sample and the solution was spiked with internal standards
- The sample was ultrasonically extracted for 2h; PVC material swells and softens in acetone
- After 12h the supernatant solution was poured into 75 ml of hexane to precipitate the dissolved PVC fraction
- The solution was concentrated to 5 ml under a gentle stream of nitrogen and centrifuged
- The upper layer was transferred to a vial and concentrated to dryness (to remove all aceton)
- 1 ml of hexane was added and the phenols were derivatised by adding 100 µl MSTFA (10% in hexane); the mixture was allowed to react for 15 min
- ^{13}C-tetrachlorobenzene was added as injection standard and the solution was injected into the GC-MS
- Remark: evaporation of the extract to dryness leads to precipation of polymeric residue, which does not dissolve in hexane

11.5.3. RESULTS

→ Repeatability

The sample was analysed in five fold. The results are given in Table 50. The concentrations of 4-t-octylphenol, nonylphenol mono-ethoxylate and all chlorophenols were lower than LOD. For the other phenols the repeatability was calculated. The %RSD for phenol was good (9.6%) although the concentration exceeds the linear range. For nonylphenol the %RSD was acceptable (22.1%). For bisphenol A and NP diethoxylate the %RSD was too high (>30%) but the concentration of these components was close to LOD.

→ Check on method performance

The concentration of the phenols in the procedure blank was lower than the LOD, except for nonylphenol (0.01 mg/kg).
The recoveries of the internal standards are given in Table 51. Only for ^{13}C-4-chlorophenol the recovery is acceptable. For all other internal standards the recovery is too low (2% - 29%).

→ Sensitivity

The sensitivity of the method was calculated with S/N using the response of 2,3,4-trichlorophenol in the sample. The LOD for 2,3,4-trichlorophenol was 0.002 mg/kg. Method CEN/TS 16182 specifies a LOD for nonylphenol of 0.1 mg/kg for sludge and 0.02 mg/kg for biowaste (expressed on dry matter).

11.5.4. COMMENTS

Although data are lacking for the chlorophenols, it can be concluded that because of the very low recovery of the internal standards the method can not be accepted for the measurement of phenols in water proofing sheets. The low recovery is most probably caused by the PVC matrix. It can be stated the phenols are captured in the residue of co-extracted polymers and only a limited number of phenol compounds is reconstituted in hexane and derivatised in the final step. The use of a keeper (e.g. iso-octane) when evaporating the hexane extract prior to the derivatisation step, can help to keep the phthalates in solution.

11.5.5. CHROMATOGRAMS

The GC/MS ion chromatograms of the phenols in water proofing sheets are shown in Figure 30.

11.5.6. CONCLUSION

Method CEN/TS 16182 using ultrasonic extraction with acetone and measurement with GC/MS is not suited for the measurement of phenols in water proofing sheets (PVC).

Table 50: Measured concentrations of phenols in water proofing sheets (PVC)

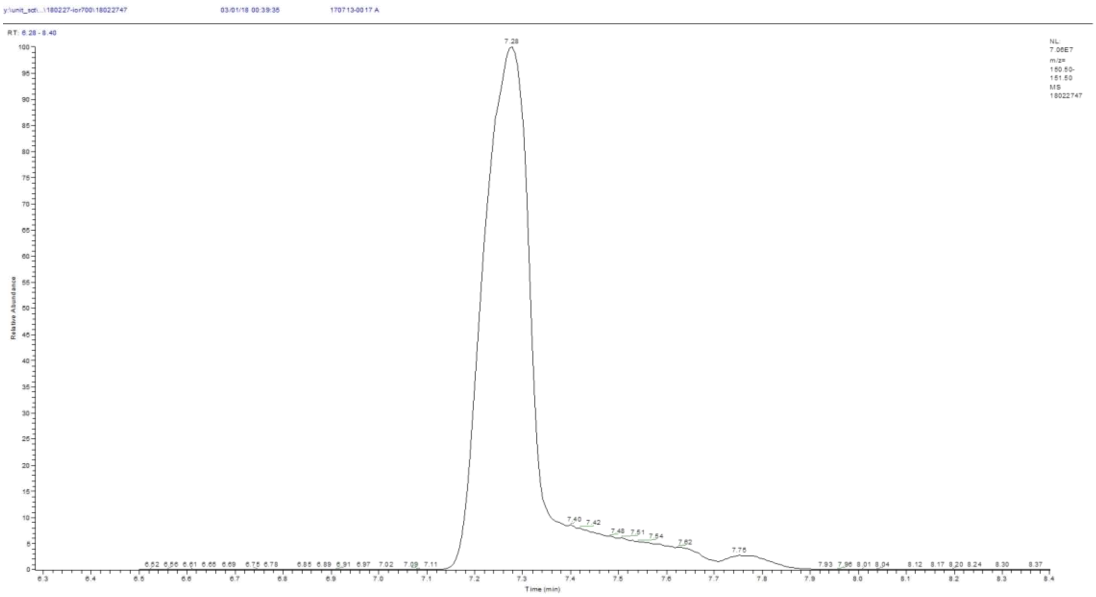
Replicate n°	**1** mg/kg	**2** mg/kg	**3** mg/kg	**4** mg/kg	**5** mg/kg	**Average** mg/kg	**Standdev** mg/kg	**CV$_r$** %
phenol	178	162	166	189	204	180	17,2	9,6
2-chloorphenol	< 0,01	< 0,01	< 0,01	< 0,01	< 0,01	-	-	-
3-chloorphenol	< 0,01	< 0,01	< 0,01	< 0,01	< 0,01	-	-	-
4-chloorphenol	< 0,01	< 0,01	< 0,01	< 0,01	< 0,01	-	-	-
2,3-dichloorphenol	< 0,01	< 0,01	< 0,01	< 0,01	< 0,01	-	-	-
(2,4+2,6)-dichloorphenol	< 0,01	< 0,01	< 0,01	< 0,01	< 0,01	-	-	-
2,5-dichloorphenol	< 0,01	< 0,01	< 0,01	< 0,01	< 0,01	-	-	-
3,4-dichloorphenol	< 0,01	< 0,01	< 0,01	< 0,01	< 0,01	-	-	-
3,5-dichloorphenol	< 0,01	< 0,01	< 0,01	< 0,01	< 0,01	-	-	-
2,3,4-trichloorphenol	< 0,01	< 0,01	< 0,01	< 0,01	< 0,01	-	-	-
2,3,5-trichloorphenol	< 0,01	< 0,01	< 0,01	< 0,01	< 0,01	-	-	-
2,3,6-trichloorphenol	< 0,01	< 0,01	< 0,01	< 0,01	< 0,01	-	-	-
2,4,5-trichloorphenol	< 0,01	< 0,01	< 0,01	< 0,01	< 0,01	-	-	-
2,4,6-trichloorphenol	< 0,01	< 0,01	< 0,01	< 0,01	< 0,01	-	-	-
3,4,5-trichloorphenol	< 0,01	< 0,01	< 0,01	< 0,01	< 0,01	-	-	-
2,3,4,5-tetrachloorphenol	< 0,01	< 0,01	< 0,01	< 0,01	< 0,01	-	-	-
2,3,4,6-tetrachloorphenol	< 0,01	< 0,01	< 0,01	< 0,01	< 0,01	-	-	-
2,3,5,6-tetrachloorphenol	< 0,01	< 0,01	< 0,01	< 0,01	< 0,01	-	-	-
pentachloorphenol	< 0,01	< 0,01	< 0,01	< 0,01	< 0,01	-	-	-
4-tert-octylphenol	< 0,01	< 0,01	< 0,01	< 0,01	< 0,01	-	-	-
bisphenol A	0,063	0,131	0,181	0,097	0,085	0,111	0,046	41,3
nonylphenol	2,09	1,94	1,83	1,38	1,22	1,69	0,37	22,1
NP monoethoxylate	< 0,005	0,006	< 0,005	< 0,005	< 0,005	-	-	-
NP diethoxylate	0,017	0,01	0,023	0,023	0,016	0,018	0,006	32,2

Table 51: Recoveries of the internal standards in water proofing sheets using method CEN/TS 16182

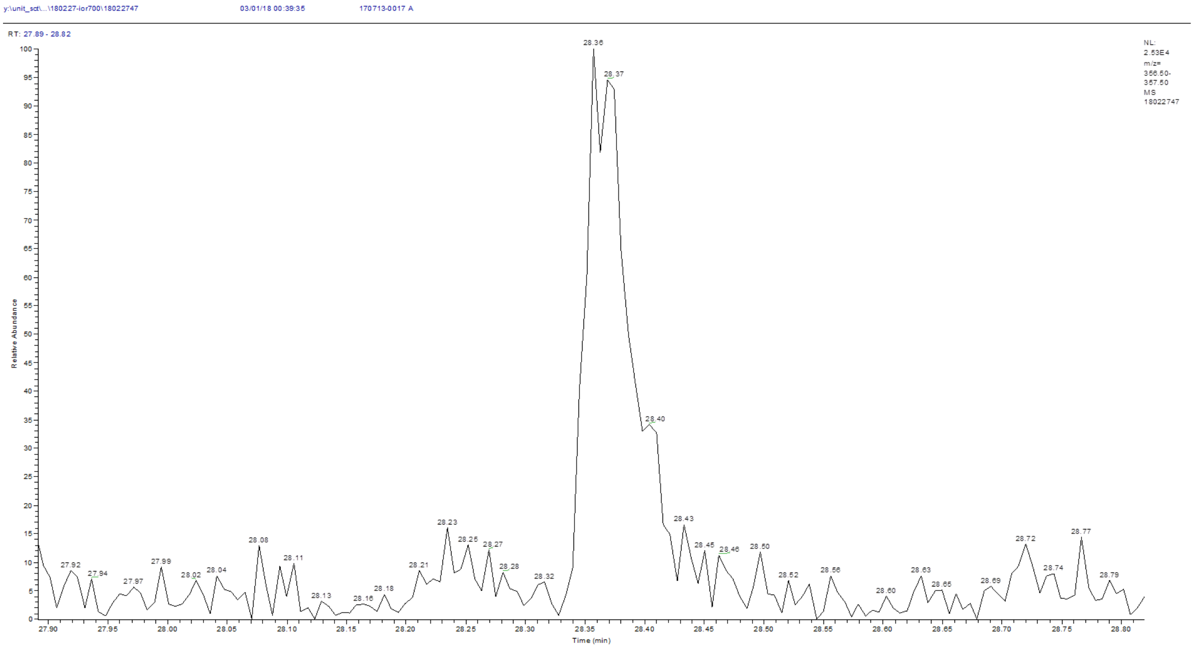
Replicate n°	**1** %	**2** %	**3** %	**4** %	**5** %
13C-phenol	24	29	25	17	21
13C-4-chlorophenol	76	62	51	51	58
13C-2,4-dichlorophenol	24	24	22	17	22
13C-2,4,5-trichlorophenol	21	22	16	14	20
13C-2,3,4,5-tetrachlorophenol	19	19	15	12	13
13C-pentachlorophenol	11	11	8	7	7
13C-octylphenol	21	22	17	14	19
D16-bisphenol A	13	6	4	6	9
13C-nonylphenol	14	16	14	15	23
13C-NP monoethoxylate	21	18	17	13	17
13C-NP diethoxylate	4	6	2	4	4

Figure 30: Chromatograms of phenols in water proofing sheets (PVC)

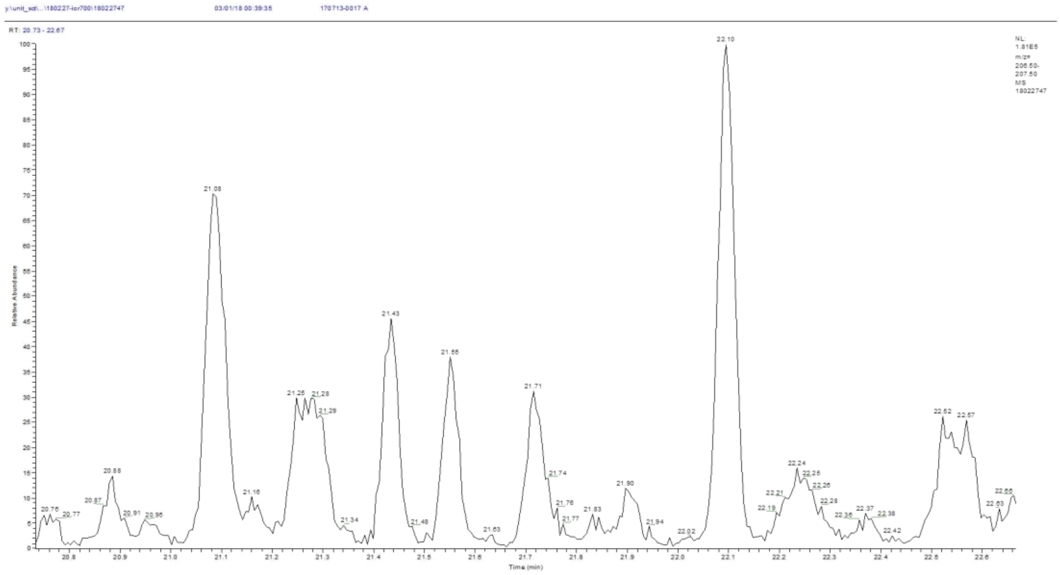
Phenol



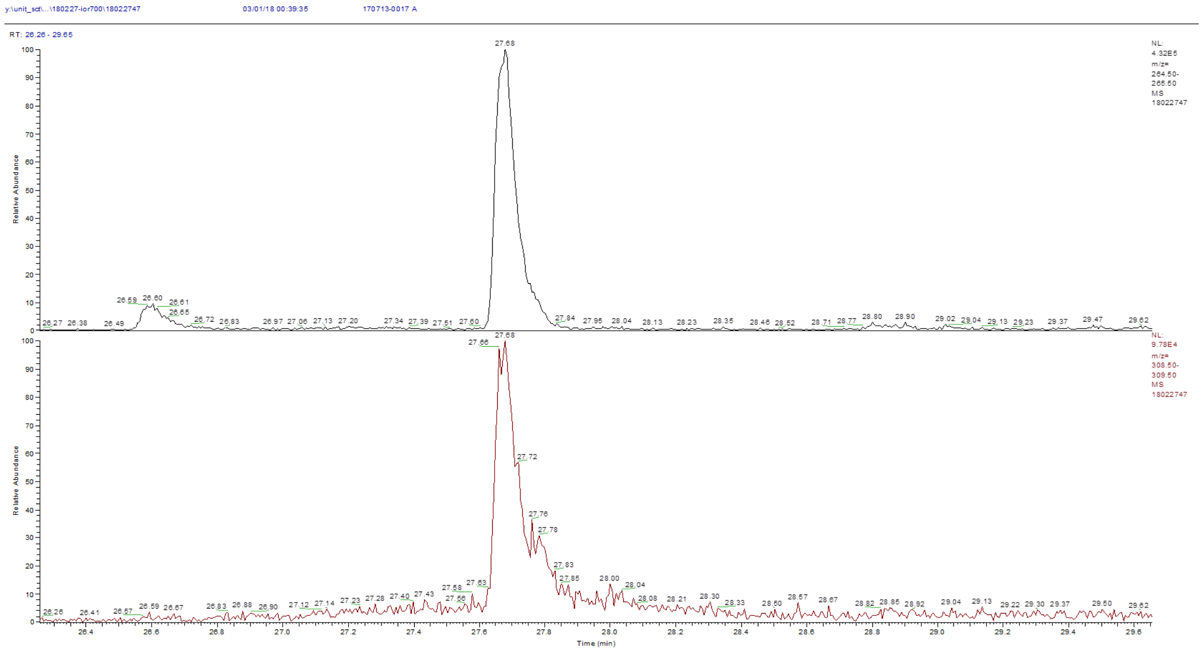
Bisphenol A



Nonylphenol



NP diethoxylate



CHAPTER 12 DETERMINATION OF MINERAL OIL IN ELUATES OF CONSTRUCTION PRODUCTS

12.1. EN ISO 9377-2 - WATER QUALITY -- DETERMINATION OF HYDROCARBON OIL INDEX -- PART 2: METHOD USING SOLVENT EXTRACTION AND GAS CHROMATOGRAPHY

12.1.1. METHOD DESCRIPTION

A summary of EN ISO 9377-2 and modifications done by VITO is given in Table 52. The method was applied for eluates of recycled mixed aggregate.

12.1.2. MEASUREMENT CONDITIONS APPLIED BY VITO

See 2.1.2

12.1.3. CALIBRATION

See 2.1.3

The calibration curve is given in Figure 1 and the curve is linear from 25 to 31000 µg/g. In case of 400 mL intake and a 1 mL final extract volume these concentrations correspond to a sample concentration of 0.075-80 mg/L mineral oil.

12.1.4. PERFORMANCE OF THE GC SYSTEM

See 2.1.4.

Table 52: Summary of EN ISO 9377-2 and method applied by VITO

Samples Parameter list	Short Description of the method to be used	Departures from method by VITO and comments
Recycled mixed aggregates Mineral oil	- Matrix: surface water, waste water, water from sewage treatment plants - Intake: 900 ml - IS: none - Extraction: acidify the sample to pH 2, add MgSO4, LLE extraction with hexane or another alkane - Clean-up: florisil column - Measurement: GC-FID - LOQ: 100 µg/l	- Matrix: eluate - Intake: 400 ml - IS: n-C40 - Clean-up: shaking with florisil

12.2. DETERMINATION OF MINERAL OIL IN ELUATES OF RECYCLED MIXED AGGREGATES

12.2.1. SAMPLE

Two series of eluates of recycled mixed aggregates were received from SGS Intron:

- PCB-Puin L/S=1.21 27-10-17 (eluate A)
- PCB-Puin L/S=8.79 6-11-17 (eluate B).

The eluates were prepared according to CEN/TS 16637-3 (T = 20°C, flow rate = 98 mL/h).
The samples were taken in dark glass bottles and transferred to VITO in coolboxes. The samples were stored in a refrigerator in expectation of analysis.

12.2.2. ANALYSIS

- Ca 400 mL of eluate was transferred to a separatory funnel
- 80 g/L $MgSO_4$, 100 µg tetracontane (C40) en 30 mL hexane were added and the mixture was shaken for 30 min
- The hexane layer was separated and the eluate was shaken another 2 times with 25 mL hexane
- The combined hexane fractions were dried with anhydrous sodium sulphate and concentrated to ca 10 g
- The hexane layer was cleaned by shaking with 2 g of activated florisil during 10 min
- The extract was filtered on a glass fiber filter, concentrated to 1 mL and analysed with GC/FID

12.2.3. COMMENTS

VITO uses an internal standard (C40) to correct for losses during sample extraction and clean up. The use of internal standard will enhance the recovery and the repeatability of the method.

12.2.4. RESULTS

→ Repeatability

The results of the replicate determinations of mineral oil in eluates of recycled mixed aggregates are given in Table 53. The results show that no mineral oil was detected in the eluates in a concentration >100 µg/L. Although no repeatability data can be given for this eluates, it can be concluded on the basis of the recovery data for the internal standard that the method can be applied reproducibly and quantitatively. The average recovery of the internal standard was 98% and the relative standard deviation 5%.

→ Check on method performance

For extraction control, a fortified sample of mineral water was analysed as QC sample. The blank water sample was spiked with mineral oil at a concentration level of 810 µg/l. The recovery the mineral oil was 98%. Remark that VITO used internal standard to correct for losses during the sample preparation. If the results are calculated with external standard calibration, the recovery is only 38%.

→ **Sensitivity**

On the basis of the lowest concentration of the linear range and assuming ~100% recovery the limit of quantification can be set to 100 µg/L, which is in agreement with the LOQ set in the standard.

Table 53: Measured concentrations for mineral oil in eluates of recycled mixed aggregates.

Sample	**conc.** µg/L	**Recovery** %	**Recovery IS** %
Blank	< 100		
QC sample	797	98%	101
170713-0020 A1	< 100		95
170713-0020 A2	< 100		92
170713-0020 A3	< 100		92
170713-0020 A4	< 100		94
170713-0020 A5	< 100		102
170713-0020 B1	< 100		98
170713-0020 B2	< 100		98
170713-0020 B3	< 100		102
170713-0020 B4	< 100		104
170713-0020 B5	< 100		100
		Average	98
		RSD	5%

12.3. CONCLUSION

Data of the repeatability study allow to conclude that EN ISO 9377-2 can be used for the determination of mineral oil in eluates of construction products. It is advised to apply internal standard calibration (e.g. with n-C40 as internal standard).

CHAPTER 13 DETERMINATION OF PAH IN ELUATES OF CONSTRUCTION PRODUCTS

13.1. ISO 28540 - DETERMINATION OF 16 POLYCYCLIC AROMATIC HYDROCARBONS (PAH) IN WATER - METHOD USING GAS CHROMATOGRAPHY WITH MASS SPECTROMETRIC DETECTION

13.1.1. METHOD DESCRIPTION

A summary of ISO 28540 and modifications done by VITO is given in Table 54. The method requires the use of minimum three internal standards, VITO applied isotope dilution with 16 deuterated internal standards. The method was applied for eluates of asphalt aggregate, recycled mixed aggregates and rubber crumbs. The method was used for the determination of the following PAH:

Naftalene
Acenaftylene
Acenaftene
Fluorene
Fenanthrene
Anthracene
Fluoranthene
Pyrene
Benzo(a)anthracene
Chrysene
Benzo(b)fluoranthene
Benzo(k)fluoranthene
Benzo(a)pyrene
Indeno(1,2,3,c,d)pyrene
Dibenzo(a,h)anthracene
Benzo(g,h,i)perylene

13.1.2. MEASUREMENT CONDITIONS APPLIED BY VITO

For the instrument settings, use of internal standards and the ions used for quantitation see 3.1.2.

13.1.3. CALIBRATION DIAGRAMS

Seven calibration solutions of PAH were prepared in a concentration range of 0.05 to 4.2 µg/ml (except benzo(k)fluoranthene: 0.07 to 5.6 µg/ml). Internal standards (deuterated PAH) and injection standards (D10-methylnaftalene and D12-perylene) were added to the calibration solutions in a fixed concentration of 0.8 µg/ml. The calibration curves are given in Figure 4 and are linear over the injected range.

In case of 500 ml intake and a 250 µl final extract volume these concentrations correspond to a sample concentration of 0.025 to 2.1 µg/l (except for benzo(k)fluoranthene: 0.035 to 2.8 µg/l).

For calibration purposes a calibration verification solution was injected before and after the measurement of the samples. The calibration verification solution contains 0.7 – 2.5 mg/l per PAH and 0.8 µg/l per internal standard. The average relative response factor of the PAH in these solutions was used to calculate the PAH concentration in the sample.

Table 54: Summary of ISO 28540 and method applied by VITO

Sample **Parameter list** **Method to be used**	**Short Description of the method to be used**	**Short description of the VITO Method**	**Method differences**	**Comment**
Asphalt concrete, Recycled mixed aggregates, Asphalt aggregate, Rubber crumbs	- Matrix: drinking water, ground water, surface water	- Matrix : eluate	- none	
PAH	- Intake: 950 ml	- Intake: 500 ml		
	- IS: min. 3 labelled PAH	- IS: 16 labelled PAH		
ISO 28540	- Extraction: LLE with hexane or another volatile solvent	- Extraction: LLE with DCM		
	- Clean-up : silica column (optional)	- Clean-up : silica/alumina column (optional)		
	- Measurement: GC-MS	- Measurement: GC-MS		
	- LOQ: 5 – 10 ng/l per component	- LOQ: 10 ng/l per component		

13.2. DETERMINATION OF PAH IN ELUATE OF ASPHALT AGGREGATE WITH METHOD ISO 28540

13.2.1. SAMPLE

Two eluates of asphalte aggregate were received from SGS Intron:

- L/S=1.09 22-11-17 (eluate A)
- L/S=8.91 4-12-17 (eluate B).

The eluates were prepared according to CEN/TS 16637-3 (T = 20°C, flow rate = 98 mL/h).
The samples were taken in dark glass bottles and transferred to VITO in coolboxes. The samples were stored in a refrigerator in expectation of analysis.

13.2.2. ANALYSIS

- 500 ml eluate is transferred to a separatory funnel
- The sample is spiked with internal standards (16 deuterated PAH)
- The sample was extracted with 25 ml of hexane by shaking for 1h
- The hexane extract was dried with anhydrous sodium sulphate and concentrated under a gentle stream of nitrogen to 1 ml
- The extract was concentrated to 250 µl with a solvent exchange to toluene
- The injection standards were added to the extract
- Due to the high PAH concentrations in the sample, the extract was diluted 20 times before it was analysed with GC/MS

13.2.3. RESULTS

→ Repeatability

Both eluates were analysed in five fold. The results are given in Table 55 and Table 56. For all the PAH in both samples the %RSD is higher than 10%. For 6 PAH in eluate A the %RSD is higher than 15%, but for some of them the concentration is near the detection limit of 0.01 µg/L and therefore acceptable. For 11 PAH in eluate B the %RSD is above 15%, with 5 of them slightly above 20%. Given the fact that the concentrations in eluate B are low (0.01-0.2 µg/L) the repeatabilities are considered to be acceptable.
Remark that SGS Intron did not deliver one (homogeneous) sample from which VITO took 5 subsamples for the determination of the repeatability. Instead VITO received 5 different recipients of eluate from SGS Intron. So the repeatability of the production of the eluate is to some extent included in the %RSD.

→ Check on method performance

The recoveries of the internal standards in each sample were calculated using the calibration standard as a reference (100%). The results are given in Table 57 and Table 58. The recoveries are sometimes lower than 70% (but higher than 50%). Because isotope dilution was used the recoveries are acceptable. For D8-naftalene in eluate A the recovery is sometimes lower than 50%, probably because of evaporation loss during the extract concentration step.

Remark that the repeatabilities of the internal standard recoveries are much better than those of the native compounds.

→ **Sensitivity**

The sensitivity of the method was calculated with S/N using the response of fluorene in eluate A. The LOD for fluorene was 0.01 µg/l. This is equal to the detection limit of PAH in surface water in method NEN ISO 28540 (0.01 µg/l).

13.2.4. COMMENTS

The %RSD of ISO 28540 using liquid/liquid extraction with hexane is rather high, but acceptable. For some PAH the high %RSD is caused by the low concentration (near the detection limit). For the other PAH the higher %RSD can be explained by the fact that the spread also includes the variances of the eluate production. From the good repeatability of the recovery of the internal standards it can be concluded that the analytical method is suited for the analysis of PAH in eluate of asphalt aggregate.

13.2.5. CHROMATOGRAMS

The GC/MS ion chromatograms of PAH in eluate of asphalt aggregate are shown in Figure 31.

13.2.6. CONCLUSION

Method ISO 28540 is suited for the analysis of PAH in eluates of asphalt aggregate.

Table 55: Measured concentrations of PAH in eluate A (asphalt aggregate) using method ISO 28540

Replicate n°	**1** µg/l	**2** µg/l	**3** µg/l	**4** µg/l	**5** µg/l	**Average** µg/l	**St.Dev.** µg/l	**CV$_r$** %
Naftalene	<0,01	<0,01	<0,01	<0,01	<0,01	-	-	-
Acenaftylene	0,02	0,02	0,01	0,02	0,01	0,02	0,004	22,3
Acenaftene	0,0582	0,077	0,0312	0,037	0,0289	0,05	0,02	44,4
Fluorene	0,031	0,0357	0,018	0,02	0,0196	0,03	0,01	29,9
Fenanthrene	0,18	0,149	0,121	0,1	0,125	0,14	0,02	16,3
Anthracene	0,072	0,058	0,058	0,0728	0,058	0,06	0,01	12,8
Fluoranthene	0,906	0,65	0,59	0,681	0,593	0,68	0,13	19,1
Pyrene	0,58	0,419	0,388	0,463	0,388	0,45	0,08	17,9
Benzo(a)anthracene	0,381	0,285	0,273	0,356	0,294	0,32	0,05	15,0
Chrysene	0,469	0,351	0,338	0,432	0,38	0,39	0,06	14,0
Benzo(b)fluoranthene	0,615	0,49	0,52	0,63	0,528	0,56	0,06	11,0
Benzo(k)fluoranthene	0,31	0,23	0,24	0,31	0,27	0,27	0,04	13,4
Benzo(a)pyrene	0,76	0,53	0,64	0,73	0,63	0,66	0,09	14,0
Indeno(1,2,3,c,d)pyrene	0,58	0,44	0,49	0,59	0,48	0,52	0,07	12,9
Dibenzo(a,h)anthracene	0,077	0,065	0,073	0,099	0,091	0,08	0,01	16,9
Benzo(g,h,i)perylene	0,576	0,43	0,47	0,57	0,476	0,51	0,07	12,9

Table 56: Measured concentrations of PAH in eluate B (asphalt aggregate)

Replicate n°	**1** µg/l	**2** µg/l	**3** µg/l	**4** µg/l	**5** µg/l	**Average** µg/l	**St.Dev** µg/l	**CV$_r$** %
Naftalene	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	-	-	-
Acenaftylene	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	-	-	-
Acenaftene	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	-	-	-
Fluorene	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	-	-	-
Fenanthrene	0,015	0,024	0,022	0,021	0,025	0,02	0,004	17,4
Anthracene	0,020	0,024	0,022	0,021	0,026	0,02	0,002	10,4
Fluoranthene	0,100	0,150	0,129	0,111	0,150	0,13	0,02	17,8
Pyrene	0,063	0,100	0,083	0,077	0,100	0,08	0,02	18,9
Benzo(a)anthracene	0,045	0,070	0,060	0,056	0,070	0,06	0,01	17,5
Chrysene	0,059	0,092	0,081	0,069	0,089	0,08	0,01	17,7
Benzo(b)fluoranthene	0,182	0,273	0,233	0,177	0,256	0,22	0,04	19,3
Benzo(k)fluoranthene	0,069	0,105	0,089	0,069	0,105	0,09	0,02	20,6
Benzo(a)pyrene	0,196	0,291	0,252	0,187	0,289	0,24	0,05	20,4
Indeno(1,2,3,c,d)pyrene	0,125	0,198	0,161	0,121	0,186	0,16	0,03	22,0
Dibenzo(a,h)anthracene	0,024	0,036	0,032	0,023	0,033	0,03	0,01	20,7
Benzo(g,h,i)perylene	0,123	0,192	0,159	0,114	0,185	0,15	0,04	22,8

Table 57: Recoveries of the internal standards in eluate A (asphalt aggregate)

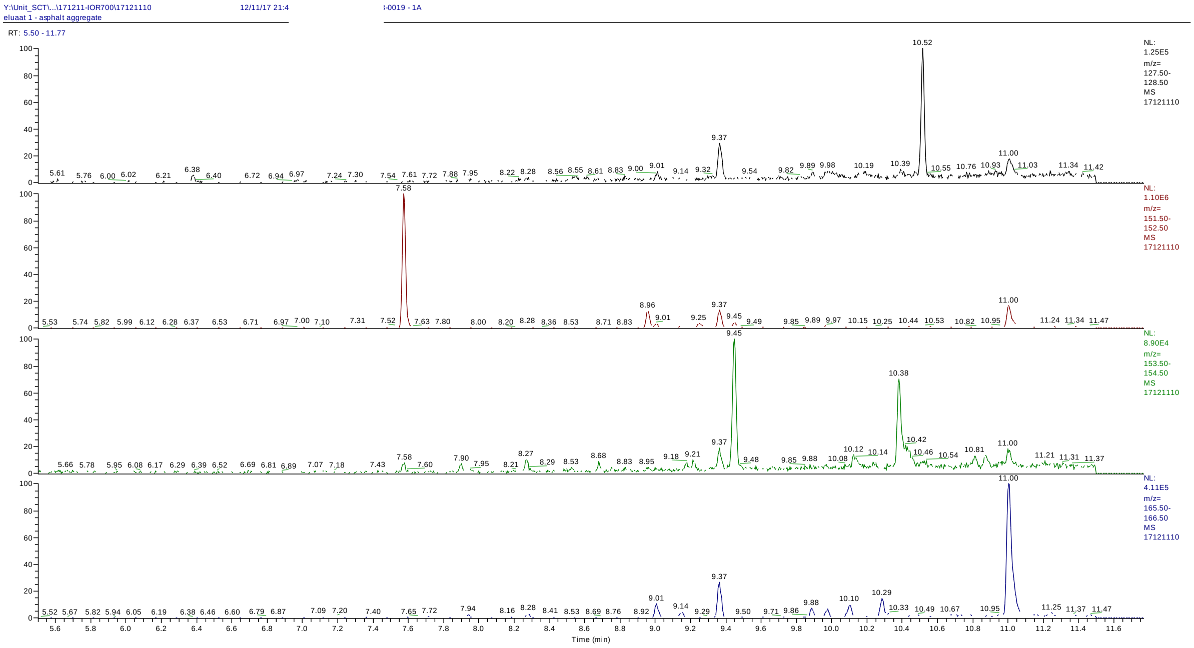
Replicate n°	**1** %	**2** %	**3** %	**4** %	**5** %	**RSD**
D8-naftalene	38	39	61	18	57	40
D8-acenaftylene	64	67	76	56	78	13
D10-acenaftene	65	65	76	53	79	15
D10-fluorene	75	75	83	69	84	8
D10-fenanthrene	84	79	89	76	91	8
D10-anthracene	93	91	98	87	102	6
D10-fluoranthene	104	102	110	96	114	7
D10-pyrene	109	106	115	99	123	8
D12-benzo(a)anthracene	125	126	136	118	154	11
D12-chrysene	101	101	110	94	123	11
D12-benzo(b)fluoranthene	85	80	87	84	92	5
D12-benzo(k)fluoranthene	67	68	70	67	73	4
D12-benzo(a)pyrene	76	79	80	79	85	4
D12-indeno(1,2,3,c,d)pyrene	71	69	73	73	82	7
D14-dibenzo(a,h)anthracene	73	70	73	71	81	6
D12-benzo(g,h,i)perylene	70	69	74	73	82	7
Average recovery	81	80	88	76	94	9

Table 58: Recoveries of the internal standards in eluate B (asphalt aggregate)

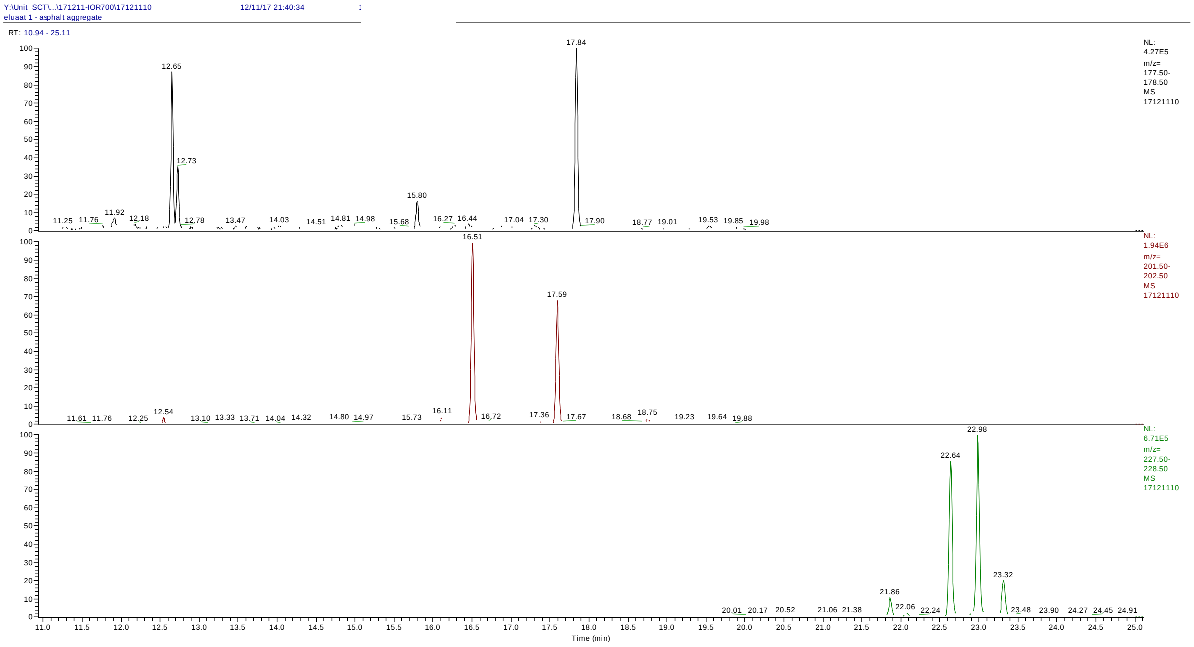
Replicate n°	**1** %	**2** %	**3** %	**4** %	**5** %	**RSD** %
D8-naftalene	51	61	61	62	62	8
D8-acenaftylene	65	71	72	73	74	5
D10-acenaftene	70	77	77	77	81	5
D10-fluorene	76	79	77	79	83	3
D10-fenanthrene	89	87	84	87	94	4
D10-anthracene	101	96	96	98	103	3
D10-fluoranthene	110	108	104	106	114	4
D10-pyrene	116	111	110	110	118	3
D12-benzo(a)anthracene	135	130	132	127	142	4
D12-chrysene	113	111	110	109	118	3
D12-benzo(b)fluoranthene	85	84	83	79	89	4
D12-benzo(k)fluoranthene	69	69	68	66	71	3
D12-benzo(a)pyrene	77	79	76	76	80	2
D12-indeno(1,2,3,c,d)pyrene	69	69	68	66	74	4
D14-dibenzo(a,h)anthracene	67	68	65	66	72	4
D12-benzo(g,h,i)perylene	68	70	68	68	74	4
Average recovery	85	86	84	84	91	3

Figure 31: GC/MS ion chromatograms of PAH in eluate A asphalt aggregate

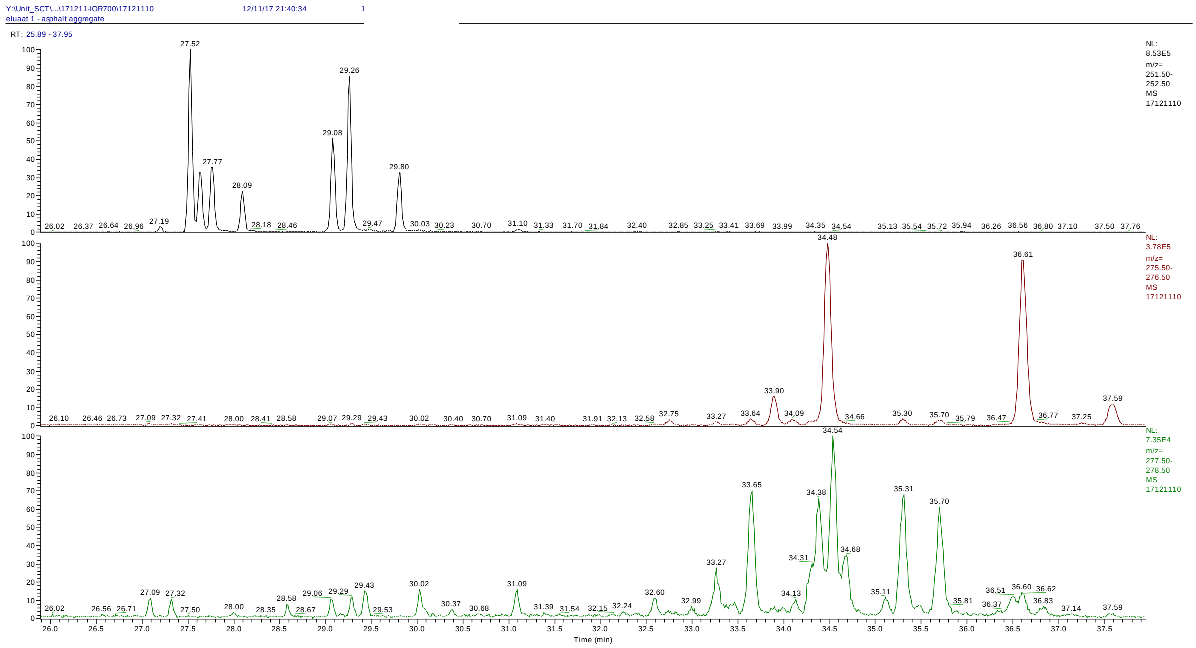
- Naftalene; acenaftylene; acenaftene; fluorene



- Fenanthreen and anthraceen; fluorantheen and pyreen; benzo(a)anthraceen and chryseen



- Benzo(b)fluoranthene, benzo(k)fluoranthene and benzo(a)pyrene; indeno(1,2,3,c,d)pyrene and benzo(g,h,i)perylene; dibenzo(a,h)anthracene



13.3. DETERMINATION OF PAH IN ELUATE OF RECYCLED MIXED AGGREGATES WITH METHOD ISO 28540

13.3.1. SAMPLE

Two series of eluates of recycled mixed aggregates were received from SGS Intron:

- PCB-Puin L/S=1.21 27-10-17 (eluate A)
- PCB-Puin L/S=8.79 6-11-17 (eluate B).

The eluates were prepared according to CEN/TS 16637-3 (T = 20°C, flow rate = 98 mL/h).
The samples were taken in dark glass bottles and transferred to VITO in coolboxes. The samples were stored in a refrigerator in expectation of analysis.

13.3.2. ANALYSIS

- 500 ml eluate is transferred to a separatory funnel
- The sample is spiked with internal standards (16 deuterated PAH)
- The sample was extracted with 25 ml of hexane by shaking for 1h
- The hexane extract was dried with anhydrous sodium sulphate and concentrated under a gentle stream of nitrogen to 1 ml
- The extract was concentrated to 250 µl with a solvent exchange to toluene
- The injection standards were added to the extract
- Due to the high PAH concentrations in the sample, the extract was diluted 20 times before it was analysed with GC/MS

13.3.3. RESULTS

→ Repeatability

Both eluates were analysed in five fold. The results are given in Table 59 and Table 60. For eluate A, the results of the higher boiling PAH are outliers (indicated in red). The concentrations of the PAH are very low (maximum around 10 times the LOD), but even at these low concentrations the repeatability is good for most PAH : in eluate A the %RSD is generally below 10%, for eluate B below 20%. Only for benzo(a)anthracene and chrysene the %RSD is high but given that concentrations are near the LOD and considering that the spread also includes the variances in eluate production, the repeatability is accepatable for all PAH.

→ Check on method performance

The recoveries of the internal standards in each sample were calculated using the calibration standard as a reference (100%). The results are given in Table 61 and Table 62. The recoveries are sometimes lower than 70% (but higher than 50%) and sometimes higher than 130%. Because isotope dilution was used the recoveries are acceptable. For D8-naftalene the recovery is sometimes lower than 50%, probably because of evaporation loss during the extract concentration step.

Remark that the %RSD of the internal standard recoveries are mostly lower than 15% (with a maximum of 19%). The good repeatability of the internal standard recoveries confirms that there are no analytical problems with the analysis of PAH in eluate of recycled mixed aggregates.

→ **Sensitivity**

The sensitivity of the method was calculated with S/N using the response of fluorene in eluate A. The LOD for fluorene was 0.01 µg/l. This is equal to the detection limit of PAH in surface water in method NEN ISO 28540 (0.01 µg/l).

13.3.4. CHROMATOGRAMS

The GC/MS ion chromatograms of PAH in eluate of recycled mixed aggregates are shown in Figure 32.

13.3.5. CONCLUSION

The repeatability and sensitivity of ISO 28540 using liquid/liquid extraction with hexane is acceptable for the analysis of PAH in eluates of recycled mixed aggregates.

Table 59: Measured concentrations of PAH in eluate A (recycled mixed aggregates) using method ISO 28540

Replicate n°	**1** µg/l	**2** µg/l	**3** µg/l	**4** µg/l	**5** µg/l	**Average** µg/l	**St.Dev.** µg/l	**C.V.** %
Naftalene	0,08	0,08	0,08	0,09	0,09	0,08	0,005	5,7
Acenaftylene	0,01	0,01	0,01	0,01	0,01	0,01	0,001	5,6
Acenaftene	0,11	0,10	0,10	0,11	0,11	0,10	0,003	3,4
Fluorene	0,06	0,05	0,05	0,06	0,06	0,06	0,002	3,7
Fenanthrene	0,12	0,13	0,14	0,13	0,14	0,13	0,007	5,3
Anthracene	0,02	0,02	0,02	0,02	0,02	0,02	0,002	7,0
Fluoranthene	0,10	0,12	0,16	0,11	0,11	0,11	0,007	6,2
Pyrene	0,11	0,12	0,17	0,11	0,11	0,11	0,008	7,0
Benzo(a)anthracene	< 0.01	0,04	0,11	0,01	0,02	0,02	0,012	53,0
Chrysene	< 0.01	0,05	0,13	0,02	0,03	0,03	0,013	42,0
Benzo(b)fluoranthene	< 0.01	0,03	0,10	< 0.02	< 0.03	-	-	-
Benzo(k)fluoranthene	< 0.02	0,04	0,14	< 0.02	< 0.03	-	-	-
Benzo(a)pyrene	< 0.01	0,02	0,09	< 0.01	< 0.03	-	-	-
Indeno(1,2,3,c,d)pyrene	< 0.01	0,03	0,09	< 0.01	0,01	-	-	-
Dibenzo(a,h)anthracene	< 0.01	0,03	0,12	< 0.01	0,02	-	-	-
Benzo(g,h,i)perylene	< 0.01	0,03	0,10	< 0.01	0,02	-	-	-

RED = outlier

Table 60: Measured concentrations of PAH in eluate B (recycled mixed aggregates)

Replicate n°	**1** µg/l	**2** µg/l	**3** µg/l	**4** µg/l	**5** µg/l	**Average** µg/l	**St.Dev.** µg/l	**C.V.** %
Naftalene	0,04	0,03	0,04	0,04	0,03	0,04	0,004	10,4
Acenaftylene	< 0,01	< 0,01	< 0,01	< 0,01	< 0,01	< 0,01	-	-
Acenaftene	0,09	0,08	0,09	0,08	0,08	0,08	0,005	6,4
Fluorene	0,04	0,04	0,04	0,04	0,04	0,04	0,001	1,9
Fenanthrene	0,12	0,12	0,17	0,11	0,11	0,13	0,026	20,5
Anthracene	0,01	0,02	< 0.01	0,02	0,02	0,02	0,003	14,2
Fluoranthene	0,11	0,13	0,14	0,10	0,10	0,12	0,019	16,1
Pyrene	0,11	0,14	0,14	0,10	0,10	0,12	0,022	18,8
Benzo(a)anthracene	0,01	0,05	0,06	< 0.01	< 0.01	0,04	0,024	59,7
Chrysene	0,02	0,08	0,09	0,01	0,01	0,04	0,037	85,5
Benzo(b)fluoranthene	< 0.02	0,05	0,06	< 0.01	< 0.01	-	-	-
Benzo(k)fluoranthene	< 0.02	0,05	0,06	< 0.01	< 0.01	-	-	-
Benzo(a)pyrene	< 0.01	0,04	0,04	< 0.01	< 0.01	-	-	-
Indeno(1,2,3,c,d)pyrene	< 0.01	0,04	0,05	< 0.01	< 0.01	-	-	-
Dibenzo(a,h)anthracene	< 0.01	0,05	0,06	< 0.01	< 0.01	-	-	-
Benzo(g,h,i)perylene	< 0.01	0,05	0,06	< 0.01	< 0.01	-	-	-

Table 61: Recoveries of the internal standards in eluate A (recycled mixed aggregates)

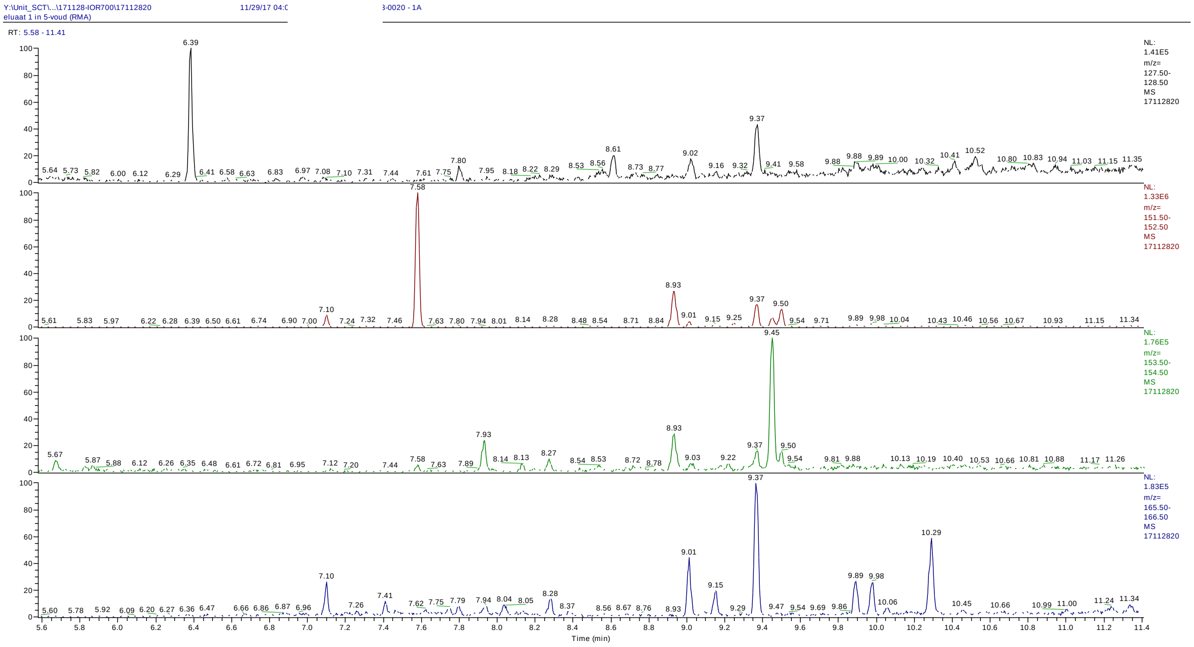
Replicate n°	**1** %	**2** %	**3** %	**4** %	**5** %	**RSD** %
D8-naftalene	51	45	53	50	45	7
D8-acenaftylene	65	63	68	71	65	5
D10-acenaftene	66	63	69	72	66	5
D10-fluorene	66	67	70	76	71	6
D10-fenanthrene	78	77	90	86	84	7
D10-anthracene	83	83	89	91	90	4
D10-fluoranthene	87	89	116	96	98	12
D10-pyrene	89	93	121	100	103	12
D12-benzo(a)anthracene	98	110	160	120	130	19
D12-chrysene	92	103	147	110	120	18
D12-benzo(b)fluoranthene	74	75	94	81	80	10
D12-benzo(k)fluoranthene	64	63	78	68	66	9
D12-benzo(a)pyrene	68	71	91	77	77	12
D12-indeno(1,2,3,c,d)pyrene	63	71	94	77	79	15
D14-dibenzo(a,h)anthracene	63	71	92	78	80	14
D12-benzo(g,h,i)perylene	66	73	99	82	84	15
Average recovery	73	76	96	83	84	11

Table 62: Recoveries of the internal standards in eluate B (recycled mixed aggregates)

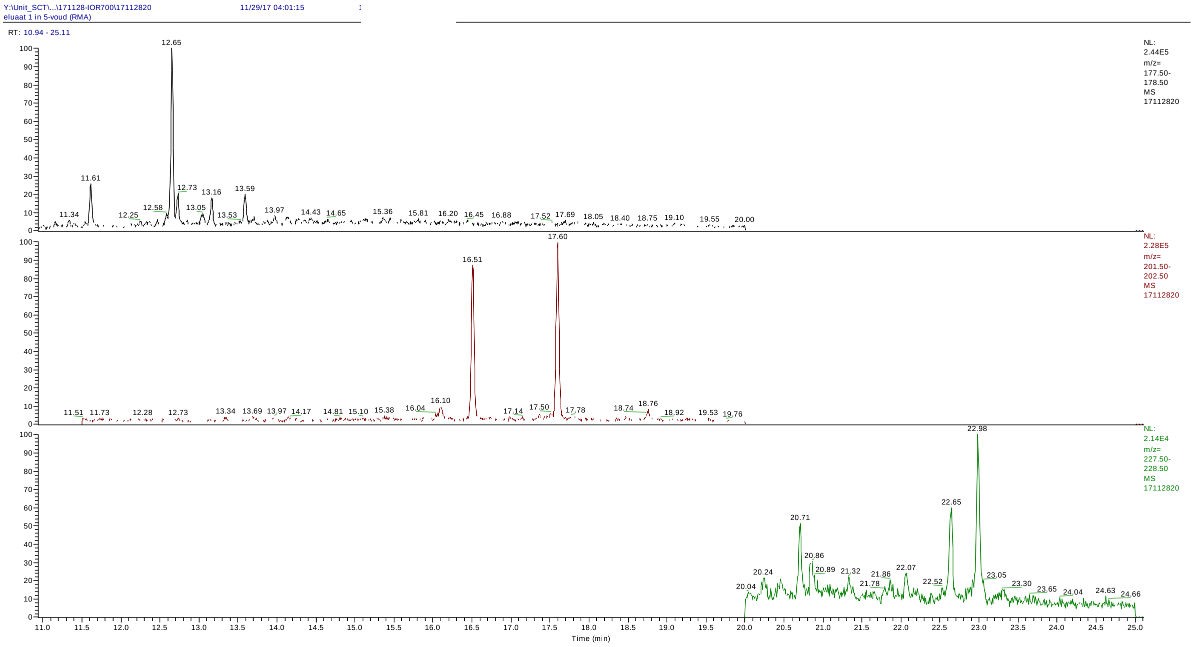
Replicate n°	**1** %	**2** %	**3** %	**4** %	**5** %	**RSD** %
D8-naftalene	47	58	48	55	61	11
D8-acenaftylene	61	68	60	65	69	6
D10-acenaftene	63	70	61	67	71	7
D10-fluorene	66	71	66	70	71	4
D10-fenanthrene	80	82	60	76	76	12
D10-anthracene	86	91	110	84	84	12
D10-fluoranthene	91	99	101	85	84	8
D10-pyrene	94	102	105	88	86	9
D12-benzo(a)anthracene	108	121	129	99	93	14
D12-chrysene	102	114	121	93	89	13
D12-benzo(b)fluoranthene	86	86	91	74	74	9
D12-benzo(k)fluoranthene	73	79	76	69	69	6
D12-benzo(a)pyrene	82	83	86	72	71	9
D12-indeno(1,2,3,c,d)pyrene	77	82	87	68	65	12
D14-dibenzo(a,h)anthracene	79	82	85	68	66	11
D12-benzo(g,h,i)perylene	80	86	90	70	69	12
Average recovery	80	86	86	75	75	7

Figure 32: GC/MS ion chromatograms of PAH in eluate A recycled mixed aggregates

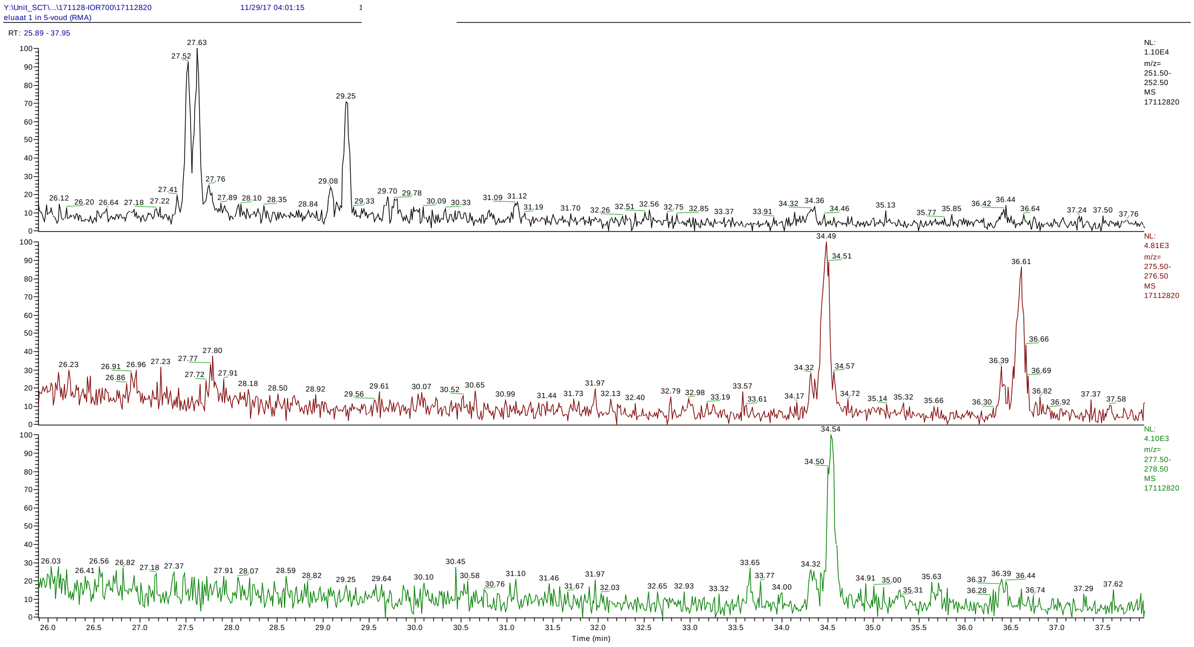
- Naftalene; acenaftylene; acenaftene; fluorene



- Fenanthrene and anthracene; fluoranthene and pyrene; benzo(a)anthracene and chrysene



- Benzo(b)fluoranthene, benzo(k)fluoranthene and benzo(a)pyrene; indeno(1,2,3,c,d)pyrene and benzo(g,h,i)perylene; dibenzo(a,h)anthracene



13.4. DETERMINATION OF PAH IN ELUATE OF RUBBER CRUMBS WITH METHOD ISO 28540

13.4.1. SAMPLE

Two series of eluates of rubber crumbs were received from SGS Intron:
- SBR-crumb L/S=1.46 20-9-17 (eluate A)
- SBR-crumb L/S=8.48 25-9-17 (eluate B).

The eluates were prepared according to CEN/TS 16637-3 (T = 20°C, flow rate = 98 mL/h).
The samples were taken in dark glass bottles and transferred to VITO in coolboxes. The samples were stored in a refrigerator in expectation of analysis.

13.4.2. ANALYSIS

- 500 ml eluate is transferred to a separatory funnel
- The sample is spiked with internal standards (16 deuterated PAH)
- The sample was extracted with 25 ml of hexane by shaking for 1h
- The hexane extract was dried with anhydrous sodium sulphate and concentrated under a gentle stream of nitrogen to 1 ml
- For eluates of rubber crumbs, the extract was cleaned up:
    - A glas column was filled with 0.5 g silica
    - The column was rinsed with 10 ml of dichloromethane/hexane (1/1) and 10 ml of hexane
    - The extract was transferred to the column and the vial was rinsed with with 0.5 ml of hexane, the hexane was also transferred to the column
    - The PAH were eluted with 6 ml of dichloromethane/hexane (1/1)
- The extract was concentrated to 250 µl with a solvent exchange to toluene
- The injection standards were added to the extract
- Due to the high PAH concentrations in the sample, the extract was diluted 20 times before it was analysed with GC/MS

13.4.3. RESULTS

→ Repeatability

Both eluates were analysed in five fold. The results are given in Table 63 and Table 64. Except for the more volatile PAH, most of the concentrations are below the LOD. For the volatile PAH the %RSD is lower than 10%. This is a very good result, the more so if we take into account the low concentrations (near the LOD). Although data for the higher boiling PAH are lacking, the available results indicate that the method is suited for the analysis of eluates of rubber crumbs.

→ Check on method performance

The recoveries of the internal standards in each sample were calculated using the calibration standard as a reference (100%). The results are given in Table 65 and Table 66. The recoveries are sometimes lower than 70% but higher than 50% (except for D8-naftalene). Because isotope dilution was used the recoveries are acceptable. The repeatability of the recoveries is good, the %RSD is for most internal standard lower than 10% and with a maximum lower than 20%.

→ **Sensitivity**

The sensitivity of the method was calculated with S/N using the response of fluorene in the eluate A. The LOD for fluorene was 0.002 µg/l. This is lower than the detection limit of PAH in surface water in method NEN ISO 28540 (0.01 µg/l).

13.4.4. COMMENTS

The recovery of the internal standards and the LOD are good, and the repeatability of the PAH with concentrations above the LOD is very good. It can be concluded that method ISO 28540 is suited for the analysis of PAH in eluates of rubber crumbs.

13.4.5. CHROMATOGRAMS

The GC/MS ion chromatograms of PAH in eluate of rubber crumbs are shown in Figure 33.

13.4.6. CONCLUSION

Method ISO 28540 is suited for the analysis of PAH in eluates of rubber crumbs.

Table 63: Measured concentrations of PAH in eluate A (rubber crumbs) using method ISO 28540

Replicate n°	**1** µg/l	**2** µg/l	**3** µg/l	**4** µg/l	**5** µg/l	**Average** µg/l	**St.Dev.** µg/l	**C.V.** %
Naftalene	0,11	0,11	0,11	0,11	0,11	0,11	0,00	0,0
Acenaftylene	0,05	0,05	0,05	0,05	0,05	-	-	-
Acenaftene	0,039	0,040	0,039	0,036	0,039	0,04	0,002	4,1
Fluorene	0,017	0,016	0,018	0,016	0,017	0,02	0,001	5,1
Fenanthrene	0,034	0,032	0,033	0,032	0,034	0,03	0,001	3,3
Anthracene	0,010	0,012	0,012	0,011	0,010	0,01	0,001	7,5
Fluoranthene	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	-	-	-
Pyrene	0,016	0,016	0,016	0,016	0,017	0,02	0,0004	2,4
Benzo(a)anthracene	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	-	-	-
Chrysene	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	-	-	-
Benzo(b)fluoranthene	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	-	-	-
Benzo(k)fluoranthene	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	-	-	-
Benzo(a)pyrene	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	-	-	-
Indeno(1,2,3,c,d)pyrene	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	-	-	-
Dibenzo(a,h)anthracene	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	-	-	-
Benzo(g,h,i)perylene	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	-	-	-

Table 64: Measured concentrations of PAH in eluate B (rubber crumbs)

Replicate n°	**1** µg/l	**2** µg/l	**3** µg/l	**4** µg/l	**5** µg/l	**Average** µg/l	**St.Dev.** µg/l	**C.V.** %
Naftalene	0,11	0,10	0,10	0,10	0,11	0,11	0,003	2,5
Acenaftylene	0,08	0,08	0,07	0,08	0,08	0,08	0,002	-
Acenaftene	0,048	0,050	0,050	0,050	0,052	0,05	0,002	3,0
Fluorene	0,040	0,039	0,038	0,038	0,040	0,04	0,001	2,3
Fenanthrene	0,106	0,103	0,099	0,101	0,100	0,10	0,003	2,9
Anthracene	0,022	0,024	0,024	0,024	0,025	0,02	0,01	5,4
Fluoranthene	0,028	0,028	0,028	0,028	0,030	0,03	0,001	3,8
Pyrene	0,061	0,059	0,057	0,059	0,059	0,06	0,001	2,3
Benzo(a)anthracene	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	-	-	-
Chrysene	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	-	-	-
Benzo(b)fluoranthene	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	-	-	-
Benzo(k)fluoranthene	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	-	-	-
Benzo(a)pyrene	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	-	-	-
Indeno(1,2,3,c,d)pyrene	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	-	-	-
Dibenzo(a,h)anthracene	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	-	-	-
Benzo(g,h,i)perylene	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	-	-	-

Table 65: Recoveries of the internal standards in eluate A (rubber crumbs)

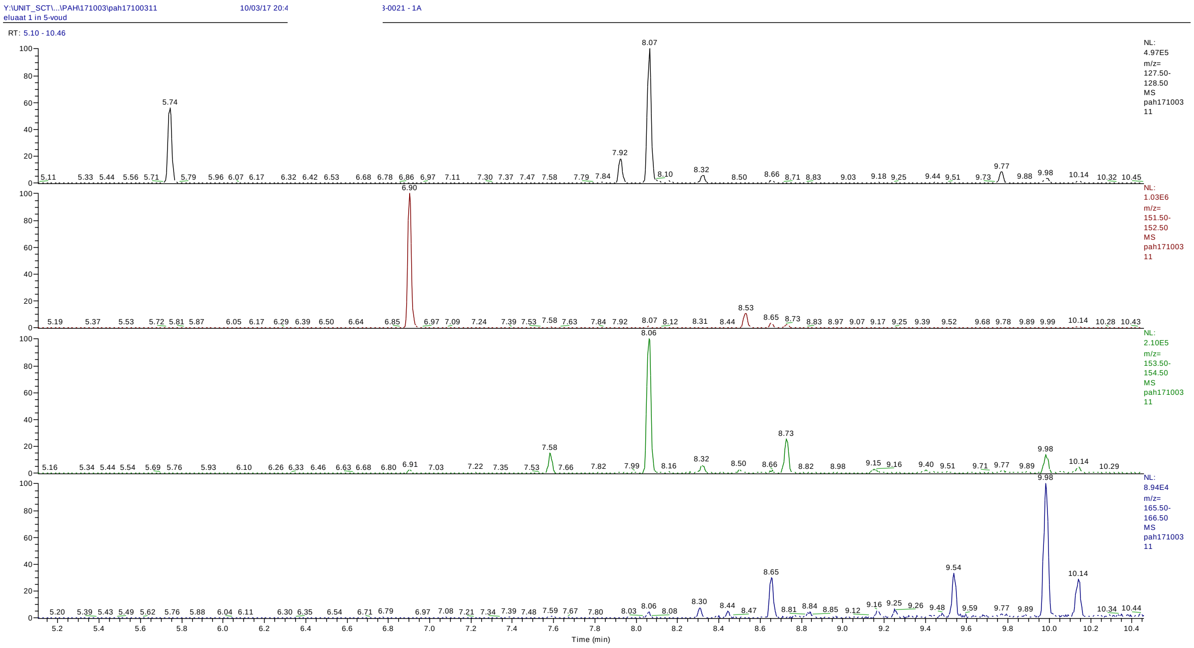
Replicate n°	**1** %	**2** %	**3** %	**4** %	**5** %	**RSD** %
D8-naftalene	55	50	47	51	51	5,5
D8-acenaftylene	64	63	56	59	62	5,4
D10-acenaftene	59	56	51	56	56	5,1
D10-fluorene	68	66	60	66	66	4,6
D10-fenanthrene	78	75	68	77	75	5,2
D10-anthracene	84	82	75	83	82	4,5
D10-fluoranthene	99	95	87	94	96	4,4
D10-pyrene	98	92	88	92	94	4,2
D12-benzo(a)anthracene	96	82	91	92	102	7,7
D12-chrysene	83	74	79	80	87	6,1
D12-benzo(b)fluoranthene	78	83	69	80	76	6,9
D12-benzo(k)fluoranthene	66	69	59	65	64	5,9
D12-benzo(a)pyrene	66	67	58	64	60	6,4
D12-indeno(1,2,3,c,d)pyrene	96	60	79	94	91	17,7
D14-dibenzo(a,h)anthracene	95	60	81	96	92	17,9
D12-benzo(g,h,i)perylene	94	58	80	95	92	18,7
Average recovery	55	50	47	51	51	5,5

Table 66: Recoveries of the internal standards in eluate B (rubber crumbs)

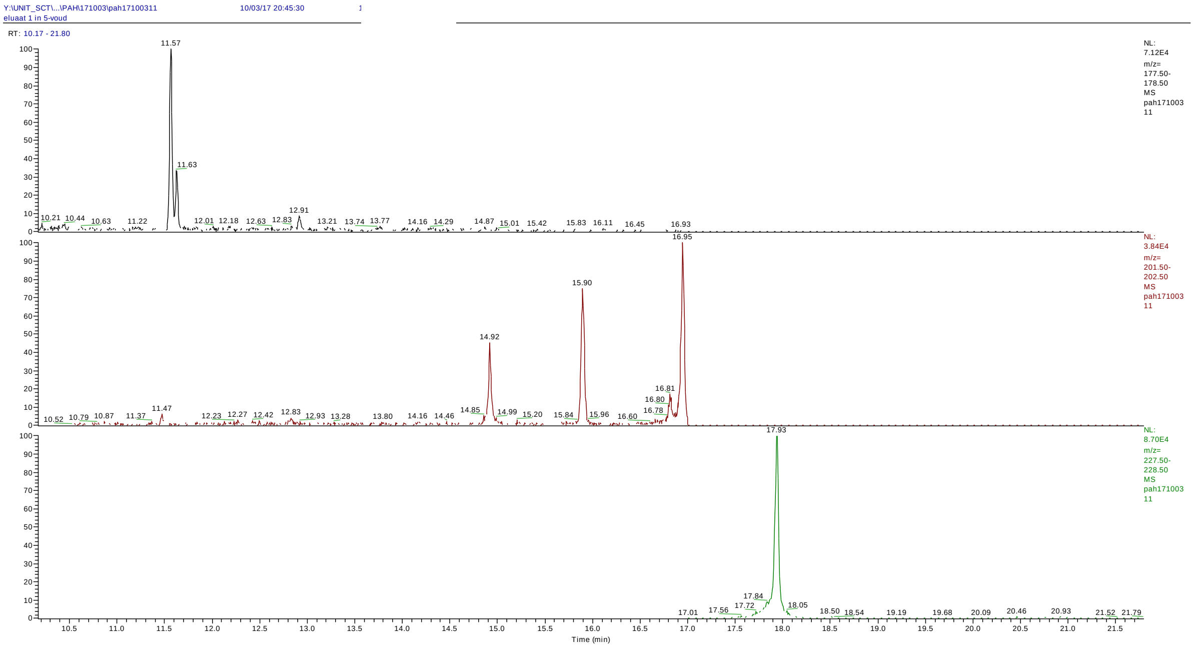
Replicate n°	**1** %	**2** %	**3** %	**4** %	**5** %	**RSD** %
D8-naftalene	41	48	49	45	51	8,5
D8-acenaftylene	48	49	53	51	61	9,8
D10-acenaftene	47	48	49	49	56	6,8
D10-fluorene	52	54	56	58	67	9,7
D10-fenanthrene	56	60	65	64	73	10,3
D10-anthracene	60	64	69	69	78	10,0
D10-fluoranthene	65	71	82	77	87	11,5
D10-pyrene	64	72	85	78	88	12,7
D12-benzo(a)anthracene	58	68	87	77	88	17,1
D12-chrysene	52	61	77	70	77	16,3
D12-benzo(b)fluoranthene	68	70	76	71	83	8,0
D12-benzo(k)fluoranthene	55	57	62	57	68	9,1
D12-benzo(a)pyrene	55	53	60	54	63	7,1
D12-indeno(1,2,3,c,d)pyrene	71	70	78	72	83	7,3
D14-dibenzo(a,h)anthracene	69	69	76	71	80	6,9
D12-benzo(g,h,i)perylene	67	69	76	70	83	8,8
Average recovery	41	48	49	45	51	8,5

Figure 33: GC/MS ion chromatograms of PAH in eluate A of rubber crumbs

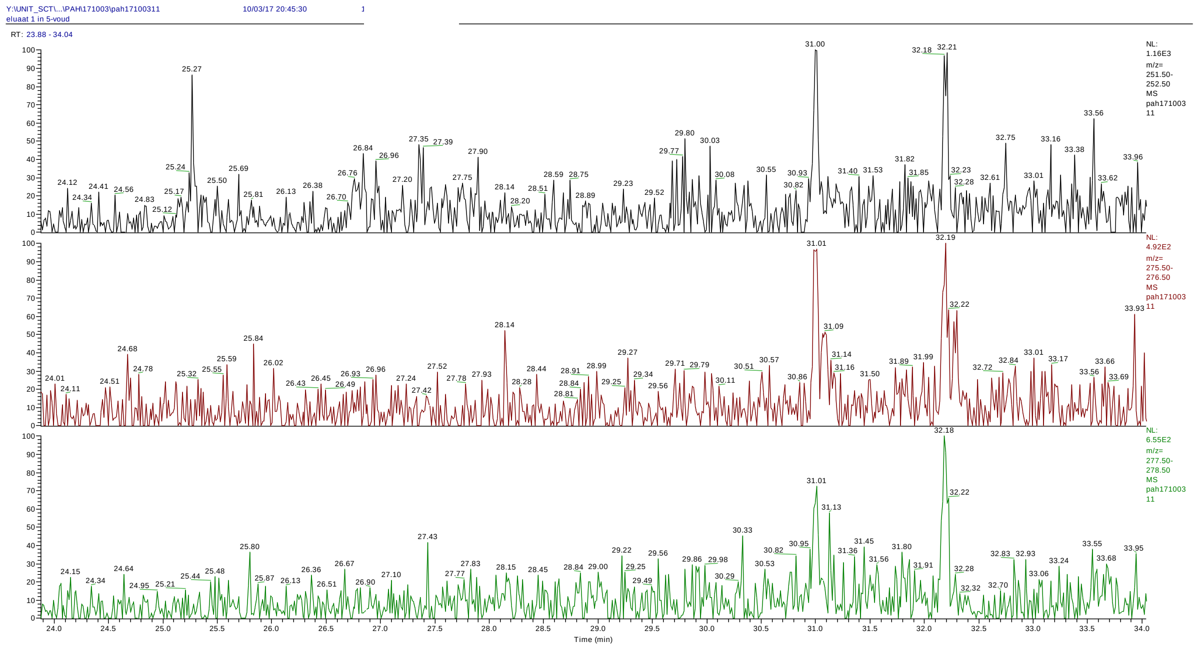
- Naftalene; acenaftylene; acenaftene; fluorene



- Fenanthrene and anthracene; fluoranthene and pyrene; benzo(a)anthracene and chrysene



- Benzo(b)fluoranthene, benzo(k)fluoranthene and benzo(a)pyrene; indeno(1,2,3,c,d)pyrene and benzo(g,h,i)perylene; dibenzo(a,h)anthracene



CHAPTER 14 DETERMINATION OF POLYBROMINATED DIPHENYL ETHERS IN ELUATES OF CONSTRUCTION PRODUCTS

14.1. EN 16694 - WATER QUALITY - DETERMINATION OF PENTABROMODIPHENYL ETHER (PBDE) IN WHOLE WATER SAMPLES USING SOLID PHASE EXTRACTION (SPE) WITH SPE-DISKS COMBINED WITH GAS CHROMATOGRAPHY - MASS SPECTROMETRY (GC-MS)

14.1.1. METHOD DESCRIPTION

A summary of EN 16694 and modifications done by VITO is given in Table 67.

14.1.2. MEASUREMENT CONDITIONS

See 6.1.2.

14.1.3. CALIBRATION DIAGRAMS

See 6.1.3.

Table 67: Summary of EN 16694 and method applied by VITO

Samples (eluates) Parameter list	Short description of the method	Departures from method by VITO and comments
Plastic product (CRM) PBDE	- Matrix: Surface water, drinking water and groundwater	
	- Compounds: BDE-28, 47, 99, 100, 153, 154	
	- Intake: 1000 mL	- Intake: only 10 mL due to limited availability of eluate
	- IS: EI-MS: 13C-BDEs (e.g. 28, 47, 99, 153); NCI-MS: F-BDEs (e.g. 28, 47, 100, 160)	
	- Extraction: disk solid phase extraction (SPE); methanol and hexane elution	
	- Clean-up (optional): multilayer silica (NaOH, H2SO4)	
	- Measurement: GC-HRMS, PTV-GC-MS/MS, PTV-NCI-MS	- Measurement: PTV-GC-MS/MS
	- LOQ: 0.025 ng/L	- Required LOQ not achievable with 10 mL intake

14.2. DETERMINATION OF PBDE IN ELUATES OF PLASTIC PRODUCT

14.2.1. SAMPLE

Only one eluate (L/S=10) of the plastic material (polyethylene, ERM-EC560) was prepared by SGS Intron (Sittard, NL), due to the limited amount of available PE material (ca 10 g). The eluate was prepared according to EN 12457. The volume of the sample was no more than 100 mL. The sample was stored at 4°C in expectation of analysis.

14.2.2. ANALYSIS

The limited amount of eluate only allows to take 5 subsamples of max 20 mL to check the repeatability of the method. This volume is by far insufficient to reach the limit of quantitation of EN 16694 (recommended intake = 1 L, LOQ = 25 pg/L). In addition it is expected that only very low quantities of BDE's will leach from the PE plastic. Therefore we believed that it was not meaningful to carry out the analyses.

14.2.3. COMMENTS

N/A

14.2.4. CHROMATOGRAMS

N/A

14.2.5. RESULTS

N/A

14.3. CONCLUSION

Although na data are available which prove the suitability of EN 16694 for the determination of BDE congeners in eluates of construction products, we are convinced that EN 16694, which is a highly selective method, can be used, if a sufficient volume of eluate is produced.

CHAPTER 15 DETERMINATION OF DIOXINS AND FURANS (PCDD/F) AND DIOXIN-LIKE PCB'S (dl-PCB) IN ELUATES OF CONSTRUCTION PRODUCTS

15.1. ISO 18073- WATER QUALITY - DETERMINATION OF TETRA- TO OCTA-CHLORINATED DIOXINS AND FURANS - METHOD USING ISOTOPE DILUTION HRGC/HRMS AND ISO 17858 - WATER QUALITY -- DETERMINATION OF DIOXIN-LIKE POLYCHLORINATED BIPHENYLS -- METHOD USING GAS CHROMATOGRAPHY/MASS SPECTROMETRY

15.1.1. METHOD DESCRIPTION

A summary of the method is given in Table 68. The analyses were carried out by SGS-IAC (Antwerp). The modifications applied by SGS are given in the same table.

15.1.2. MEASUREMENT CONDITIONS

The measurement conditions applied by SGS were not communicated. They were in compliance with the requirements set for HRGC-HRMS analysis in existing dioxin standards.

15.1.3. CALIBRATION DIAGRAMS

Calibration diagrams were submitted by SGS and will be made availibale on request.

Table 68: Summary of ISO 18073 and ISO 17858 and method applied in this study

Samples Parameter list	Short Description of the method	Departures from method by SGS and comments
Rubber crumbs Recycled mixed aggregates Polychlorodibenzodioxins Polychlorodibenzofurans Dioxin-like PCBs	- Matrix: water, waste water - Intake: 1 liter - IS: 13C-PCDDF (17) and 13C-PCB (12) - Extraction: - no visible particles: LLE with DCM - visible particles: glass fiber filtration - LLE extraction of filtrate with DCM - soxhlet extraction of filter with toluene - *or* glass fiber filtration on top of SPE - desorption with suitable solvent or soxlet extraction of filter and disk - Clean-up: - acid/base wash - GPC - alumina, silica, florisil and/or activated carbon column - HPLC fractionnation - Measurement: GC-HRMS	- Matrix: eluate - Intake: 1 liter - IS: 13C-PCDDF (16) and 13C-PCB (12) - Extraction: - glas fiber filtration - LLE extraction of filtrate with toluene - soxhlet extraction of filter with toluene -Clean-up: - multilayer column - alumina column - Measurement: GC-HRMS

	- LOQ: - DL-PCB: 10 pg/L per congener except PCB-105 en PCB-118 (50 pg/L) - PCDD/F: 50 pg/L per congener except 2,3,7,8-TCDF and 2,3,7,8-TCDD (10 pg/L) OCDD en OCDF (100 pg/l)	- LOQ: - DL-PCB: 25 – 500 pg/L - PCDD/F: 1 – 12.5 pg/L

15.2. DETERMINATION OF PCDD/F AND DL-PCB'S IN ELUATES OF RUBBER CRUMBS AND IN ELUATES OF RECYLED MIXED AGREGATES

15.2.1. SAMPLES

Eluates of rubber crumbs were prepared by SGS Intron (Sittart, NL). 2 types of eluates according to CEN/TS 16637-3 were prepared in 5-fold, namely L/S=1.46 and L/S=8.41. VITO received 1 L of each eluate for PCDD/F analysis.

Eluates of recycled mixed aggregates were also prepared by SGS Intron. 2 types of eluates according to CEN/TS 16637-3 were prepared in 5-fold, namely L/S=1.21 and L/S=8.79. VITO received 1 L of each eluate for PCDD/F analysis.

The eluates were collected in dark glass bottles and sent to SGS-IAC in coolboxes for analysis.

15.2.2. ANALYSIS

Sample extraction and clean up were carried out by SGS according to ISO 18073 and ISO 17858, with the exception of the use toluene as solvent instead of DCM for the extraction of the filtered water sample.
Other details of the extraction and clean up method were not communicated by SGS.

15.2.3. COMMENTS

The use of toluene instead of DCM is considered to have no impact on the repeatability of the method.

15.2.4. CHROMATOGRAMS

Chromatograms of PCDD/F and dl-PCB congeners in eluates of rubber crumbs and recycled mixed aggregates are given in B en C.

15.2.5. RESULTS

The analysis reports provided by SGS are given in annex of this report.

→ Repeatabilities

Results of the repeatability determinations of PCDD/F and dl-PCB are given in Table 69 and Table 70 for resp. the L/S=1.46 and L/S=8.41 eluates of rubber crumbs. In none of the eluates PCDD/F nor dl-PCB congeners could be detected in concentrations >LOQ.

Results of the repeatability determinations of PCDD/F and dl-PCB are given in Table 71 and Table 72 for resp. the L/S=1.21 and L/S=8.79 eluates of recycled mixed aggregates. In none of the eluates PCDD/F nor dl-PCB congeners could be detected in concentrations >LOQ, except some 2,3,4,7,8-

PeCDF in the L/S=1.21 eluate (CV_r = 11%, excluding outlier 0.016) and the L/S=8.79 eluate (CV_r = 29%) and 1,2,3,7,8-PCDD in the L/S=8.79 eluate (CV_r = 20%).

Although no repeatability data can be generated for the native PCDD/F and d,l-PCB congeners, repeatabilities can be calculated on the basis of the recovery data reported for the internal standards (concentration of 4 ng/L and 1.5 ng/L for resp. PCDD/F and dl-PCB congeners). These recovery data are listed in Table 73 and repeatabilities have been calculated. The repeatabilities are generally good (excluding some outlier values), so that it can be accepted, as isotope dilution is applied, that the precison of the method will also be acceptable for all native congeners.

→ Recoveries

No data of matrix additions have been made available by SGS. Nevertheless the recovery data for the internal standards indicate that there will be no issue of insufficient extraction yields.

→ Sensitivity

SGS reports LOQ-values of <2 pg/L for non-detected PCDD/F congeners. These values are lower than the limit of detection of 4 pg/L given in ISO 18073.

For dl-PCB's the reported LOQ values are strongly dependent on congener and range from 30 (PCB-81) to 1000 pg/L (PCB-118). These LOQ-values are much higher than the values given in Table 2 of ISO 17858 (10-50 pg/L). No explanation has been given so far by SGS.

15.3. CONCLUSION

On the basis of the recovery data of the isotope labelled internal standards ISO 18073 and ISO 17858 can be considered appropriate for the determination of dioxins and dioxinlike PCBs in eluates of construction products. The method is sufficiently sensitive for dioxins, but for dioxinlike PCBs higher LOQ-values are applicable, most probably due to matrix interferences.

Table 69: Concentrations of PCDD/F and dl-PCBs in eluates of rubber crumbs (fraction L/S 1.46)

PCDD/F	**1** ng/L	**2** ng/L	**3** ng/L	**4** ng/L	**5** ng/L
2378-TCDF	< 0,0018	< 0,0021	< 0,0016	< 0,0027	< 0,0022
2378-TCDD	< 0,00091	< 0,0011	< 0,00079	< 0,0013	< 0,0011
12378-PeCDF	< 0,00091	< 0,0011	< 0,00079	< 0,0013	< 0,0011
23478-PeCDF	< 0,00091	< 0,0011	< 0,00079	< 0,0013	< 0,0011
12378-PeCDD	< 0,00091	< 0,0011	< 0,00079	< 0,0013	< 0,0011
123478-HxCDF	< 0,0015	< 0,0017	< 0,0013	< 0,0021	< 0,0018
123678-HxCDF	< 0,0015	< 0,0017	< 0,0013	< 0,0021	< 0,0018
234678-HxCDF	< 0,0015	< 0,0017	< 0,0013	< 0,0021	< 0,0018
123789-HxCDF	< 0,0015	< 0,0017	< 0,0013	< 0,0021	< 0,0018
123478-HxCDD	< 0,0015	< 0,0017	< 0,0013	< 0,0021	< 0,0018
123678-HxCDD	< 0,0015	< 0,0017	< 0,0013	< 0,0021	< 0,0018
123789-HxCDD	< 0,0015	< 0,0017	< 0,0013	< 0,0021	< 0,0018
1234678-HpCDF	< 0,0091	< 0,011	< 0,0079	< 0,013	< 0,011
1234789-HpCDF	< 0,0091	< 0,011	< 0,0079	< 0,013	< 0,011
1234678-HpCDD	< 0,0091	< 0,011	< 0,0079	< 0,013	< 0,011
OCDF *	< 0,018	< 0,021	< 0,016	< 0,027	< 0,022
OCDD	< 0,018	< 0,021	< 0,016	< 0,027	<0,022

dl-PCB's	**1** ng/L	**2** ng/L	**3** ng/L	**4** ng/L	**5** ng/L
PCB-81	< 0,036	< 0,043	< 0,032	< 0,054	< 0,044
PCB-77	< 0,073	< 0,085	< 0,063	< 0,11	< 0,088
PCB-126 *	< 0,018	< 0,021	< 0,016	< 0,027	< 0,022
PCB-169	< 0,018	< 0,021	< 0,016	< 0,027	< 0,022
PCB-123	< 0,073	< 0,085	< 0,063	< 0,11	< 0,088
PCB-118	< 0,73	< 0,85	< 0,63	< 1,1	< 0,88
PCB-114	< 0,073	< 0,085	< 0,063	< 0,11	< 0,088
PCB-105	< 0,36	< 0,43	< 0,32	< 0,54	< 0,44
PCB-167	< 0,36	< 0,43	< 0,32	< 0,54	< 0,44
PCB-156	< 0,36	< 0,43	< 0,32	< 0,54	< 0,44
PCB-157	< 0,073	< 0,085	< 0,063	< 0,11	< 0,088
PCB-189	< 0,073	< 0,085	< 0,063	< 0,11	< 0,088

Table 70: Concentrations of PCDD/F and dl-PCBs in eluates of rubber crumbs (fraction L/S 8.41)

PCDD/F	**1** ng/L	**2** ng/L	**3** ng/L	**4** ng/L	**5** ng/L
2378-TCDF	< 0,0026	< 0,0021	< 0,0022	< 0,0021	< 0,0023
2378-TCDD	< 0,0013	< 0,0010	< 0,0011	< 0,0010	< 0,0011
12378-PeCDF	< 0,0013	< 0,0010	< 0,0011	< 0,0010	< 0,0011
23478-PeCDF	< 0,0013	< 0,0010	< 0,0011	< 0,0010	< 0,0011
12378-PeCDD	< 0,0013	< 0,0010	< 0,0011	< 0,0010	< 0,0011
123478-HxCDF	< 0,0020	< 0,0017	< 0,0018	< 0,0017	< 0,0018
123678-HxCDF	< 0,0020	< 0,0017	< 0,0018	< 0,0017	< 0,0018
234678-HxCDF	< 0,0020	< 0,0017	< 0,0018	< 0,0017	< 0,0018
123789-HxCDF	< 0,0020	< 0,0017	< 0,0018	< 0,0017	< 0,0018
123478-HxCDD	< 0,0020	< 0,0017	< 0,0018	< 0,0017	< 0,0018
123678-HxCDD	< 0,0020	< 0,0017	< 0,0018	< 0,0017	< 0,0018
123789-HxCDD	< 0,0020	< 0,0017	< 0,0018	< 0,0017	< 0,0018
1234678-HpCDF	< 0,013	< 0,010	< 0,011	< 0,010	< 0,011
1234789-HpCDF	< 0,013	< 0,010	< 0,011	< 0,010	< 0,011
1234678-HpCDD	< 0,013	< 0,010	< 0,011	< 0,010	< 0,011
OCDF *	< 0,026	< 0,021	< 0,022	< 0,021	< 0,023
OCDD	< 0,026	< 0,021	< 0,022	< 0,021	< 0,023
dl-PCB's	**1** ng/L	**2** ng/L	**3** ng/L	**4** ng/L	**5** ng/L
PCB-81	< 0,051	< 0,042	< 0,045	< 0,042	< 0,046
PCB-77	< 0,10	< 0,084	< 0,090	< 0,083	< 0,092
PCB-126 *	< 0,026	< 0,021	< 0,022	< 0,021	< 0,023
PCB-169	< 0,026	< 0,021	< 0,022	< 0,021	< 0,023
PCB-123	< 0,10	< 0,084	< 0,090	< 0,083	< 0,092
PCB-118	< 1,0	< 0,84	< 0,90	< 0,83	< 0,92
PCB-114	< 0,10	< 0,084	< 0,090	< 0,083	< 0,092
PCB-105	< 0,51	< 0,42	< 0,45	< 0,42	< 0,46
PCB-167	< 0,51	< 0,42	< 0,45	< 0,42	< 0,46
PCB-156	< 0,51	< 0,42	< 0,45	< 0,42	< 0,46
PCB-157	< 0,10	< 0,084	< 0,090	< 0,083	< 0,092
PCB-189	< 0,10	< 0,084	< 0,090	< 0,083	< 0,092

Table 71: Concentrations of PCDD/F and dl-PCBs in eluates of recycled mixed aggregates (fraction L/S 1.21)

PCDD/F	**1** ng/L	**2** ng/L	**3** ng/L	**4** ng/L	**5** ng/L
2378-TCDF	0,031	< 0,011	0,011	< 0,0099	0,019
2378-TCDD	< 0,0020	< 0,016	< 0,0014	< 0,0014	< 0,0025
12378-PeCDF	0,014	< 0,0054	< 0,0048	< 0,0048	< 0,0025
23478-PeCDF	0,016	0,0063	0,0066	0,0076	0,0059
12378-PeCDD	0,002	< 0,0016	< 0,0014	0,0037	< 0,0025
123478-HxCDF	0,0087	< 0,0025	< 0,0022	0,0035	< 0,0041
123678-HxCDF	0,0051	< 0,0025	< 0,0022	0,0039	< 0,0041
234678-HxCDF	0,0076	0,0028	< 0,0022	0,0042	< 0,0041
123789-HxCDF	< 0,0033	< 0,0025	< 0,0022	0,003	< 0,0041
123478-HxCDD	< 0,0033	< 0,0025	< 0,0022	0,004	< 0,0041
123678-HxCDD	< 0,0033	< 0,0025	< 0,0022	0,0032	< 0,0041
123789-HxCDD	< 0,0033	0,0026	< 0,0022	0,004	< 0,0041
1234678-HpCDF	< 0,020	< 0,016	< 0,014	< 0,014	< 0,025
1234789-HpCDF	< 0,020	< 0,016	< 0,014	< 0,014	< 0,025
1234678-HpCDD	< 0,020	< 0,016	< 0,014	< 0,014	< 0,025
OCDF *	< 0,041	< 0,032	< 0,028	< 0,028	< 0,051
OCDD	< 0,041	< 0,032	< 0,028	< 0,028	< 0,051
dl-PCB's	**1** ng/L	**2** ng/L	**3** ng/L	**4** ng/L	**5** ng/L
PCB-81	< 0,081	< 0,063	< 0,056	< 0,096	< 0,092
PCB-77	< 0,16	< 0,13	< 0,11	< 0,19	< 0,18
PCB-126 *	< 0,041	< 0,032	< 0,028	< 0,048	< 0,046
PCB-169	< 0,041	< 0,032	< 0,028	< 0,048	< 0,046
PCB-123	< 0,16	< 0,13	< 0,11	< 0,19	< 0,18
PCB-118	< 1,6	< 1,3	< 1,1	< 1,9	< 1,8
PCB-114	< 0,16	< 0,13	< 0,11	< 0,19	< 0,18
PCB-105	< 0,81	< 0,63	< 0,56	< 0,96	< 0,92
PCB-167	< 0,81	< 0,63	< 0,56	< 0,96	< 0,92
PCB-156	< 0,81	< 0,63	< 0,56	< 0,96	< 0,92
PCB-157	< 0,16	< 0,13	< 0,11	< 0,19	< 0,18
PCB-189	< 0,16	< 0,13	< 0,11	< 0,19	< 0,18

Table 72: Concentrations of PCDD/F and dl-PCBs in eluates of recycled mixed aggregates (fraction L/S 8.79)

PCDD/F	**1** ng/L	**2** ng/L	**3** ng/L	**4** ng/L	**5** ng/L
2378-TCDF	0,032	0,029	0,03	0,039	0,037
2378-TCDD	< 0,0029	< 0,0024	< 0,0025	< 0,0038	< 0,0033
12378-PeCDF	< 0,0084	< 0,0079	0,0089	< 0,0082	0,0099
23478-PeCDF	0,015	0,015	0,13	0,022	0,025
12378-PeCDD	< 0,0029	0,0062	0,0042	0,0061	< 0,0033
123478-HxCDF	< 0,0047	< 0,0038	< 0,0041	< 0,0061	< 0,0053
123678-HxCDF	< 0,0047	< 0,0038	< 0,0041	< 0,0061	< 0,0053
234678-HxCDF	< 0,0047	0,0042	< 0,0041	< 0,0061	< 0,0053
123789-HxCDF	< 0,0047	< 0,0038	< 0,0041	< 0,0061	< 0,0053
123478-HxCDD	< 0,0047	< 0,0038	< 0,0041	0,0076	< 0,0053
123678-HxCDD	< 0,0047	< 0,0038	< 0,0041	< 0,0061	0,0055
123789-HxCDD	< 0,0047	< 0,0038	< 0,0041	< 0,0061	< 0,0053
1234678-HpCDF	< 0,029	< 0,024	< 0,025	< 0,038	< 0,033
1234789-HpCDF	< 0,029	< 0,024	< 0,025	< 0,038	< 0,033
1234678-HpCDD	< 0,029	< 0,024	< 0,025	< 0,038	0,036
OCDF *	< 0,058	< 0,048	< 0,051	< 0,077	< 0,066
OCDD	< 0,058	< 0,048	< 0,051	< 0,077	< 0,066
dl-PCB's	**1** ng/L	**2** ng/L	**3** ng/L	**4** ng/L	**5** ng/L
PCB-81	< 0,097	< 0,092	< 0,10	< 0,096	< 0,10
PCB-77	< 0,19	< 0,18	< 0,20	< 0,19	< 0,20
PCB-126 *	< 0,049	< 0,046	< 0,051	< 0,048	< 0,051
PCB-169	< 0,049	< 0,046	< 0,051	< 0,048	< 0,051
PCB-123	< 0,19	< 0,18	< 0,20	< 0,19	< 0,20
PCB-118	< 1,9	< 1,8	< 2,0	< 1,9	< 2,0
PCB-114	< 0,19	< 0,18	< 0,20	< 0,19	< 0,20
PCB-105	< 0,97	< 0,92	< 1,0	< 0,96	< 1,0
PCB-167	< 0,97	< 0,92	< 1,0	< 0,96	< 1,0
PCB-156	< 0,97	< 0,92	< 1,0	< 0,96	< 1,0
PCB-157	< 0,19	< 0,18	< 0,20	< 0,19	< 0,20
PCB-189	< 0,19	< 0,18	< 0,20	< 0,19	< 0,20

Table 73: Recoveries of internal standards for eluates of construction products

%	1	2	3	4	5	Average	CV_r
Rubber crumbs L/S=1.46							
13C-2378-TCDF	92,6	92,8	97,9	90,4	90,8	93	3%
13C-2378-TCDD	83,1	84,1	87,8	79	82,9	83	4%
13C-12378-PeCDF	90,6	90,1	94,1	85,9	87,7	90	3%
13C-23478-PeCDF	89,9	93,4	95,4	88,6	92,6	92	3%
13C-12378-PeCDD	95	101	103	91,4	97	97	5%
13C-123478-HxCDF	87,6	86,3	87,8	84,6	85,8	86	2%
13C-123678-HxCDF	92,6	90,1	93,1	89,4	92,3	92	2%
13C-234678-HxCDF	93,1	89,4	90,8	86,3	89,5	90	3%
13C-123789-HxCDF	92,1	92	90,8	86,7	89,6	90	2%
13C-123478-HxCDD	85,2	85	81,7	80,5	86,6	84	3%
13C-123678-HxCDD	98,2	97,1	101	92,3	97,2	97	3%
13C-1234678-HpCDF	89,3	86,5	89,9	83,9	87,5	87	3%
13C-1234789-HpCDF	78,9	75,2	78,4	72,3	75,9	76	4%
13C-1234678-HpCDD	91,7	90,1	89,6	84,4	92,8	90	4%
13C-OCDF	61,4	61,4	64,9	57,4	64,5	62	5%
13C-OCDD	73,5	70,5	73,5	66,5	74,1	72	4%
13C-PCB-81	66,7	65	80,7	67,6	76	71	10%
13C-PCB-77	68,2	65,5	96,5	68,9	80,4	76	17%
13C-PCB-126	72,6	73,4	84,1	71,4	83,6	77	8%
13C-PCB-169	74,1	78,9	89,4	74,1	79,2	79	8%
13C-PCB-123	74,6	76	89,2	77,8	84,1	80	8%
13C-PCB-118	72,3	73	84,6	76	81,8	78	7%
13C-PCB-114	74,2	75,5	87,7	75,1	84,1	79	8%
13C-PCB-105	70,5	71,4	83	70,6	78,2	75	8%
13C-PCB-167	84,3	89,4	96,2	80,3	81,8	86	7%
13C-PCB-156	89,1	90,8	98,3	82,4	85,9	89	7%
13C-PCB-157	91,2	93,7	103	87,9	87,7	93	7%
13C-PCB-189	66	69,1	78,2	66	75,6	71	8%
Rubber crumbs L/S=8.41							
13C-2378-TCDF	95,2	96,1	82,8	89,1	93,4	91	6%
13C-2378-TCDD	86,9	87,1	75,8	79,5	84,1	83	6%
13C-12378-PeCDF	89,8	91,6	78,8	84,3	87,9	86	6%
13C-23478-PeCDF	94,8	96,1	84,6	87,2	90,1	91	5%
13C-12378-PeCDD	99,1	103	89,5	93,2	96,7	96	5%
13C-123478-HxCDF	86,2	89,4	80,8	78,4	86,3	84	5%
13C-123678-HxCDF	94,4	96,8	84,1	85,8	90,1	90	6%
13C-234678-HxCDF	92,3	93,4	84,2	82	89,1	88	6%

13C-123789-HxCDF	90,4	95,3	86,4	85,5	90,3	90	4%
13C-123478-HxCDD	82,9	88,2	77,2	75,9	83,1	81	6%
13C-123678-HxCDD	99,7	99,6	90,6	90,3	97,2	95	5%
13C-1234678-HpCDF	91,1	91,7	81,7	82,5	87,8	87	5%
13C-1234789-HpCDF	75,4	79,6	73,7	73,4	77,3	76	3%
13C-1234678-HpCDD	91,2	94,1	88,6	84,8	89,9	90	4%
13C-OCDF	62,3	64,5	62,6	59,2	61,8	62	3%
13C-OCDD	72,4	76,4	71,8	70,7	74,3	73	3%
13C-PCB-81	68,9	71,4	63,7	65,7	65,7	67	5%
13C-PCB-77	74,3	71,4	67,6	67,6	71,2	70	4%
13C-PCB-126	76,7	78,3	69,7	71,7	71,8	74	5%
13C-PCB-169	67	78,5	65,2	66,3	69,4	69	8%
13C-PCB-123	80,5	83,7	72,7	73,9	74,3	77	6%
13C-PCB-118	77,8	81	70,4	73	74,1	75	6%
13C-PCB-114	79,6	84	72,7	72,1	75	77	7%
13C-PCB-105	77,5	78,7	69,9	72,4	71,8	74	5%
13C-PCB-167	80,2	83,3	72,2	73,8	77,5	77	6%
13C-PCB-156	79,8	86,4	77,3	76,7	81,7	80	5%
13C-PCB-157	83,5	88,6	77	81	83,6	83	5%
13C-PCB-189	71,4	74,1	67,7	68	67,4	70	4%
Recycled mixed aggregates L/S=1.21							
13C-2378-TCDF	86,9	93,3	83,5	94,6	~~35~~	90	6%
13C-2378-TCDD	74,5	79,3	71	80,8	~~30,8~~	76	6%
13C-12378-PeCDF	81,2	84,4	77,6	86,6	~~30,5~~	82	5%
13C-23478-PeCDF	84,2	89,5	81,2	90,4	~~31,2~~	86	5%
13C-12378-PeCDD	84,9	89,7	81,5	92,7	~~32,8~~	87	6%
13C-123478-HxCDF	79,2	85,7	76,4	86,2	~~36,4~~	82	6%
13C-123678-HxCDF	78,1	84,1	72,9	82,2	~~29,4~~	79	6%
13C-234678-HxCDF	83,2	88,5	79,2	89,1	~~33,3~~	85	6%
13C-123789-HxCDF	85,8	90,8	82,2	91,6	~~33,2~~	88	5%
13C-123478-HxCDD	79,8	84,9	73,8	85,6	~~40,2~~	81	7%
13C-123678-HxCDD	80,5	86,1	77,6	86,9	~~32,6~~	83	5%
13C-1234678-HpCDF	79,4	87,3	77,9	85,7	~~30,9~~	83	6%
13C-1234789-HpCDF	71,1	76,6	69,1	76,3	~~25,3~~	73	5%
13C-1234678-HpCDD	80	86,6	76,8	85,9	~~30,5~~	82	6%
13C-OCDF	71,7	78,5	70,6	76,6	~~24,7~~	74	5%
13C-OCDD	76,2	83,4	74	82,1	~~27,3~~	79	6%
13C-PCB-81	75,7	92,5	79,3	82,5	~~31,4~~	83	9%
13C-PCB-77	73,2	87,9	72,2	62,1	~~31,9~~	74	14%
13C-PCB-126	64,9	73,9	65,3	67,3	~~20,5~~	68	6%
13C-PCB-169	63,1	72,8	62,5	64,5	~~29,3~~	66	7%

13C-PCB-123	71,5	87,5	73,4	79,8	~~30,8~~	78	9%
13C-PCB-118	66	78,2	67,1	74,8	~~28,9~~	72	8%
13C-PCB-114	78,9	89,8	77,2	86,5	~~32,4~~	83	7%
13C-PCB-105	72,2	83,6	75,8	79,4	~~30,8~~	78	6%
13C-PCB-167	64	70,8	62,1	66,3	~~23,8~~	66	6%
13C-PCB-156	68,9	74,3	67,6	72,4	~~24,7~~	71	4%
13C-PCB-157	39,2	74,9	69,6	73,1	~~27,3~~	64	26%
13C-PCB-189	66,4	81,9	67,8	74,3	~~30,8~~	73	10%
Recycled mixed aggregates L/S=8.76							
13C-2378-TCDF	42,8	42,3	43,9	46	38,1	43	7%
13C-2378-TCDD	37,3	36,4	38,1	40,7	34	37	7%
13C-12378-PeCDF	36	36,1	37,8	40,4	34,4	37	6%
13C-23478-PeCDF	37,9	38,8	38,9	39,5	33,9	38	6%
13C-12378-PeCDD	39,6	40,5	40,6	43,5	34,3	40	8%
13C-123478-HxCDF	45,8	40,3	46,3	49,8	42,3	45	8%
13C-123678-HxCDF	37,2	33,8	38,3	40	34	37	7%
13C-234678-HxCDF	40,7	37,8	41,7	42,8	37,8	40	6%
13C-123789-HxCDF	39,1	37,8	40,6	43,6	36,4	40	7%
13C-123478-HxCDD	46	44,4	47	52,9	43,5	47	8%
13C-123678-HxCDD	40,2	37,9	40,5	43,2	36,6	40	6%
13C-1234678-HpCDF	35,9	34,5	37,8	38,6	33,1	36	6%
13C-1234789-HpCDF	29,5	28,2	28,7	33,8	25,9	29	10%
13C-1234678-HpCDD	34,9	34,7	36,6	37,6	31,3	35	7%
13C-OCDF	28	29	27,3	27,1	24,2	27	7%
13C-OCDD	28,5	31,6	31,7	31,3	27,4	30	7%
13C-PCB-81	46,4	34,2	37,7	~~20,8~~	33,6	38	16%
13C-PCB-77	46,8	35,3	38,3	~~19,3~~	31,6	38	17%
13C-PCB-126	31,1	22,3	24,5	~~12~~	21,8	25	17%
13C-PCB-169	42,5	30,3	33,2	~~17,1~~	29,5	34	18%
13C-PCB-123	46	33,4	37,3	~~18,7~~	33,1	37	16%
13C-PCB-118	43	31,3	35,4	~~17,8~~	31,4	35	16%
13C-PCB-114	49,2	36,6	39,9	~~19,8~~	35	40	16%
13C-PCB-105	44,6	33,4	36,9	~~18,2~~	33,4	37	14%
13C-PCB-167	35,4	25,8	25	~~13,7~~	24,5	28	19%
13C-PCB-156	36,5	26,4	26,1	~~14,4~~	25,2	29	19%
13C-PCB-157	39	28,2	27,5	~~16,5~~	27,4	31	19%
13C-PCB-189	45,4	32,7	32,6	~~18,2~~	30,8	35	19%

CHAPTER 16 DETERMINATION OF SELECTED PHTHALATES IN ELUATES OF CONSTRUCTION PRODUCTS

16.1. ISO 18856 – WATER QUALITY – DETERMINATION OF SELECTED PHTHALATES USING GAS CHROMATOGRAPHY/MASS SPECTROMETRY

16.1.1. METHOD DESCRIPTION

A summary of ISO 18856 and modifications done by VITO is given in Table 74.

The method was used for the determination of the following compounds:
- Dimethylphthalate
- Diethylphthalate
- Dipropylphthalate
- Di-(2-methylpropyl)phthalate
- Dibutylphthalate
- Butylbenzylphthalate
- Dicyclohexylphthalate
- Di-(2-ethylhexyl)phthalate
- Dioctylphthalate
- Didecylphthalate
- Diundecylphthalate

Note that ISO 18856 states that the applicability of the method to other phthalates is not excluded except the isomeric mixtures e.g. DiNP (di-isononylphthalate), but shall be verified in each case.

16.1.2. MEASUREMENT CONDITIONS APPLIED BY VITO

For the measurement conditions we refer to 8.1.2

16.1.3. CALIBRATION DIAGRAMS

For the calibration diagrams we refer to 8.1.3. The working ranges are:

- DMP, DEP, DPP, DiBP, BBP: 0,01-2 mg/L
- DBP, DCHP, DOP: 0,02-2 mg/L
- DEHP, DDP, DUP: 0,05-2 mg/L

For an intake of 200 mL and a final extract volume of 1 mL this corresponds to a lowest quantification limit for a water sample of 0.05 to 0.25 µg/L depending on phthalate.

Table 74: Summary of ISO 18856 and method applied by VITO

Samples (eluates) Parameter list	Short description of the method	Departures from method by VITO and comments
~~PVC flooring (old)~~ Sealant 1 DMP DEP DPP DiBP DBP BBzP DCHP DEHP DOP DDP DUP	- Matrix: groundwater, surface water, waste water, drinking water - Intake: 250 mL - IS: e.g. diallyl phthalate, d4-DBP, d4-DOP - Extraction: Clean, heated glassware (400°C); deactivate with iso-octane; extract with SPE (250 mg C18); elute with ethyl acetate spiked with IS - Clean-up (optional): Waste water: activated alumina - Measurement: GC-MS - LOQ: 0.02–0.15 µg/L	- VITO applied SPE in this study but used DCM instead of ethyl acetate for the elution of the phthalates because of lower solvent blanks

16.2. DETERMINATION OF PHTHALATES IN ELUATES OF SEALANT 1

16.2.1. SAMPLES

Eluates of sealant 1 were prepared by SGS Intron (Sittard, NL) according to CEN/TS 16637-2 (T = 20°C, L/A = 80 L/m^2). The eluates were collected in dark glass bottles. 5 samples of fraction 1 and 5 samples of fraction 3 of a leaching test were sent to VITO in coolboxes. The sample volumes were 450 mL. The samples were stored at 4°C in expectation of analysis.

16.2.2. ANALYSIS

- Glassware was rinsed in the dishwasher and heated at 400°C followed by rinsing with iso-octane to deactivate the glass wall
- The eluate samples were extracted using glass SPE cartridges (Supelclean™ ENVI™-18 (500 mg, 3 mL)
- The SPE phase was conditioned with 3 times 5 mL DCM and 2 times 5 mL methanol, taking care that the adsorbent wouldn't run dry
- 225 mL eluate was extracted with a flow rate of 2-10 mL/min and after extracton the SPE cartridge was dried during 5 min on the vacuum device and subsequently by centrifugation
- The phthalates were desorbed from the adsorbent with 15 mL DCM to which internal standards were added (500 ng).
- The extract was dried with Na_2SO_4 and evaporated with solvent change to hexane to a final volume of 1 mL and injected into a GC-MS

16.2.3. COMMENTS

DCM was used for elution of the phthalates instead of ethyl acetate because no phthalate free ethyl acetate could be found. For the elution of the longer chain phthalates an elution volume of 15 ml was needed.
All tested SPE cartridges contained phthalates. This resulted in relatively high blanks for DiBP, DBP and DEHP (see Table 76). The use of liquid-liquid extraction can reduce this blank contribution.
Internal standards were added to the elution solvent according to ISO 18856; it is advisable to add the internal standards to the water sample instead in order to correct for extraction recoveries.

16.2.4. CHROMATOGRAMS

Chromatograms for the eluate fractions 1 and 3 are given in Figure 34. The main phthalates which are found in the eluates are DEP, DiBP, DBP and DEHP. Other phthalates

16.2.5. RESULTS

→ Repeatabilities

The results of the replicate determinations of phthalates in both eluate fractions are given in Table 75. The %RSD range from 6 to 34% depending on concentration and phthalate compound. The repeatabilities are better for fraction 1, but the %RSD is still too high for some phthalates. For fraction 3 only acceptable results (<15%) were obtained for DEP and DBP.
DiNP was also determined and was present in an average concentration of resp. 3 and 9 µg/L in eluate fraction 1 and 3.

Remarks
- Outlier values were observed for DiBP and DEHP for fraction 1 eluates and for DBP for fraction 2 eluates.
- The observed concentrations of phthalates may have a contribution resulting from contamination which occurred during the leaching process.
- DiBP, DBP and DEHP showed to high blank values, nevertheless these blanks stayed well below the eluate concentrations (see Table 76).

→ Recoveries

Recoveries which were obtained for additions of phthalates (2.5 µg/L) to mineral water are given in Table 77. The table shows that the recoveries are not quantitative (ca 70% except DUP 36%). This can be attributed to the fact that the internal standards are added to the SPE elution solvent and not to the water, making that there is no correction for losses due to adsorption on glas wall and breakthrough.

→ Sensitivity

On the basis of measured signal-to-noise ratios of the eluate extracts the limit of detection can be set to 0.02 µg/L.

16.3. CONCLUSION

On the basis of the results obtained for the eluates of sealant 1 no decision can be made with regard to suitability of ISO 18856 for the analysis of phthalates in eluates of construction products. The %RSD values are too high but improvement can most probably be obtained after optimization of the analytical method and with a better control of the leaching process.

Table 75: Measured concentrations for phthalates in eluates of sealant 1.

Replicate	***A1*** µg/l	***A2*** µg/l	***A3*** µg/l	***A4*** µg/l	***A5*** µg/l	***average*** µg/l	***CV$_r$*** %
DMP	0,026	0,030	0,052	0,028	0,049	0,04	34
DEP	0,73	0,65	0,66	0,76	0,70	0,70	7
DPropP	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	-
DIBP	2,6	2,5	2,3	~~4,0~~	2,9	2,58	10
DBP	6,2	6,8	6,8	7,2	7,0	6,80	6
BBP	0,032	0,022	0,022	0,028	<0,02	0,03	19
DEHP	1,3	1,1	~~2,6~~	1,4	1,1	1,23	12
DCHP	0,021	0,031	0,028	0,037	0,028	0,03	20
DOP	0,082	0,068	0,072	0,07	0,065	0,07	9
DDcP	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	-
DUP	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	-
DiNP	2,3	2,8	2,8	3,2	2,7	2,9	11

Replicate	***B1*** µg/l	***B2*** µg/l	***B3*** µg/l	***B4*** µg/l	***B5*** µg/l	***average*** µg/l	***CV$_r$*** %
DMP	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	-
DEP	0,32	0,35	0,40	0,34	0,38	0,36	9
DPropP	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	-
DIBP	2,0	2,1	2,9	2,1	2,9	2,40	19
DBP	~~2,0~~	3,0	3,3	3,1	3,3	3,18	5
BBP	<0,02	0,021	0,026	<0,02	0,030	0,03	18
DEHP	0,54	0,89	0,85	1,1	1,1	0,90	26
DCHP	0,054	0,089	0,081	0,049	0,058	0,07	27
DOP	0,16	0,25	0,23	0,16	0,17	0,19	22
DDcP	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	-
DUP	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	-
DiNP	6,8	12,0	12,0	7,6	8,4	9,36	26

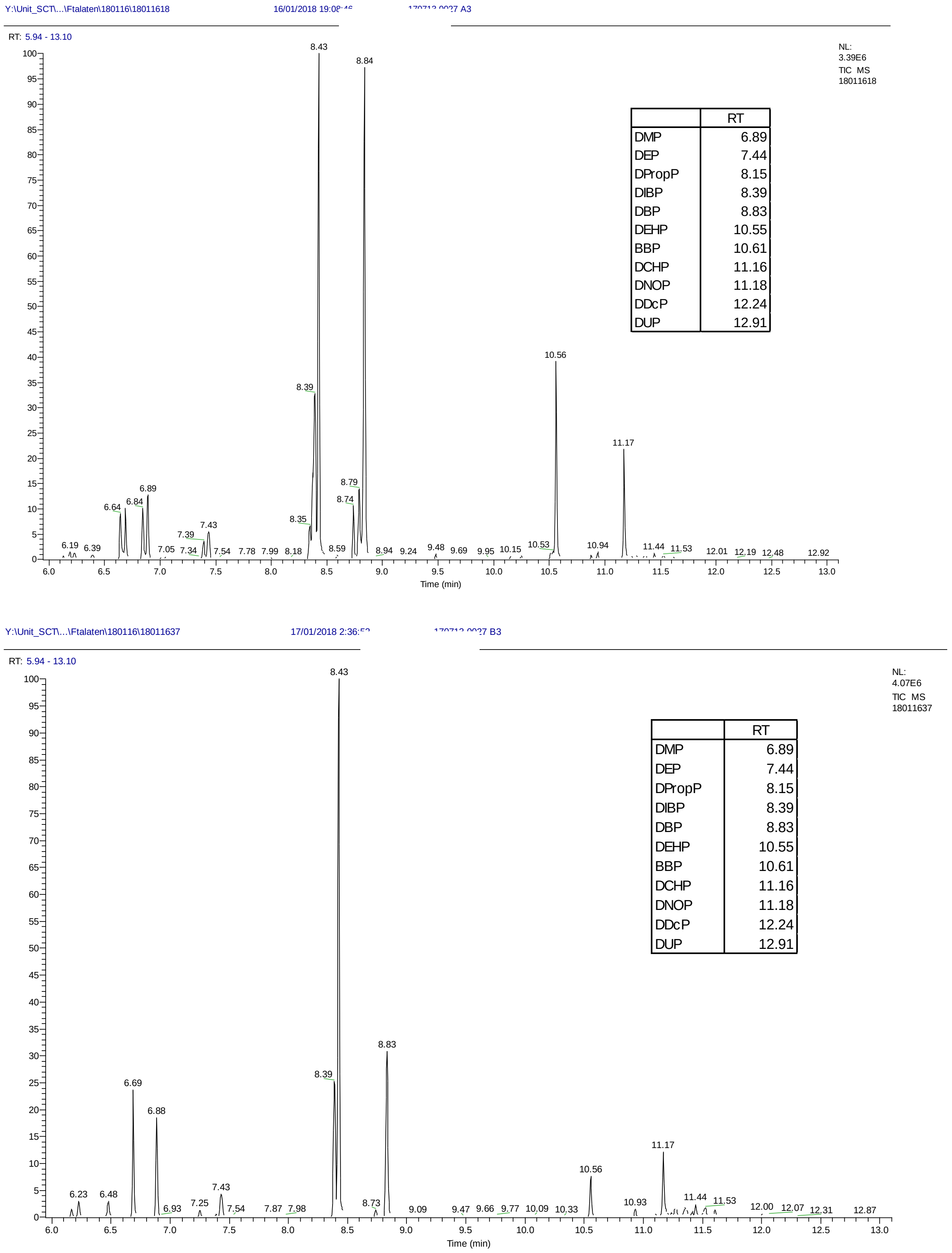
Table 76: Phthalate procedural blanks

	Blank 1 conc. µg/l	**Blank 2** conc. µg/l
DMP	<0,02	<0,02
DEP	0,07	0,07
DPropP	<0,02	<0,02
DIBP	0,72	0,59
DBP	0,25	0,21
BBP	<0,02	<0,02
DEHP	0,58	0,48
DCHP	<0,02	<0,02
DOP	<0,02	<0,02
DDcP	<0,02	<0,02
DUP	<0,02	<0,02

Table 77: Recoveries of phthalate additions to water using SPE extraction according to ISO 18856

	Added conc	**Measured conc.**		**Recovery**	
		QC 1	**QC 2**	**QC 1**	**QC 2**
	µg/L	µg/L	µg/L	%	%
DMP	2,58	2,02	1,95	78	76
DEP	2,77	2,11	2,13	76	77
DPropP	2,56	2,05	2,04	80	80
DIBP	2,54	1,99	1,93	79	76
DBP	2,51	2,04	2,13	81	85
DEHP	2,60	1,60	1,71	62	66
BBP	2,21	1,66	1,63	75	73
DCHP	2,30	1,48	1,29	65	56
DOP	2,52	1,85	1,99	73	79
DDcP	2,79	1,73	1,86	62	67
DUP	2,53	0,78	0,92	31	36

Figure 34: Total ion chromatograms for phthalates in eluates of sealant 1



	RT
DMP	6.89
DEP	7.44
DPropP	8.15
DIBP	8.39
DBP	8.83
DEHP	10.55
BBP	10.61
DCHP	11.16
DNOP	11.18
DDcP	12.24
DUP	12.91

	RT
DMP	6.89
DEP	7.44
DPropP	8.15
DIBP	8.39
DBP	8.83
DEHP	10.55
BBP	10.61
DCHP	11.16
DNOP	11.18
DDcP	12.24
DUP	12.91

CHAPTER 17 DETERMINATION OF PCP IN ELUATES OF CONSTRUCTION PRODUCTS

17.1. EN 12673 – WATER QUALITY – GAS CHROMATOGRAPHIC DETERMINATION OF SOME SELECTED CHLOROPHENOLS IN WATER

17.1.1. METHOD DESCRIPTION

A summary of EN 12673 and the method applied by VITO is given in Table 78. EN 12673 allows the detection of chlorophenols either by GC-ECD or GC-MS. VITO used GC-MS. Only PCP was determined. Quantification was done relative to ^{13}C-PCP, which was added as internal standard.

17.1.2. MEASUREMENT CONDITIONS

For the measurement conditions we refer to 9.1.2.

17.1.3. CALIBRATION DIAGRAM

For a calibration diagram we refer to 9.1.3. Good linearity is obtained in the range of 10 – 1000 µg/l extract. This corresponds to a working range of 0.5 – 50 µg/L water sample, based on 10 mL intake and 0.5 mL final extract volume.

Table 78: Summary of EN 12673 and method applied by VITO

Samples (eluates) Parameter list	Short description of the method	Departures from method by VITO and comments
Wood powder (beech) Chlorinated phenols including pentachlorophenol (PCP)	- Matrix: drinking water, groundwater, rainwater, waste water, sea water, surface water - Intake: 200 ml - IS: tribromophenol and trichlorophenol (ECD) or labelled chlorophenols (MS) - Extraction/Clean-up: extraction with toluene (pH=4), re-extraction with K2CO3 0.1M - Derivatization: acetylation with acetic anhydride followed by extraction of acetate esters with hexane - Measurement: GC-ECD or GC-MS - LOQ: 0.1 µg/l	- None - GC-MS detection using ^{13}C-PCP as internal standard

17.2. DETERMINATION OF PCP IN ELUATES OF BEECHWOOD POWDER

17.2.1. SAMPLE

Only one eluate (L/S=10) of wood powder (BCR-683) was prepared by SGS Intron (Sittard, NL), due to the limited amount of available material. The eluate was prepared according to EN 12457. The sample was taken in a dark glass bottle and transferred to VITO in a coolbox. The volume of the sample was no more than 250 mL. The sample was stored at 4°C in expectation of analysis.

17.2.2. ANALYSIS

- The eluate was neutralised (pH 7) with 1N NaOH
- 10 mL test portions were taken
- 40 mL mineral water was added to 10 mL eluate, followed by addition of 250 ng ^{13}C-PCP and 5mL 1M K_2CO_3
- 1mL acetic anhydride was added and the mixture was shaken for 5 min
- After 10min 5ml hexane was added and the mixture was shaken for another 5 min
- The hexane layer was separated and washed with ultrapure water and subsequently dried with sodium sulfate
- The hexane volume was evaporated to 0.5 mL and transferred to an injection vial, followed by addition of ^{13}C-tetrachlorobenzene (injection standard)

17.2.3. COMMENTS

A washing step of the hexane layer was added to the procedure in order to remove excess acetic anhydride and possible polar interferences

17.2.4. CHROMATOGRAM

A total ion chromatogram and chromatogram for m/z 266 is shown in Figure 35 for a beechwood eluate.

17.2.5. RESULTS

→ Repeatability

The results of the replicate determinations of PCP in eluates of wood are summarised in Table 79. The results show a very good repeatability of 6 %.

→ Recoveries

The recovery was determined for a water sample spiked with 800 µg/l PCP. The recovery was 98%.

→ **Sensitivity**

With a concentration factor of 20 the lowest calibration standard corresponds to a sample concentration of 0.5 µg/L. This value is in agreement with the LOD calculated on the basis of a signal-to-noise of 3 for the eluate sample (see Figure 35). Lower LODs are achievable with higher concentration factors. A concentration factor of 100 will be sufficient to reach the LOD of 0.1 µg/L mentioned in EN 12673.

Table 79: Measured PCP concentrations in eluates of wood powder

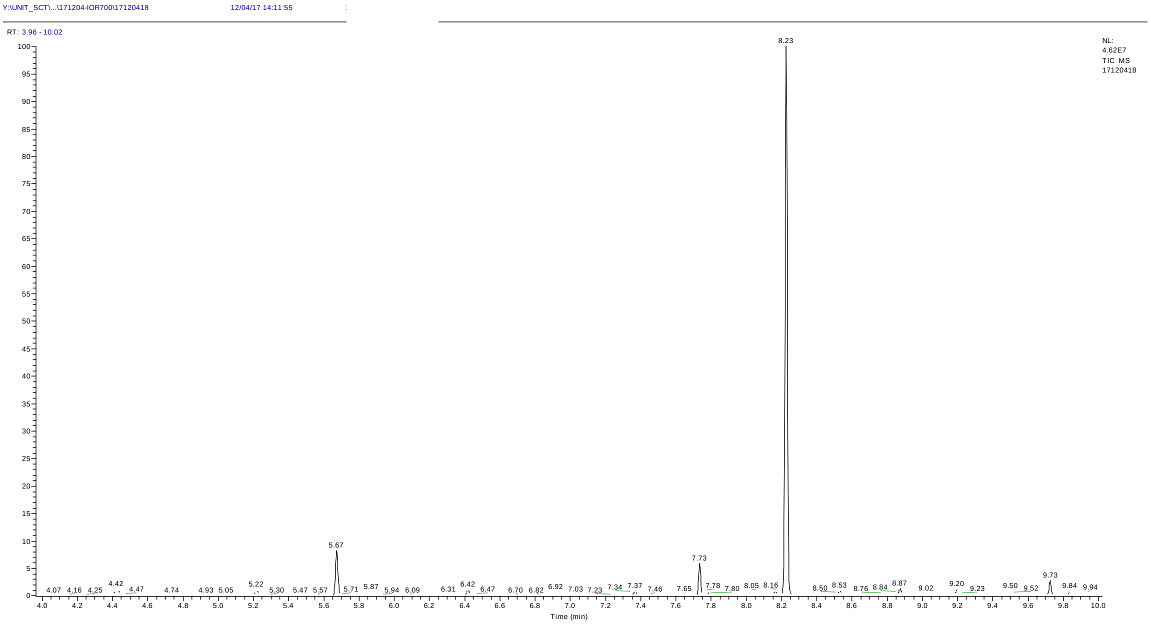
	Measured conc. µg/L	***Theor. conc*** µg/L	***Recovery***
Replicate A	5,26		
Replicate B	4,47		
Replicate A	4,68		
Replicate A	4,90		
Replicate A	4,95		
Average	4,85		
St. Dev.	0,299		
CV_r	**6,2%**		
QC sample	827	838	98%

17.3. CONCLUSION

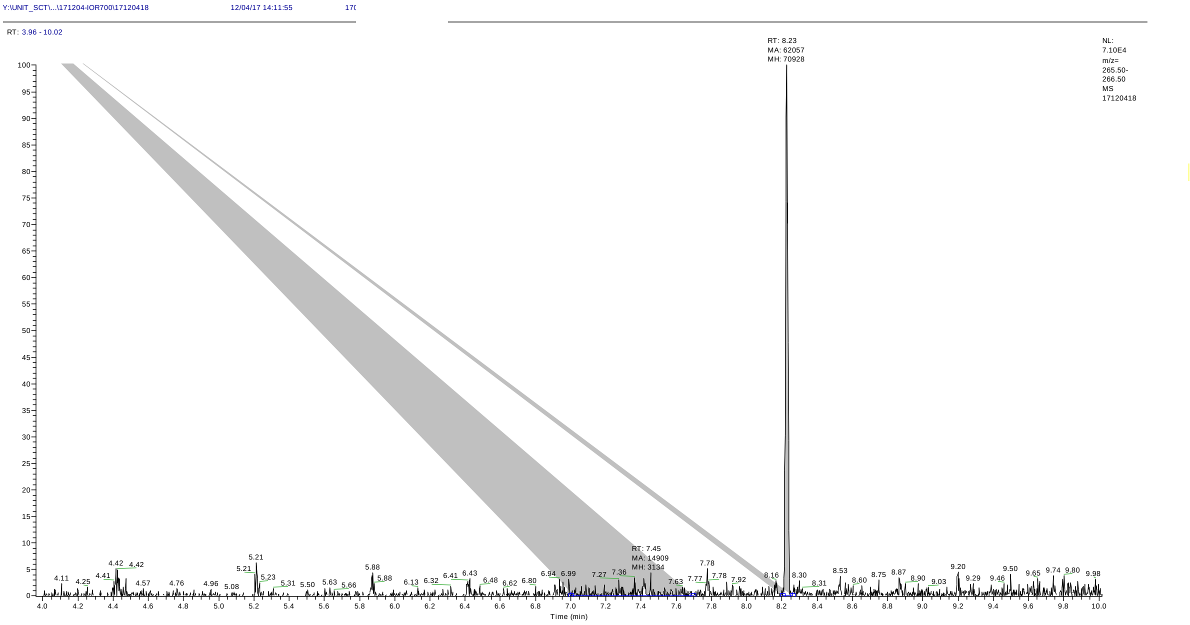
EN 12673 is suited for the analysis of PCP and other chlorophenols in eluates of wood.
An advised modification is the inclusion of a hexane extract washing step for the removal of interferences.
Lower detection limits can be obtained in case of larger intakes.

Figure 35: Total ion (TIC) and ion chromatogram (m/z 266) of PCP in wood powder eluate

TIC



m/z 266



CHAPTER 18 DETERMINATION OF SELECTED PESTICIDES IN ELUATES OF CONSTRUCTION PRODUCTS

18.1. EN 15637 FOODS OF PLANT ORIGIN - DETERMINATION OF PESTICIDE RESIDUES USING LC-MS/MS FOLLOWING METHANOL EXTRACTION AND CLEAN-UP USING DIATOMACEOUS EARTH

For the method description and the LC-MS conditions applied by VITO we refer to 10.1.1.

18.2. DETERMINATION OF PROPICONAZOLE AND TEBUCONAZOLE IN ELUATES OF TREATED WOOD

18.2.1. SAMPLES

2 frozen eluate samples (A and B) of ca 250 mL were received from BAM. The eluates were prepared according to EN 16637-2; eluates A and B correspond to different immersion periods. The samples were kept frozen in expectation of analysis.

18.2.2. ANALYSIS

- A quantity of eluate was diluted with an equal amount of methanol
- 5 test potions of 1 mL were transferred to injection vials and analysed using LC-MS/MS according to the method given in 10.1.2.
- The concentrations of the target analytes were determined using the external standard method
- A procedural blank as well as 2 matrix additions (10 µg/L) were analysed as well.

18.2.3. COMMENTS

- EN 15637 is not a standard for water analysis
- The chromatographic peaks of propiconazole and tebuconazole were out of range. The extracts were diluted 10 times with 1/1 methanol/water.
- The use of triphenylphosphate or tris-(1,3-dichlorisopropyl)-phosphate as internal standard is inappropriate because of:
  - high blank values
  - retention times and consequently matrix suppression/enhancement effects differing from those of the target analytes
- Bis-nitrophenyl urea (nicarbazin) is neither a suitable internal standard because this compound has to be analysed in negative mode

18.2.4. CHROMATOGRAMS:

Chromatograms of propiconazole and tebuconazole in eluate A are given in Figure 36.

18.2.5. RESULTS

→ Repeatability

In Table 80 the concentrations which were determined for the different wood eluate test portions are given. For each compound the repeatability (CV_r) was calculated. For both propiconazole and tebuconazole the repeatability is <4%.

→ Recovery

The results of the matrix additions are given in Table 81. The recoveries are ~100% on average. No correction has to be made for reasons of ionisation suppression. Note that the results of the repeatability study are lower than the concentrations determined by BAM (for eluate A 54 and 75 µg/L for tebuconazole and propiconazole resp.; for eluate B resp. 68 and 97 µg/L). This would indicate to some losses occurred during transport and storage.

→ Sensitivity

The lowest concentration of the linear range is 0.1 µg/L (using a UPLC-Xevo TQ-S), with signal-to-noise ratios of 35 and 10 for resp. propiconazole and tebuconazole.

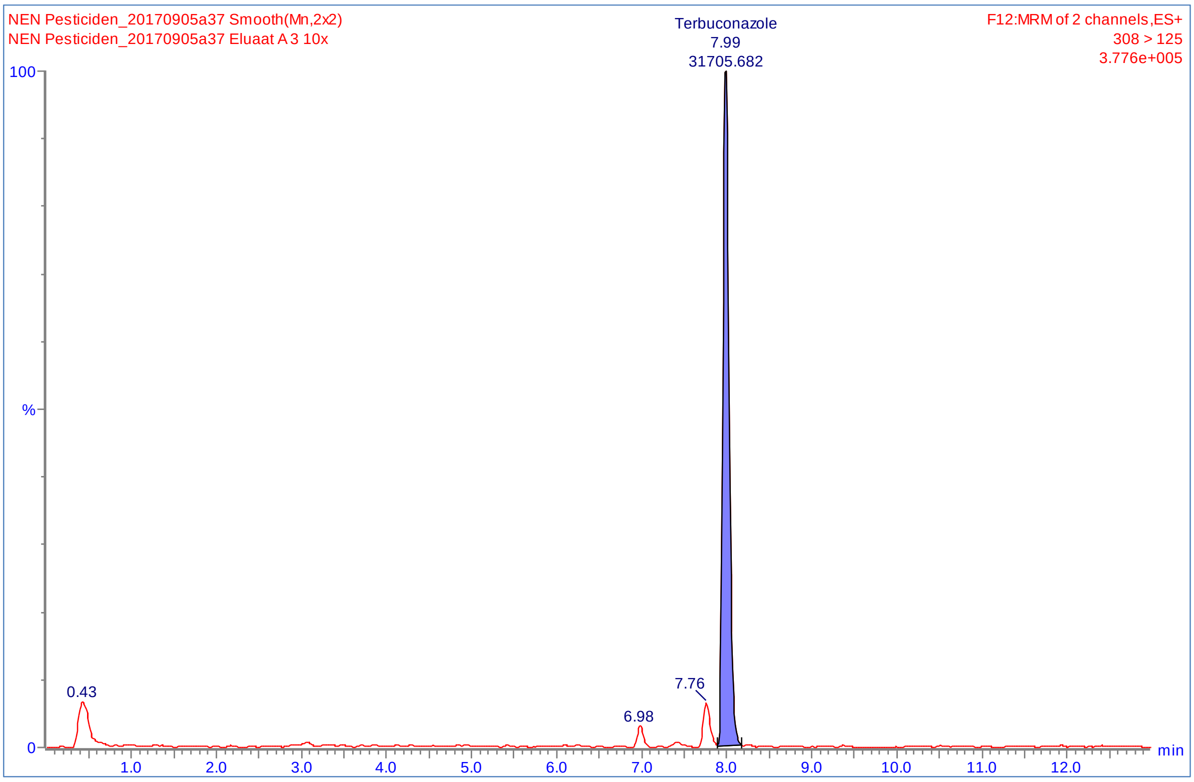
Table 80: Measured concentrations of propiconazole and tebuconazole in eluates of treated wood (in µg/L)

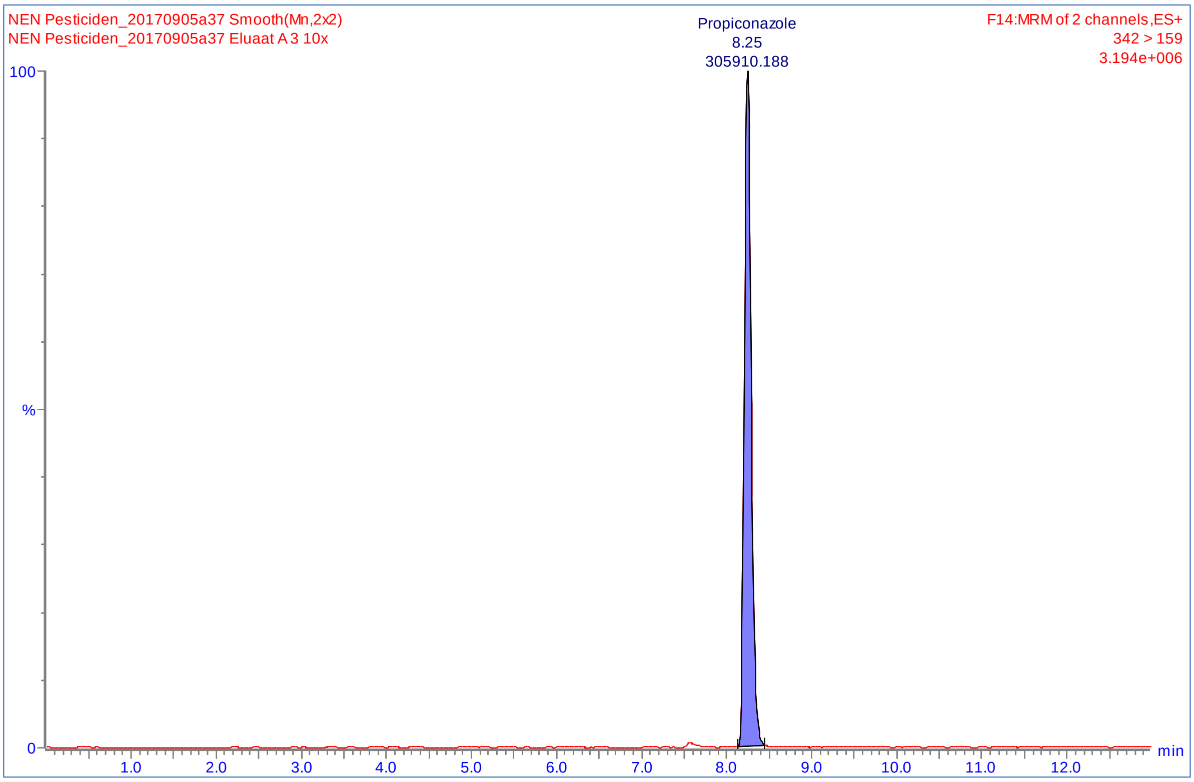
ID	Tebuconazole	Propiconazole
eluate A 1	38,4	48,2
eluate A 2	37,3	48,7
eluate A 3	40,9	50,8
eluate A 4	41,3	51,5
eluate A 5	40,0	50,8
Average	39,6	50,0
St.dev	1,53	1,29
CV_r%	3,9	2,6
eluate B 1	52,2	66,8
eluate B 2	49,9	66,1
eluate B 3	50,1	66,1
eluate B 4	53,7	69,3
eluate B 5	54,2	72,7
Average	52,0	68,2
St.dev	1,77	2,53
CV_r%	3,4	3,7

Table 81 : Recoveries for matrix additions in %

ID	Tebuconazole	Propiconazole
Eluaat A 6 ADD 10x	96	96
Eluaat A 7 ADD 10x	103	102
Eluaat B 6 ADD 10x	105	96
Eluaat B 7 ADD 10x	105	101

Figure 36: Chromatograms of tebuconazole and propiconazole for a 10 times diluted wood eluate





18.3. DETERMINATION OF BIOCIDES IN ELUATES OF SEALANT 2

18.3.1. SAMPLES

2 eluate samples (A and B) of ca 500 mL were received from SGS Intron. The eluates were prepared according to CEN/TS 16637-2 (T = 20°C, L/A = 80 L/m^2); eluates A and B correspond to different immersion periods. The samples were collected in dark glass bottles and transferred to VITO in coolboxes. They were frozen in expectation of analysis.

18.3.2. ANALYSIS

- A quantity of eluate was diluted with an equal amount of methanol
- 5 test portions of 1 mL were transferred to injection vials and analysed using LC-MS/MS according to the method given in 10.1.2.
- The concentrations of the target analytes were determined using resp. the external and internal standard method
- A procedural blank as well as 2 matrix additions (100 µg/L) on each eluate fraction were analysed as well.

18.3.3. COMMENTS

- The chromatographic peaks of MIT and BIT were out of range. The extracts were diluted 10 times with 1/1 methanol/water. Other biocides were not detected above LOQ.
- For other comments see 16.2.3.

18.3.4. CHROMATOGRAMS:

Chromatograms of MIT and BIT in eluate A are given in Figure 37.

18.3.5. RESULTS

→ Repeatability

In Table 82 the concentrations which were determined for the different sealant eluate test portions are given. For each compound the repeatability (CV_r) was calculated. For BIT the %RSD were 8% and 5% for resp. fraction 1 and fraction 3 eluate. For MIT which is eluting very fast, the %RSD is higher, resp. 15 and 24%.

→ Recovery

The results of the matrix additions are given in Table 83. The average recoveries range from 70-120%, depending on biocide. Note that the additions of MIT and BIT were lower than the original concentrations in the eluates which can explain the spread in the recovery data.

→ Sensitivity

The lowest concentration of the linear range is 0.1 µg/L (using a UPLC-Xevo TQ-S).

Table 82: Measured concentrations of diuron, terbutryn, MIT, BIT, OIT and CMIT in eluates of sealant 2 (in µg/L)

ID	diuron	terbutryn	MIT	BIT	OIT	CMIT
sealant 2 FR1 1	<0,1	<0,1	231	154	0,11	<0,1
sealant 2 FR1 2	<0,1	<0,1	311	140	0,12	<0,1
sealant 2 FR1 3	<0,1	<0,1	351	135	<0,1	<0,1
sealant 2 FR1 4	<0,1	<0,1	286	162	<0,1	<0,1
sealant 2 FR1 5	<0,1	<0,1	273	158	<0,1	<0,1
Average			290	150		
St.Dev.			44	12		
CV_r			15%	8%		
sealant 2 FR3 1	<0,1	<0,1	657	336	<0,1	<0,1
sealant 2 FR3 2	<0,1	<0,1	415	367	0,16	<0,1
sealant 2 FR3 3	<0,1	<0,1	414	382	<0,1	<0,1
sealant 2 FR3 4	<0,1	<0,1	440	366	<0,1	<0,1
sealant 2 FR3 5	<0,1	<0,1	622	371	<0,1	<0,1
Average			509	364		
St.Dev.			120	17		
CV_r			24%	5%		

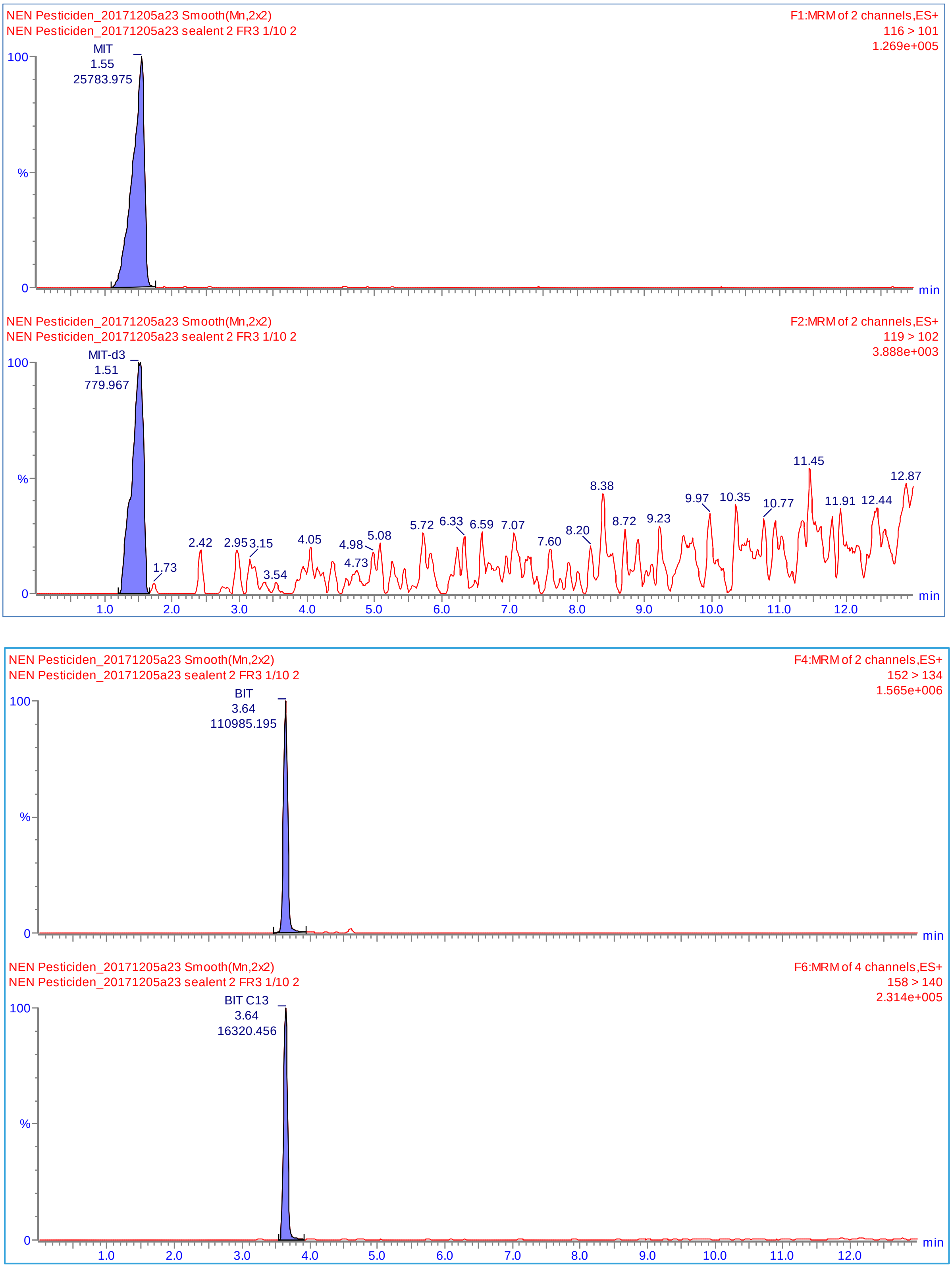
Table 83: Recoveries (in %) of biocides added to sealant 2 eluates (addition corresponding to a concentration of ca 100 µg/L)

ID	diuron	terbutryn	MIT	BIT	OIT	CMIT
sealant 2 FR1 1 ADD	59	75	59	55	98	61
sealant 2 FR1 2 ADD	94	88	184	86	123	88
sealant 2 FR3 1 ADD	88	85	93	58	117	80
sealant 2 FR3 2 ADD	80	85	145	99	109	71

Average

sealant 2 FR1 ADD	77	81	122	71	111	74
sealant 2 FR3 ADD	84	85	119	78	113	76

Figure 37: Chromatograms of MIT and BIT for a 10 times diluted sealant 2 eluate



18.4. DETERMINATION OF BIOCIDES IN ELUATES OF RENDER 2

18.4.1. SAMPLES

2 eluate samples (fraction 1 and 3) of ca 500 mL were received from SGS Intron. The eluates were prepared according to CEN/TS 16637-2 (T = 20°C, L/A = 80 L/m^2). The samples were collected in dark glass bottles and transferred to VITO in coolboxes. They were frozen in expectation of analysis.

18.4.2. ANALYSIS

- A quantity of eluate was diluted with an equal amount of methanol
- 5 test portions of 1 mL were transferred to injection vials and analysed using LC-MS/MS according to the method given in 10.1.2. The target analytes were diuron, terbutryn, MIT, BIT, OIT and carbendazim.
- The concentrations of the target analytes were determined using resp. the external and internal standard method
- A procedural blank as well as 2 matrix additions (1 mg/L) on each eluate fraction were analysed as well.

18.4.3. COMMENTS

- The chromatographic peaks of MIT and BIT were out of range. The extracts were diluted 100 times with 1/1 methanol/water.
- For other comments see 16.2.3.

18.4.4. CHROMATOGRAMS:

Chromatograms of the target biocides in fraction 1 eluate of render 2 are given in Figure 38.

18.4.5. RESULTS

→ Repeatability

In Table 84 the concentrations which were determined for the different render eluate test portions are given. The highest values are found for MIT and BIT, which are the most polar and more leachable compounds.
For each compound the repeatability (CV$_r$) was calculated. For eluate fraction 1 the %RSD range from 7 to 13%, with exclusion of 2 outlier values which were observed for resp. MIT and OIT. For eluate fraction 2 the %RSD are below 10%, with the exception of OIT. For OIT there is more variation, the %RSD are 12% and 17% for resp. fraction 1 and fraction 3.

→ Recovery

The results of the matrix additions are given in Table 85. For MIT, BIT and OIT the recoveries are acceptable (80-130%). For diuron and terbutryn the recoveries are too low. Signal suppression caused by co-eluting matrix constituents occurs in case of diuron. The concentrations of diuron in the eluates (Table 84) were not corrected for this suppression.

For terbutryn suppression cannot be the explanation as concentrations are corrected for matrix suppression effects by use of an isotope labelled internal standard. The reason for the lower recovery of terbutryn is not clear.

Carbendazim was not present in the spiking solution and no recovery data are available.

→ **Sensitivity**

The lowest concentration of the linear range is 0.1 µg/L (using a UPLC-Xevo TQ-S).

18.5. CONCLUSION

On the basis of the repeatability and recovery values which were obtained for the eluates of different types of construction products it can be concluded that biocides can be quantitatively determined by direct injection into a sensitive LC-MS/MS system. Not all results were satisfactory but improvement is possible when optimising the LC-MS conditions (e.g. to achieve more retention for MIT) and quantification method (use of isotope labelled internal standards, standard addition or matrix matched calibration). In case of less sensitive instruments concentration of the extracts will be needed by means of solid phase extraction. The suitability of this extraction technique has to be proven for each biocide of interest. As EN 15637 is not a water standard and as there is no EN or ISO LC-MS standard for biocides in water available, we advice to define a work item for the development of a standard for the determination of biocides in eluates of construction materials. DIN 38407-36 (*German standard methods for the examination of water, waste water and sludge - Jointly determinable substances (group F) - Part 36: Determination of selected active substances of plant protection products and other organic substances in water - Method using high performance liquid chromatography and mass spectrometric detection (HPLC-MS/MS) after direct injection (F 36*)) could serve as starting document.

Table 84: Measured concentrations of diuron, terbutryn, MIT, BIT, OIT and carbendazim in eluates of render 2 (in mg/L)

ID	diuron	terbutryn	MIT	BIT	OIT	Carbendazim
170713-26 FR 1 1	1,90	0,30	26,4	26,9	~~1,54~~	0,39
170713-26 FR 1 2	1,78	0,26	23,6	21,4	1,07	0,35
170713-26 FR 1 3	1,67	0,29	25,6	25,4	1,13	0,38
170713-26 FR 1 4	1,83	0,28	25,2	25,3	1,14	0,37
170713-26 FR 1 5	1,60	0,21	~~19,3~~	19,2	0,88	0,38
Average	1,756	0,270	25,22	23,63	1,054	0,375
St.Dev.	0,125	0,034	1,161	3,184	0,122	0,013
CVr	7%	13%	5%	13%	12%	3%
170713-26 FR 3 1	1,74	0,37	3,57	3,93	1,01	0,62
170713-26 FR 3 2	1,78	0,38	3,48	4,07	1,49	0,63
170713-26 FR 3 3	1,75	0,38	3,58	3,99	1,17	0,62
170713-26 FR 3 4	1,70	0,36	3,38	3,75	1,07	0,59
170713-26 FR 3 5	1,75	0,37	3,58	3,21	1,42	0,62
Average	1,746	0,373	3,519	3,788	1,231	0,615
St.Dev.	0,027	0,008	0,086	0,346	0,211	0,016
CVr	2%	2%	2%	9%	17%	3%

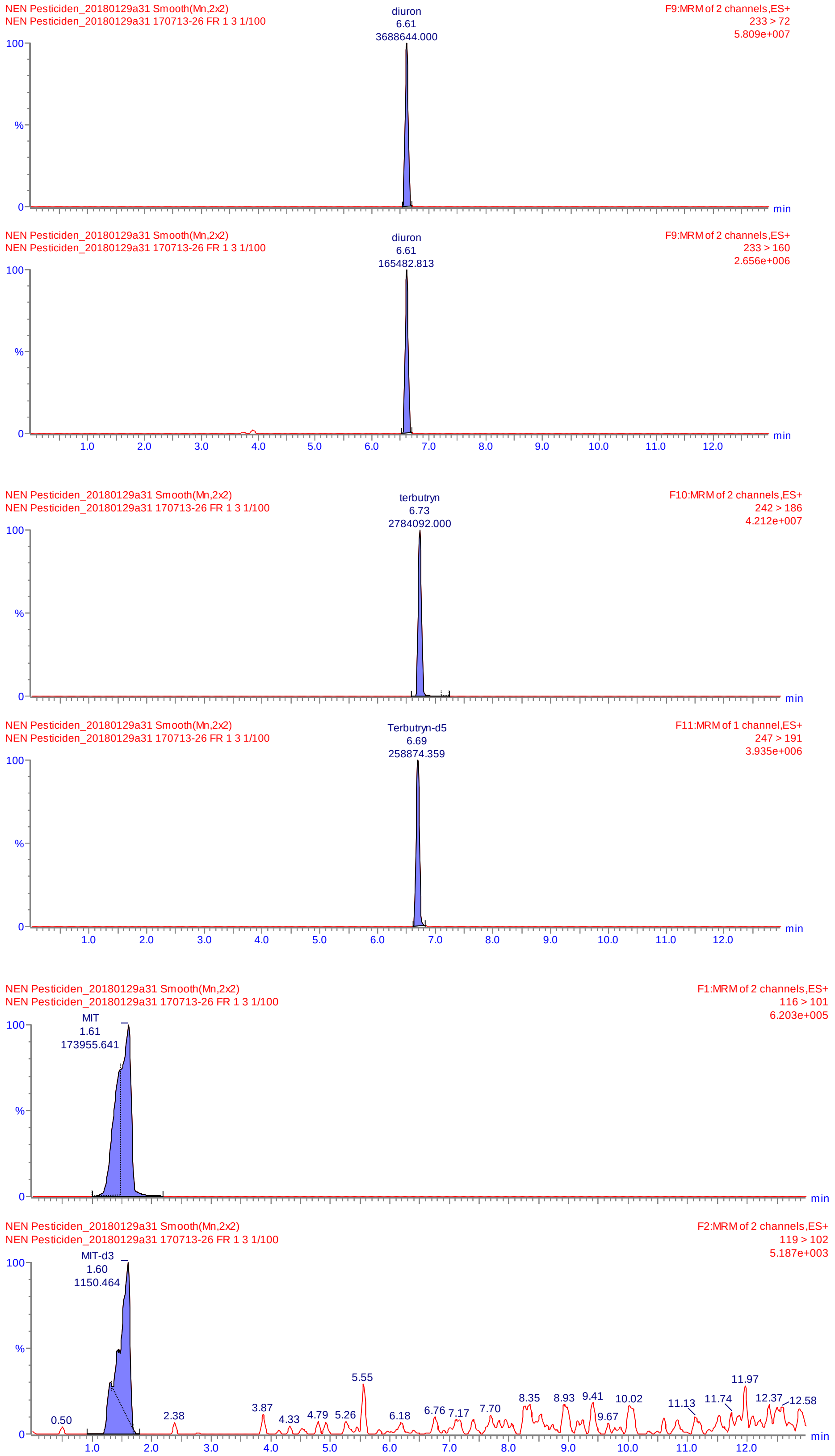
Table 85: Recoveries (in %) of pesticides added to render 2 eluates (addition corresponding to a concentration of ca 1 mg/L)

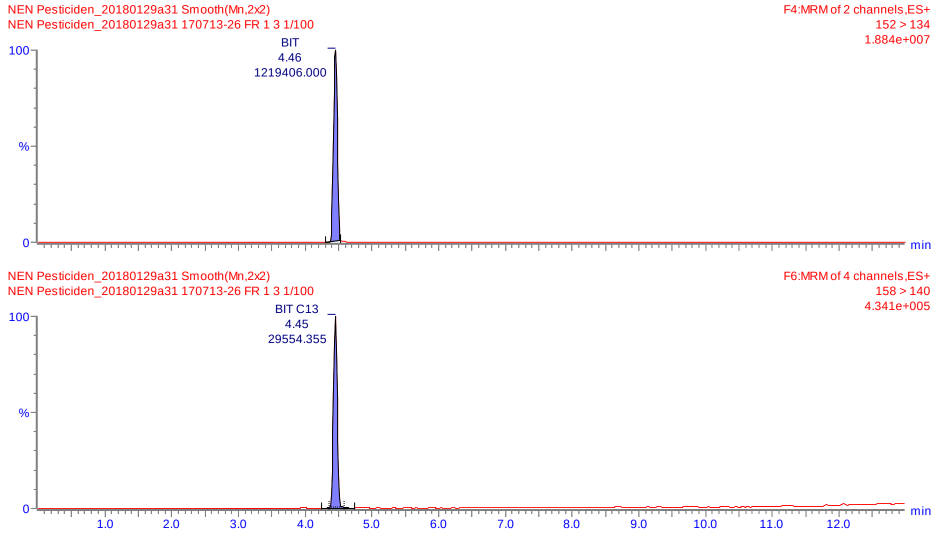
ID	diuron	terbutryn	MIT	BIT	OIT
170713-26 FR 1 ADD1	30	69	95	110	145
170713-26 FR 1 ADD2	40	78	105	145	83
170713-26 FR 3 ADD1	31	54	77	115	129
170713-26 FR 3 ADD2	39	61	84	97	133

Average

170713-26 FR 1 ADD	35	73	100	127	114
170713-26 FR 3 ADD	35	58	81	106	131

Figure 38: Chromatograms of pesticides in a 100 times diluted render eluate

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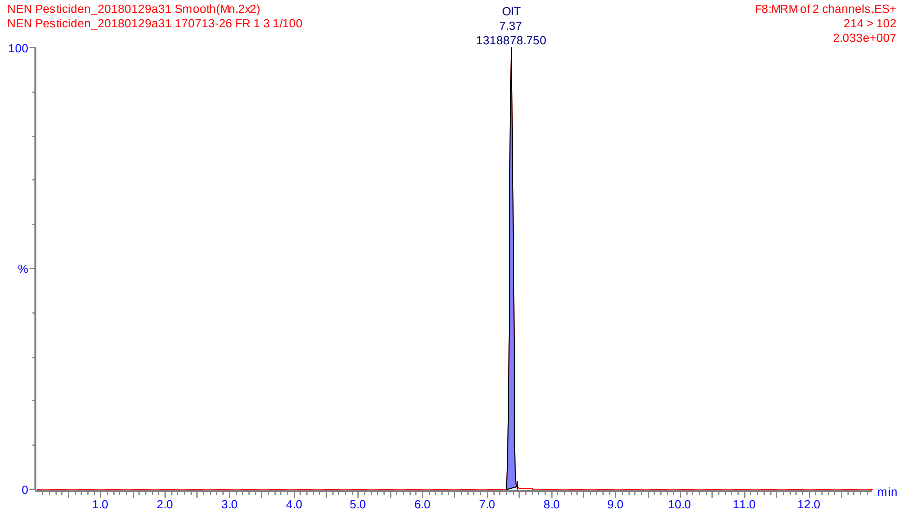
NEN Pesticiden_20180129a31 170713-26 FR 1 3 1/100
F4:MRM of 2 channels,ES+
152 > 134
1.884e+007
BIT
4.46
1219406.000
100
%
0
min
NEN Pesticiden_20180129a31 Smooth(Mn,2x2)
NEN Pesticiden_20180129a31 170713-26 FR 1 3 1/100
F6:MRM of 4 channels,ES+
158 > 140
4.341e+005
BIT C13
4.45
29554.355
100
%
0
min
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0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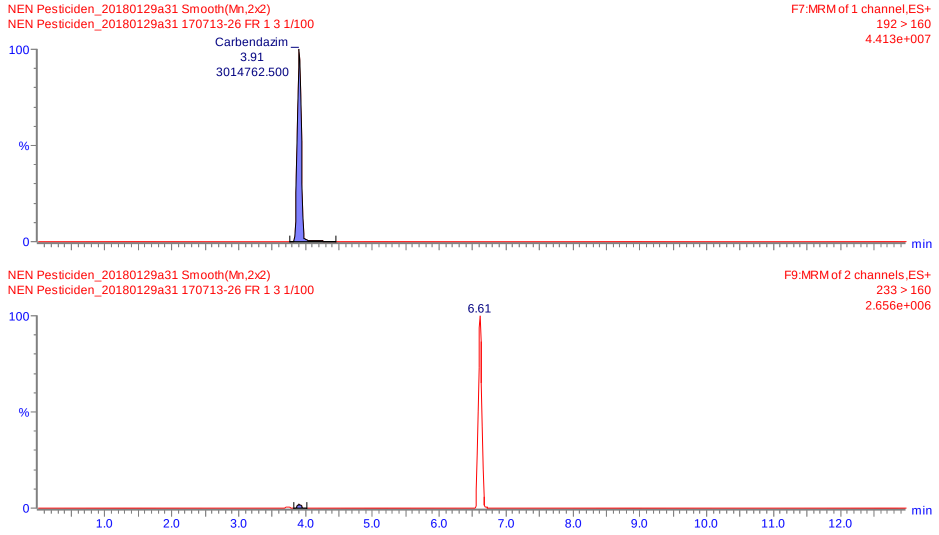
NEN Pesticiden_20180129a31 170713-26 FR 1 3 1/100
OIT
7.37
1318878.750
F8:MRM of 2 channels,ES+
214 > 102
2.033e+007
100
%
0
min
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0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NEN Pesticiden_20180129a31 170713-26 FR 1 3 1/100
F7:MRM of 1 channel,ES+
192 > 160
4.413e+007
Carbendazim
3.91
3014762.500
100
%
0
min
NEN Pesticiden_20180129a31 Smooth(Mn,2x2)
NEN Pesticiden_20180129a31 170713-26 FR 1 3 1/100
F9:MRM of 2 channels,ES+
233 > 160
2.656e+006
6.61
100
%
0
min
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0

CHAPTER 19 DETERMINATION OF BTEX IN ELUATES OF CONSTRUCTION PRODUCTS

19.1. ISO 15680 - WATER QUALITY – GAS-CHROMATOGRAPHIC DETERMINATION OF A NUMBER OF MONOCYCLIC AROMATIC HYDROCARBONS, NAPHTALENE AND SEVERAL CHLORINATED COMPOUNDS USING PURGE-AND-TRAP AND THERMAL DESORPTION

19.1.1. METHOD DESCRIPTION

A summary of ISO 15680 and modifications done by VITO is given in Table 86. The method was applied to eluate of asphalt aggregate. The method was used for the determination of the following BTEX:

Benzene
Toluene
Ethylbenzene
m/p-Xylene
o-Xylene

19.1.2. MEASUREMENT CONDITIONS APPLIED BY VITO

For the instrument settings, use of internal standards and the ions used for quantitation see 4.1.2.

19.1.3. CALIBRATION DIAGRAMS

Five calibration solutions of BTEX were prepared in a concentration range of 0.17 to 11.2 µg/l per component. D6-benzene, D8-toluene and D10-ethylbenzene were used as internal standards. The concentration of the internal standards in the calibration solutions was constant (6.5 µg/l). The calibration curves are given in Figure 39 and are linear over the injected range.

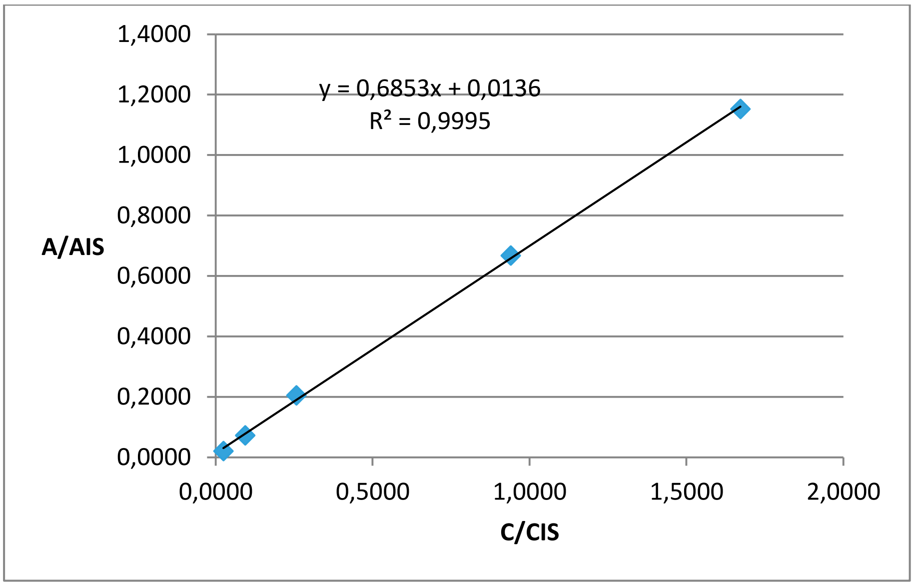
The linear range corresponds to a sample concentration of 0.17 µg/l to 11.2 µg/l (except for the sum of m/p-xylene: 0.34 to 22.4 µg/l).

Table 86: Summary of ISO 15680 and method applied by VITO

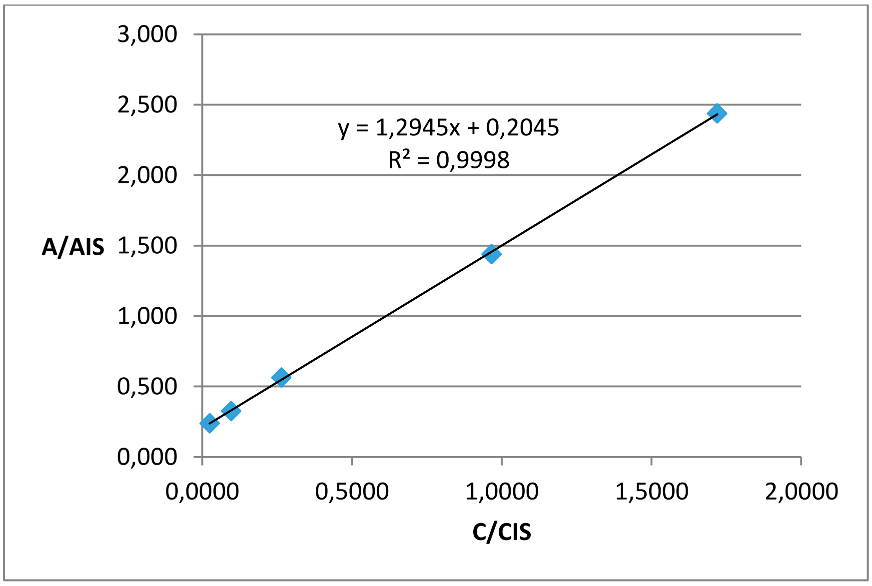
#	Sample(eluate) Parameter list Method to be used	Short Description of the method to be used	Short description of the VITO Method	Method differences	Comment
5	Asphalt aggregate BTEX EN ISO 15680	- Matrix: drinking water, groundwater, surface water, seawater, waste water - Intake: 20 ml - IS: D6-benzene, D8-toluene, D10-ethylbenzene - Measurement: Purge&Trap – GC-MS - LOQ: 10 ng/l	- Matrix: eluate of asphalt aggregate - Intake: 5 – 10 ml - IS: D6-benzene, D8-toluene, D10-ethylbenzene - Measurement: Headspace – GC-MS - LOQ: 100-200 ng/l	- VITO applies headspace instead of purge&trap	- headspace is less sensitive than purge&trap but requires less sample handling and there is less chance on carry-over

Figure 39: Calibration diagrams of the BTEX (method ISO 15680)

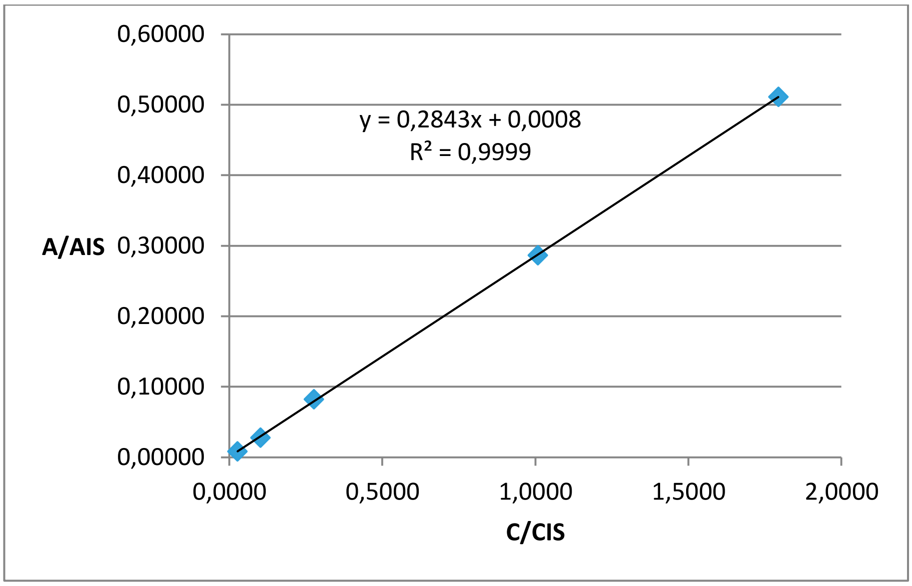
- Benzene



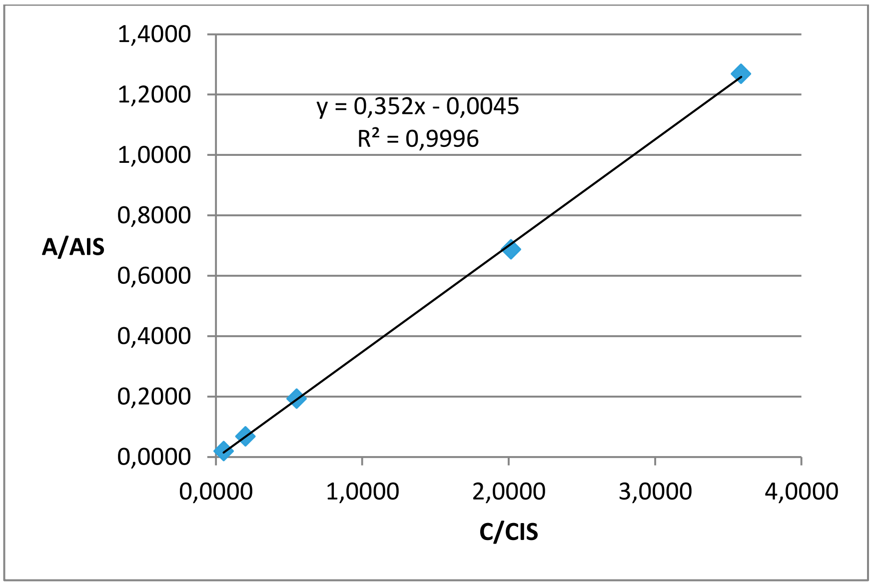
- Toluene



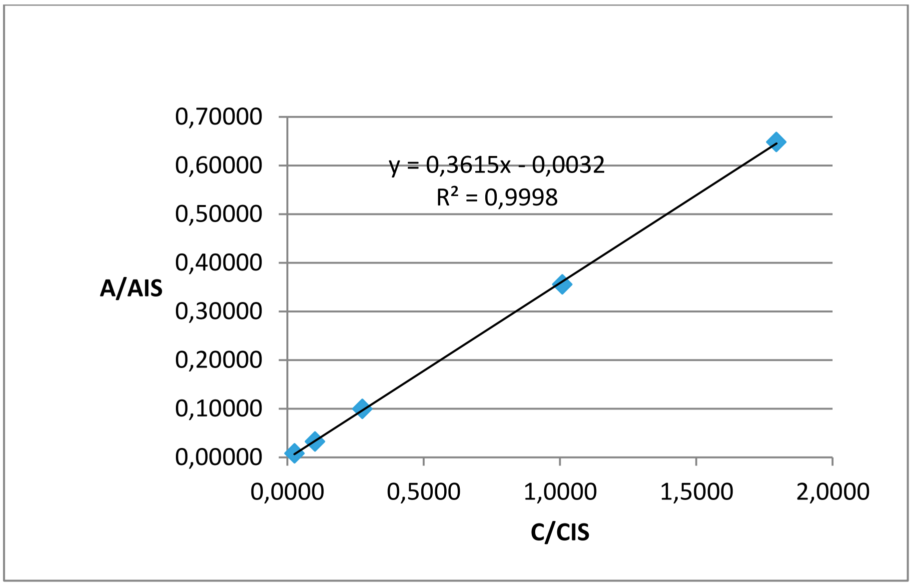
- Ethylbenzene



- m/p-Xylene



- o-Xylene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0,60000
0,50000
0,40000
0,30000
0,20000
0,10000
0,00000
A/AIS
y = 0,3615x - 0,0032
R² = 0,9998
0,0000
0,5000
1,0000
1,5000
2,0000
C/CIS

19.2. DETERMINATION OF BTEX IN ELUATE OF ASPHALT AGGREGATE WITH METHOD ISO 15680

19.2.1. SAMPLE

Two eluates of asphalte aggregate were received from SGS Intron:
- L/S=1.09 22-11-17 (eluate A)
- L/S=8.91 4-12-17 (eluate B).

The eluates were prepared according to CEN/TS 16637-3 (T = 20°C, flow rate = 98 mL/h).
The samples were taken in dark glass bottles and transferred to VITO in coolboxes. The samples were stored in a refrigerator in expectation of analysis.

19.2.2. ANALYSIS

- 5 ml of sample is transferred to a headspace vial 1.5 g sodium chloride
- The internal standard solution was adde
- The vial was closed and heated for 30 min at 70 °C
- 1 ml of the gas phase was injected in the GC/MS

19.2.3. RESULTS

→ **Repeatability**

The samples were analysed in five fold. The results are given in Table 87 and Table 88. The repeatability could not be calculated because all the results were lower than the LOD (0.1 to 0.2 µg/l per component).

→ **Check on method performance**

The recoveries of the internal standard in each sample was calculated using the calibration standard as a reference (100%). The results are given in Table 89 and Table 90. The recoveries of the internal standards range from 91% to 103%; there are no requirements in the method ISO 15680 regarding the recovery. The %RSD of the recoveries are <5%.

→ **Sensitivity**

The sensitivity of the method was calculated with the lowest calibration standard. The LOD is for all components 0.1 µg/l.

19.2.4. CONCLUSION

No conclusion can be drawn about the suitability of the method because the eluates of asphalt aggregate did not contain measurable amounts of BTEX. Nevertheless, on the basis of the recovery and repeatability data of the internal standards it is expected that there will be no issue for the quantitative determination of BTEX in eluates.

Table 87: Measured concentrations of BTEX in eluate A of asphalt aggregate using method ISO 15680

Replicate n°	**1** µg/l	**2** µg/l	**3** µg/l	**4** µg/l	**5** µg/l	**Average** µg/l	**St.Dev.** µg/l	**C.V.** %
Benzene	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	-	-	-
Toluene	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	-	-	-
Ethylhbenzene	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	-	-	-
m/p-Xylene	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	-	-	-
o-Xylene	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	-	-	-

Table 88: Measured concentrations of BTEX in eluate B of asphalt aggregate using method ISO 15680

Replicate n°	**1** µg/l	**2** µg/l	**3** µg/l	**4** µg/l	**5** µg/l	**Average** µg/l	**St.Dev.** µg/l	**C.V.** %
Benzene	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	-	-	-
Toluene	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	-	-	-
Ethylhbenzene	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	-	-	-
m/p-Xylene	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	-	-	-
o-Xylene	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	-	-	-

Table 89: Recovery of the internal standard in eluate A of asphalt aggregate

Replicate n°	**1** %	**2** %	**3** %	**4** %	**5** %	**RSD** %
D6-benzene	96	100	91	97	98	3,5
D8-toluene	102	103	96	99	102	2,9
D10-ethylbenzene	101	101	92	97	99	3,8

Table 90: Recovery of the internal standard in eluate B of asphalt aggregate

Replicate n°	**1** %	**2** %	**3** %	**4** %	**5** %	**RSD** %
D6-benzene	101	94	98	96	96	2,7
D8-toluene	101	98	100	98	100	1,3
D10-ethylbenzene	101	96	100	97	100	2,2

CHAPTER 20 DETERMINATION OF PHENOLS IN ELUATES OF CONSTRUCTION PRODUCTS

20.1. EN ISO 14402 – WATER QUALITY – DETERMINATION OF PHENOL INDEX BY FLOW ANALYSIS

20.1.1. METHOD DESCRIPTION

EN ISO 14402 specifies two methods for the automated colorimetric determination of phenolic compounds in waters of different origin. VITO used the method described in clause 4 of the standard, *determination of phenol index (without extraction) after distillation*. The automated procedure for the determination of the phenol index consists of the following steps:

- The sample is fed into a stream, mixed with phosphoric acid , and inline distilled at pH 1.4
- The distillate, containing steam volatile phenolic compounds, is mixed with continuously flowing solutions of 4-aminoantipyrine and potassium hexacyanoferrate (III)
- Phenolic compounds in the distillate are oxidised by hexacyanoferrate(III)
- The resulting quinones react with 4-amino-2,3-dimetyl-1-phenyl-3pyrazolin-5-one forming yellow condensation products
- The condensation products are measured spectrophotometrically at 505 nm

20.1.2. MEASUREMENT

The analyses were carried out using an flow segment analyser SKALAR San Plus system.

20.1.3. CALIBRATION DIAGRAM

A phenol index calibration diagram is given in Figure 40. Excellent linearity is obtained for a concentration range of 0.01-0.1 mg/L.

20.2. DETERMINATION OF PHENOL INDEX IN ELUATES OF WATER PROOFING SHEETS (PVC)

20.2.1. SAMPLES

Two eluates of water proofing sheets (PVC) were obtained from SGS Intron:

- 180207-1 PVC F-1 22-1-18 (eluate A)
- 180207-1 PVC F-3 24-1-18 (eluate B)

The eluates were prepared according to CEN/TS 16637-2 (T = 20°C, L/A = 80 L/m^2).
The samples were taken in dark glass bottles and were transferred to VITO in coolboxes and stored in a refrigerator.

20.2.2. ANALYSIS

The samples were analysed by direct injection according to ISO 14402 (§4).

20.2.3. RESULTS

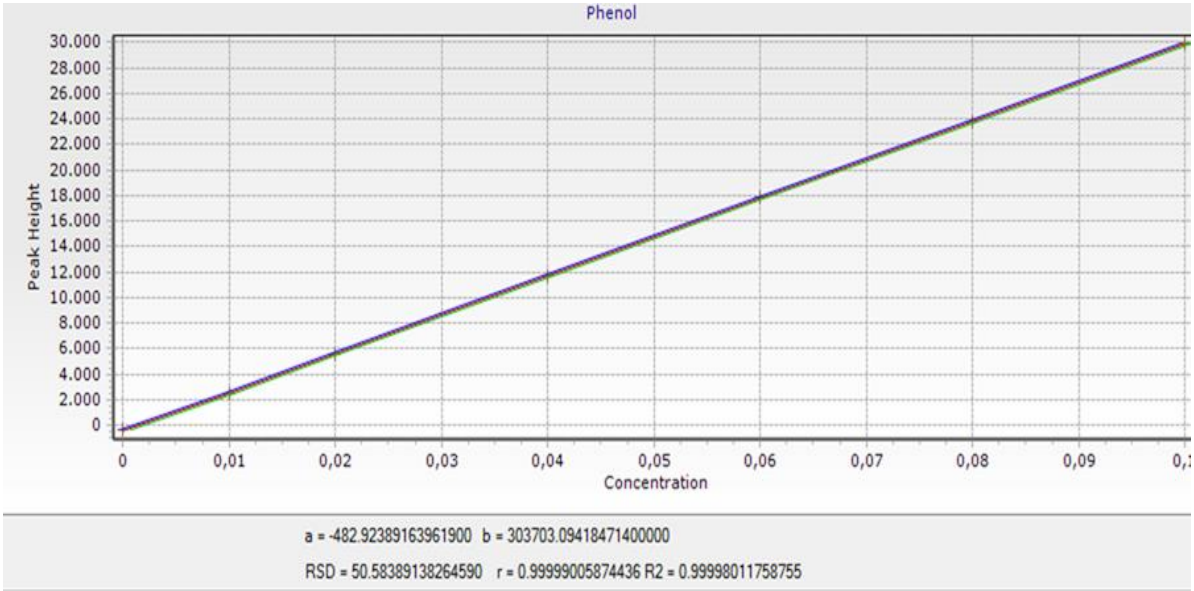
→ Repeatability

The results for phenol index are shown in Table 91. The fraction 1 eluates contain 1.8 mg/L phenol index, the fraction 3 eluates 1.7 mg/L. The %RSD is 11% for both fractions, excluding the outlier values of 4.48 and 6.41 mg/L. These outlier values have been confirmed by analysing other dilutions and result most probably from contamination of sample bottle or during the leaching process.

→ Sensitivity

LOD values of 0.001 mg phenol/L can be reached.

Figure 40: Calibration diagram for phenol determined according to ISO 14402 (§4)



a = -482.92389163961900 b = 303703.09418471400000

RSD = 50.58389138264590 r = 0.99999005874436 R2 = 0.99998011758755

Table 91: Results of the replicate determinations of phenol index for eluates of water PVC proofing sheets

sample nr	dilution factor	C6H5OH mg/L	dilution factor	C6H5OH mg/L	dilution factor	C6H5OH mg/L
Eluate A - 1	50	1,67	20	1,65		
Eluate A - 2	50	1,82				
Eluate A - 3	50	1,61				
Eluate A - 4	50	2,07				
Eluate A - 5	100	~~4,48~~	100	4,46	200	4,49
Average		1,79				
St.Dev.		0,20				
CVr		11%				

Eluate B - 1	100	~~6,41~~	100	6,38	200	6,82
Eluate B - 2	50	1,99				
Eluate B - 3	50	1,61				
Eluate B - 4	50	1,59				
Eluate B - 5	50	1,61				
Average		1,70				
St.Dev.		0,19				
CVr		11%				

20.3. EN ISO 18857-2 - WATER QUALITY -- DETERMINATION OF SELECTED ALKYLPHENOLS -- PART 2: GAS CHROMATOGRAPHIC-MASS SPECTROMETRIC DETERMINATION OF ALKYLPHENOLS, THEIR ETHOXYLATES AND BISPHENOL A IN NON-FILTERED SAMPLES FOLLOWING SOLID-PHASE EXTRACTION AND DERIVATISATION

20.3.1. METHOD DESCRIPTION

Method EN ISO 18857-2 was applied for eluates of water proofing sheets (PVC) and eluates of render 1. The method was used for the determination of the following phenols:

- 4-nonylphenol (isomeric mixture)(NP)
- 4-nonylphenol monoethoxylate (isomeric mixture)
- 4-nonylphenol diethoxylate (isomeric mixture)
- 4-tert.-octylphenol (OP)
- Bisphenol A (BPA)
- Phenol
- Chlorophenols (mono- to penta-)

Remark: in the eluate of render, only nonylphenol and its ethoxylates were analysed.
A summary of method EN ISO 18857-2 and modifications done by VITO is given in Table 92.

20.3.2. MEASUREMENT CONDITIONS APPLIED BY VITO

Instrument settings:

Hardware	Instrument GC-column	Thermo Quest Trace GC Thermo DSQ MS Agilent VF-17MS 30 m lenght, 0.25 mm ID, 0.25 um FT
Injector parameters	Injection volume Injection modus Injection temperature Pulse pressure Pulse time Purge flow Purge time	1 µl Pulsed splitless 250 °C 300 kPa 1.0 min 25 ml/min 1.0 min
GC parameters	Carrier gas Initial temperature Initial time Rate #1 Final temperature #1 Hold time #1 Rate #2 Final temperature #2 Hold time #2	Helium - const flow 1 ml/min 55 °C 1.0 min 6 °C/min 205 °C 0 min 25.0 °C/min 305 °C 5 min
MS parameters	Mode Source temperature Interface temperature Solvent delay	Full scan (120 – 400 amu) 250 °C 310 °C 6.5 min

Internal standards and ions used for quantitation:

Component	m/z	Internal standard	m/z
fenol	151	13C fenol	157
2-Chloorfenol	185	13C 4-Cl-fenol	191
3-Chloorfenol	185	13C 4-Cl-fenol	191
4-Chloorfenol	185	13C 4-Cl-fenol	191
2,3-Dichloorfenol	219	13C 2,4-diClfenol	225
2,4-Dichloorfenol	219	13C 2,4-diClfenol	225
2,5-Dichloorfenol	219	13C 2,4-diClfenol	225
2,6-Dichloorfenol	219	13C 2,4-diClfenol	225
3,4-Dichloorfenol	219	13C 2,4-diClfenol	225
3,5-Dichloorfenol	219	13C 2,4-diClfenol	225
2,3,4-Trichloorfenol	253	13C 2,4,5-triClfenol	259
2,3,5-Trichloorfenol	253	13C 2,4,5-triClfenol	259
2,3,6-Trichloorfenol	253	13C 2,4,5-triClfenol	259
2,4,5-Trichloorfenol	253	13C 2,4,5-triClfenol	259
2,4,6-Trichloorfenol	253	13C 2,4,5-triClfenol	259
3,4,5-Trichloorfenol	253	13C 2,4,5-triClfenol	259
2,3,4,5-Tetrachloorfenol	289	13C 2,3,4,5-tetraClfenol	295
2,3,4,6-Tetrachloorfenol	289	13C 2,3,4,5-tetraClfenol	295
2,3,5,6-Tetrachloorfenol	289	13C 2,3,4,5-tetraClfenol	295
Pentachloorfenol	323	13C pentaClfenol	329
4 tert-octylphenol	207	13C-OP	213
Bisfenol A	357	D16-bisphenol A	372
Nonylfenol	207	13C-NP	227
NP mono ethox	265	13C-NP mono ethox	271
NP di ethox	309	13C-NP di ethox	315

20.3.3. CALIBRATION DIAGRAMS

The same six calibration solutions were used as for the analysis of phenols in PVC water proofing sheets (see 11.4.3). The concentration range was 0.02 µg/ml to 2 µg/ml (except nonylphenol 0.13–13 µg/ml). The internal standards and the injection standard (13C-1,2,4,5-tetrachlorobenzene) were added in a fixed concentration of 0.5 µg/ml. The calibration solutions were derivatised with MSTFA in the same way as the sample extracts.

In case of an intake of 100 ml and a final volume of 0.5 ml, the concentration range of the calibrations solutions correspond to a sample concentrations range of 0.1 – 10 µg/l per phenol (except nonylphenol : 0.6 – 60 µg/l)

The calibration curves are given in Figure 29.

Table 92: Summary of EN ISO 18857-2 and modifications by VITO

Sample (eluate) Parameter list Method to be used	Short Description of the method to be used	Short description of the VITO Method	Method differences	Comment
Water proofing sheets Render 1	- Matrix: drinking water, ground water, surface water, waste water - Intake: 100 ml - IS: 4-(3,6-dimethyl-3-heptyl)phenol (ring 13C) and BPA-D16 - Extraction: bring sample at pH 2 with HCl or H2SO4, SPE with styrene-divinylbenzene phase - Derivatization: MSTFA 5% - Measurement: GC-MS - LOQ: 500 ng/l (NP), 100 ng/l (BPA)	- Matrix: eluate - Intake: 100 ml - IS: 4-(3,6-dimethyl-3-heptyl)phenol (ring 13C), BPA-D16 and 13C-(chloro)phenols - Extraction: bring sample at pH 2 with HCl, SPE with styrene-divinylbenzene phase - Derivatization: MSTFA 5% - Measurement: GC-MS	- VITO applied the method also for phenol, chlorophenols and octylphenol on eluates of water proofing sheets (PVC)	-
Bisphenol A Nonylphenol				
EN ISO 18857-2				

20.4. DETERMINATION OF PHENOLS IN ELUATES OF WATER PROOFING SHEETS (PVC) WITH METHOD EN ISO 18857-2

20.4.1. SAMPLE

Two eluates of water proofing sheets (PVC) were obtained from SGS Intron:

- 180207-1 PVC F-1 22-1-18 (eluate A)
- 180207-1 PVC F-3 24-1-18 (eluate B)

The eluates were prepared according to CEN/TS 16637-2 (T = 20°C, L/A = 80 L/m^2).
The samples were taken in dark glass bottles and were transferred to VITO in coolboxes and stored in a refrigerator.

20.4.2. ANALYSIS

- 100 ml of sample was adjusted to pH 2 with HCl
- Internal standards were added to the sample
- The SPE cartridge (Chromabond EASY) was conditioned with 2 times 10 ml acetone followed by 10 ml water (acidified to pH 2 with HCl)
- The sample was applied to the SPE cartridge
- The cartridge was rinsed with 10 ml of water (acidified to pH 2 with HCl)
- The cartridge was dried
- The cartridge was soaked with 1 ml acetone
- The cartridge was eluted with 2 times 2.5 ml acetone
- The extract was concentrated to dryness under a gentle stream of N2
- 475 µl hexane was added and the phenols were derivatised with 25 µl MSTFA (5% in hexane)
- The injection standard was added and the extract was analysed with GC/MS

20.4.3. RESULTS

→ Repeatability

Both eluates (A and B) were analysed in five fold. The results of the 5 replicates and the procedure blank are given in Table 93 (eluate A) and Table 94 (eluate B). The concentration of octylphenol, the nonylphenol ethoxylates and all the chlorophenols were lower than the LOD. For the other phenols the repeatability was calculated. For phenol, bisphenol A and nonylphenol the repeatabilities were good for both eluates (<15%). For phenol two outlier values had to be excluded, for the same samples as those with the phenol index outlier values (20.2.3). Remark that nonylphenol is also present in the procedural blank at the same concentration level. This means that the repeatability of nonylphenol is not reflecting the repeatability of the extraction, because the component is not present in the samples but is introduced as a contamination during the sample preparation. Most probably the nonylphenol contamination is caused by the SPE extraction step.

→ Check on method performance

The concentration of nonylphenol in the procedural blank was too high. This is a known phenomenon when applying extraction with SPE, as the SPE cartridges can contain nonylphenol.
The recoveries of the internal standards are given in Table 95 (eluate A) and Table 96 (eluate B). The recoveries are generally good, except for ^{13}C-phenol and ^{13}C-2,4-dichlorophenol (too low), most probably because of SPE breakthrough.

→ Sensitivity

The sensitivity of the method was calculated with S/N using the response of 2,3,6-trichlorophenol in eluate. The LOD for 2,3,6-trichlorophenol was 0.01 µg/l. Method EN ISO 18857-2 specifies an LOD in waste water of 0.1 µg/l for OP and BPA, and 0.5 µg/l for NP and NP mono- and diethoxylate.

20.4.4. COMMENTS

Because almost all phenols were absent in the eluate samples, there are not sufficient data regarding the repeatability of method EN ISO 18857-2. Also there are some problems with nonylphenol contamination from the SPE procedure, and with low recoveries of some internal standards. Only for bisphenol A the method gives acceptable results.
From the data it can not be concluded that method EN ISO 18857-2 using SPE extraction and measurement with GC/MS is suited for the analysis of phenols in eluates of water proofing sheets (PVC).

20.4.5. CHROMATOGRAMS

The GC/MS ion chromatograms of the phenols in water proofing sheets are shown in Figure 41.

Table 93: Measured concentrations of phenols in eluates A of water proofing sheets

Replicate n°	**1** µg/l	**2** µg/l	**3** µg/l	**4** µg/l	**5** µg/l	**Average** µg/l	**Standdev** µg/l	**CV_r** %	**Proc.blank** µg/l
phenol	1139	1117	883	1060	~~1704~~	1181	309,3	11,1	0,9
2-chloorphenol	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	-	-	-	< 0,1
3-chloorphenol	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	-	-	-	< 0,1
4-chloorphenol	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	-	-	-	< 0,1
2,3-dichloorphenol	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	-	-	-	< 0,1
(2,4+2,6)-dichloorphenol	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	-	-	-	< 0,1
2,5-dichloorphenol	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	-	-	-	< 0,1
3,4-dichloorphenol	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	-	-	-	< 0,1
3,5-dichloorphenol	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	-	-	-	< 0,1
2,3,4-trichloorphenol	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	-	-	-	< 0,1
2,3,5-trichloorphenol	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	-	-	-	< 0,1
2,3,6-trichloorphenol	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	-	-	-	< 0,1
2,4,5-trichloorphenol	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	-	-	-	< 0,1
2,4,6-trichloorphenol	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	-	-	-	< 0,1
3,4,5-trichloorphenol	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	-	-	-	< 0,1
2,3,4,5-tetrachloorphenol	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	-	-	-	< 0,1
2,3,4,6-tetrachloorphenol	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	-	-	-	< 0,1
2,3,5,6-tetrachloorphenol	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	-	-	-	< 0,1
pentachloorphenol	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	-	-	-	< 0,1
4-tert-octylphenol	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	-	-	-	< 0,1
bisphenol A	1,24	1,08	1,22	1,16	1,29	1,20	0,080	6,7	< 0,1
nonylphenol	2,18	2,16	2,16	2,13	1,93	2,11	0,10	4,8	2,03
NP monoethoxylate	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	-	-	-	< 0,1
NP diethoxylate	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	-	-	-	< 0,1

Table 94: Measured concentrations of phenols in eluates B of water proofing sheets

Replicate n°	**1** µg/l	**2** µg/l	**3** µg/l	**4** µg/l	**5** µg/l	**Average** µg/l	**St.dev.** µg/l	**CV$_r$** %	**Proc.blank** µg/l
phenol	~~2557~~	1186	897	1085	941	1333	693,7	12,9	0,9
2-chloorphenol	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	-	-	-	< 0,1
3-chloorphenol	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	-	-	-	< 0,1
4-chloorphenol	0,20	< 0,1	< 0,1	< 0,1	0,11	-	-	-	< 0,1
2,3-dichloorphenol	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	-	-	-	< 0,1
(2,4+2,6)-dichloorphenol	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	-	-	-	< 0,1
2,5-dichloorphenol	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	-	-	-	< 0,1
3,4-dichloorphenol	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	-	-	-	< 0,1
3,5-dichloorphenol	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	-	-	-	< 0,1
2,3,4-trichloorphenol	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	-	-	-	< 0,1
2,3,5-trichloorphenol	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	-	-	-	< 0,1
2,3,6-trichloorphenol	< 0,1	0,01	< 0,1	< 0,1	< 0,1	-	-	-	< 0,1
2,4,5-trichloorphenol	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	-	-	-	< 0,1
2,4,6-trichloorphenol	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	-	-	-	< 0,1
3,4,5-trichloorphenol	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	-	-	-	< 0,1
2,3,4,5-tetrachloorphenol	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	-	-	-	< 0,1
2,3,4,6-tetrachloorphenol	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	-	-	-	< 0,1
2,3,5,6-tetrachloorphenol	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	-	-	-	< 0,1
pentachloorphenol	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	-	-	-	< 0,1
4-tert-octylphenol	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	-	-	-	< 0,1
bisphenol A	0,70	0,64	0,59	0,65	0,66	0,65	0,038	5,9	< 0,1
nonylphenol	1,72	2,03	1,92	2,51	1,93	2,02	0,29	14,6	2,03
NP monoethoxylate	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	-	-	-	< 0,1
NP diethoxylate	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	-	-	-	< 0,1

Table 95: Recoveries of the internal standards in eluate A of water proofing sheets

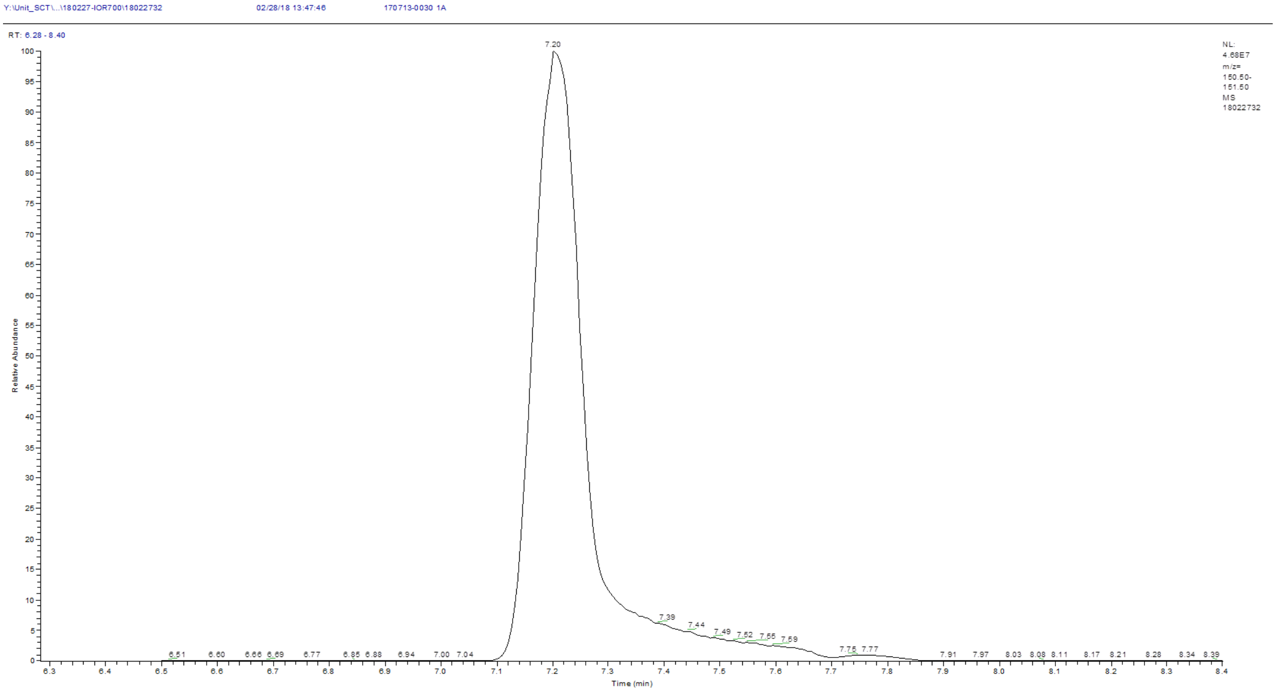
Replicate n°	**1** %	**2** %	**3** %	**4** %	**5** %
13C-phenol	13	9	16	13	23
13C-4-chlorophenol	71	66	74	82	85
13C-2,4-dichlorophenol	8	12	16	34	54
13C-2,4,5-trichlorophenol	54	59	63	62	75
13C-2,3,4,5-tetrachlorophenol	78	80	81	71	91
13C-pentachlorophenol	75	76	76	74	87
13C-octylphenol	68	64	71	63	75
D16-bisphenol A	122	138	128	148	131
13C-nonylphenol	43	43	46	40	46
13C-NP monoethoxylate	86	82	82	86	85
13C-NP diethoxylate	87	82	82	99	100

Table 96: Recoveries of the internal standards in eluate B of water proofing sheets

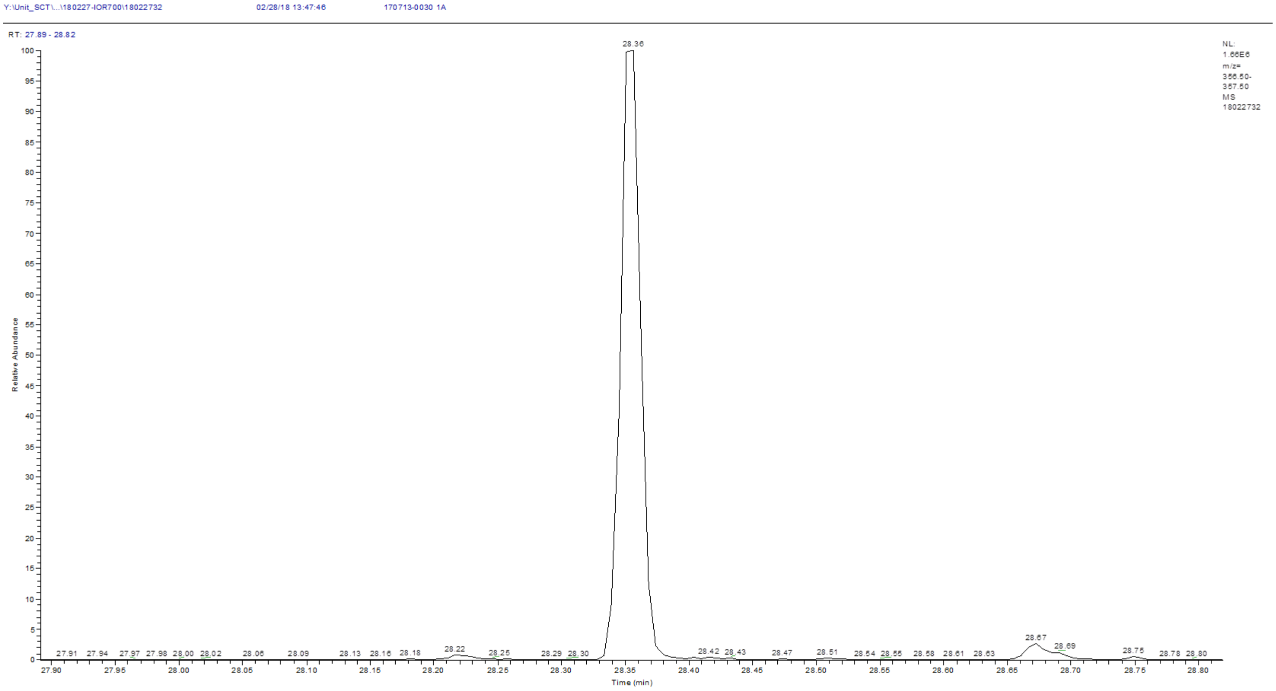
Replicate n°	**1** %	**2** %	**3** %	**4** %	**5** %
13C-phenol	22	9	12	7	14
13C-4-chlorophenol	89	63	70	67	74
13C-2,4-dichlorophenol	60	15	19	13	37
13C-2,4,5-trichlorophenol	71	54	66	61	64
13C-2,3,4,5-tetrachlorophenol	82	75	80	76	82
13C-pentachlorophenol	78	74	76	72	75
13C-octylphenol	81	62	72	66	71
D16-bisphenol A	134	128	127	118	113
13C-nonylphenol	51	41	47	40	44
13C-NP monoethoxylate	101	86	86	77	81
13C-NP diethoxylate	54	48	46	41	39

Figure 41: GC/MS ionchromatograms of phenols in eluate of water proofing sheets (PVC)

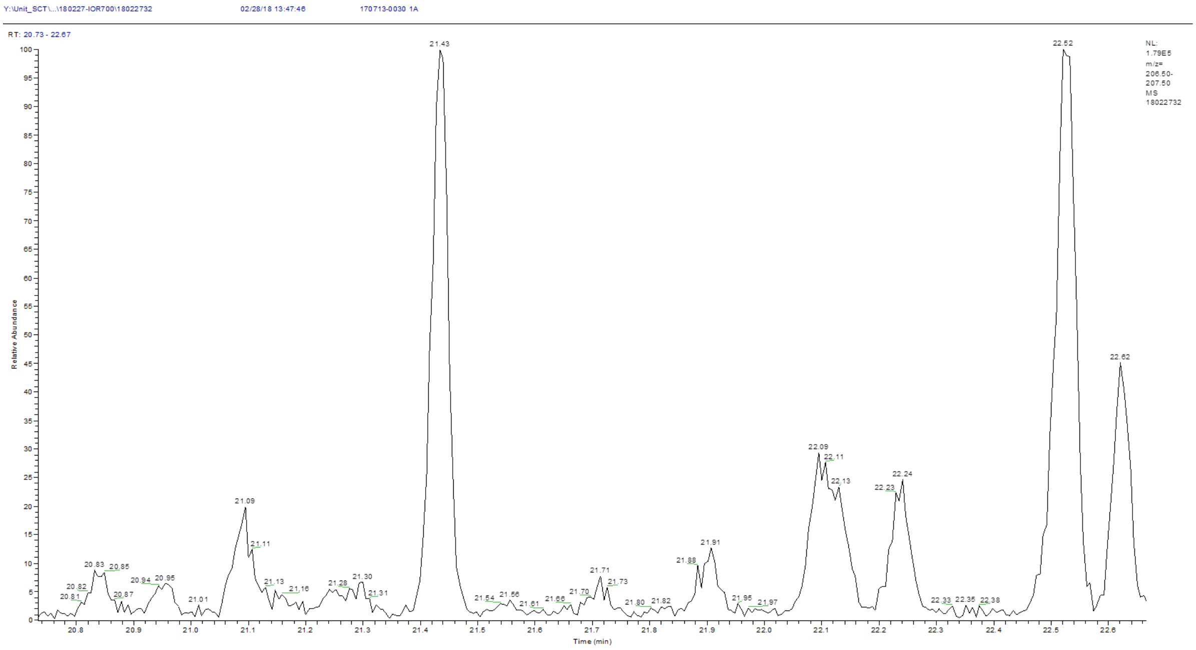
Phenol



bisphenol A



Nonylphenol



20.5. DETERMINATION OF NONYLPHENOL AND ITS ETHOXYLATES IN ELUATES OF RENDER 1 WITH METHOD EN ISO 18857-2

20.5.1. SAMPLE

Two eluates of render 1 were obtained from SGS Intron:

- 180092-1 F-1 22-1-18 (eluate A)
- 180092-1 F-3 24-1-18 (eluate B)

The eluates were prepared according to CEN/TS 16637-2 (T = 20°C, L/A = 80 L/m^2).
The samples were taken in dark glass bottles and were transferred to VITO in coolboxes and stored in a refrigerator.

20.5.2. ANALYSIS

See 19.4.2.

20.5.3. RESULTS

→ Repeatability

Both eluate samples were analysed in five fold. The results are given in Table 97 (eluate A) and Table 98 (eluate B). The ethoxylates were absent in the sample and no repeatability can be calculated. For nonylphenol the repeatability was very good (4.1% and 3.1% in eluate A and B respectively) but the concentration in the procedure blank is as high as in the sample. This means that the repeatability does not reflect the repeatability of the method (including extraction).

→ Check on method performance

The concentration of nonylphenol in the procedural blank was high. This is a known phenomenon when applying extraction with SPE, as the SPE cartiridges can contain nonylphenol.
The recoveries of the internal standards are given in Table 99 and Table 100. The recovery of the nonylphenol internal standard is low (+-50%) but acceptable. The recoveries of the ethoxylate internal standards are very good (90-110%).
For extraction control, a fortified eluate sample was analysed. Eluate B was spiked with native nonylphenol and NP-ethoxylates at a concentration level of 2.5 µg/l (35 µg/l for nonylphenol). The recoveries of the native phenols are summarized in Table 101. The recovery of nonylphenol is too high (154%), probably as a consequence of the lower internal standard recovery and the different behaviour of the nonylphenol isomers.

20.5.4. COMMENTS

Because of the high blank value for nonylphenol, no conclusions can be made with regard to the suitability of method EN ISO 18857-2 for this compound. For the NP-ethoxylates the method is suited.

20.5.5. CHROMATOGRAMS

GC/MS ion chromatograms of the phenols in eluate of Render 1 are shown in Figure 42.

20.6. CONCLUSION

Method EN ISO 18857-2 using SPE extraction and measurement with GC/MS is suited for the analysis of NP-ethoxylates. For nonylphenol no conclusion could be drawn because of the high blank value.

Table 97: Measured concentrations of phenols in eluates A of Render 1

Replicate n°	**1** µg/l	**2** µg/l	**3** µg/l	**4** µg/l	**5** µg/l	**Average** µg/l	**Standdev** µg/l	**CVr** %	**Proc.blank** µg/l
nonylphenol	2,76	2,60	2,79	2,73	2,91	2,76	0,11	4,1	2,76
NP monoethoxylate	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	-	-	-	< 0,1
NP diethoxylate	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	-	-	-	< 0,1

Table 98: Measured concentrations of phenols in eluates B of Render 1

Replicate n°	**1** µg/l	**2** µg/l	**3** µg/l	**4** µg/l	**5** µg/l	**Average** µg/l	**Standdev** µg/l	**CVr** %	**Proc.blank** µg/l
nonylphenol	2,48	2,62	2,49	2,54	2,66	2,56	0,08	3,1	2,76
NP monoethoxylate	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	-	-	-	< 0,1
NP diethoxylate	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	-	-	-	< 0,1

Table 99: Recoveries of the internal standards in eluate A of Render 1

Replicate n°	**1** %	**2** %	**3** %	**4** %	**5** %
13C-nonylphenol	54	53	50	54	48
13C-NP monoethoxylate	100	97	95	99	91
13C-NP diethoxylate	107	101	103	105	98

Table 100: Recoveries of the internal standards in eluate B of Render 1

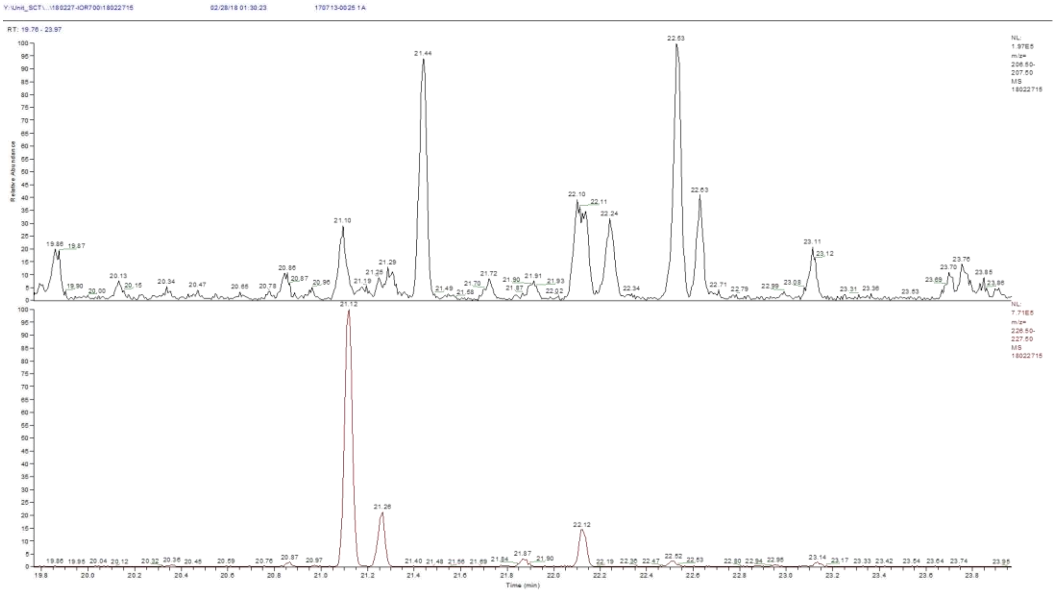
Replicate n°	**1** %	**2** %	**3** %	**4** %	**5** %
13C-nonylphenol	53	58	53	56	59
13C-NP monoethoxylate	92	105	93	98	99
13C-NP diethoxylate	97	108	105	104	102

Table 101: Recovery of native nonylphenols spiked in eluate of render 1

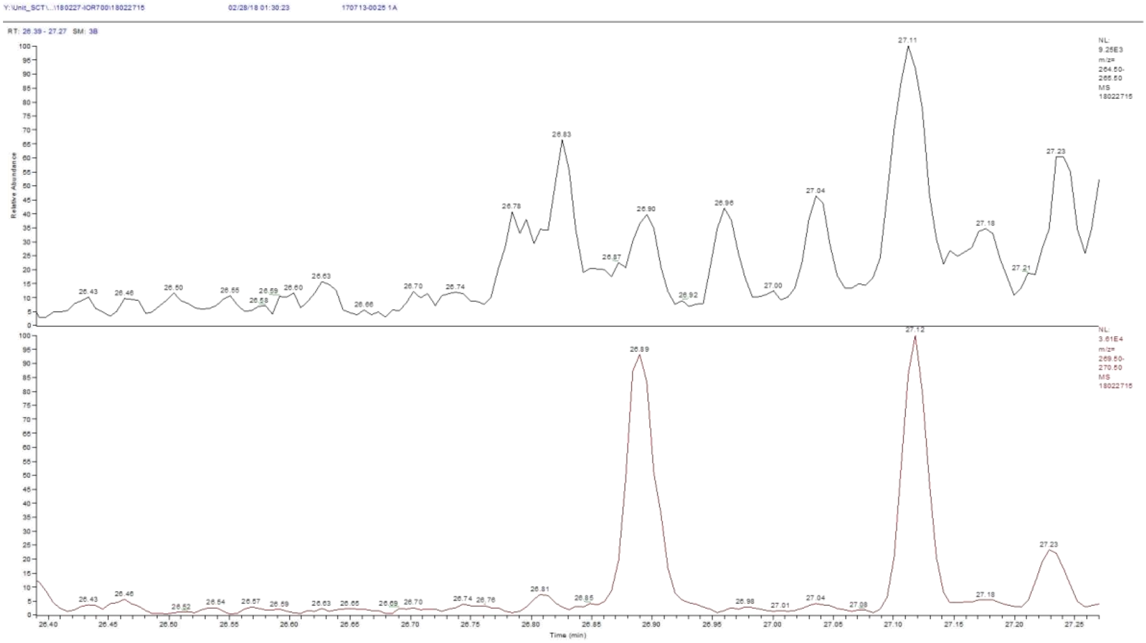
	Measured µg/l	**Spiked** µg/l	**Recovery** %
nonylphenol	52,2	34,0	154
NP monoethoxylate	2,5	2,5	98
NP diethoxylate	2,6	2,5	103

Figure 42: GC/MS ionchromatograms of nonylphenol and its ethoxylates in eluate A of render 1

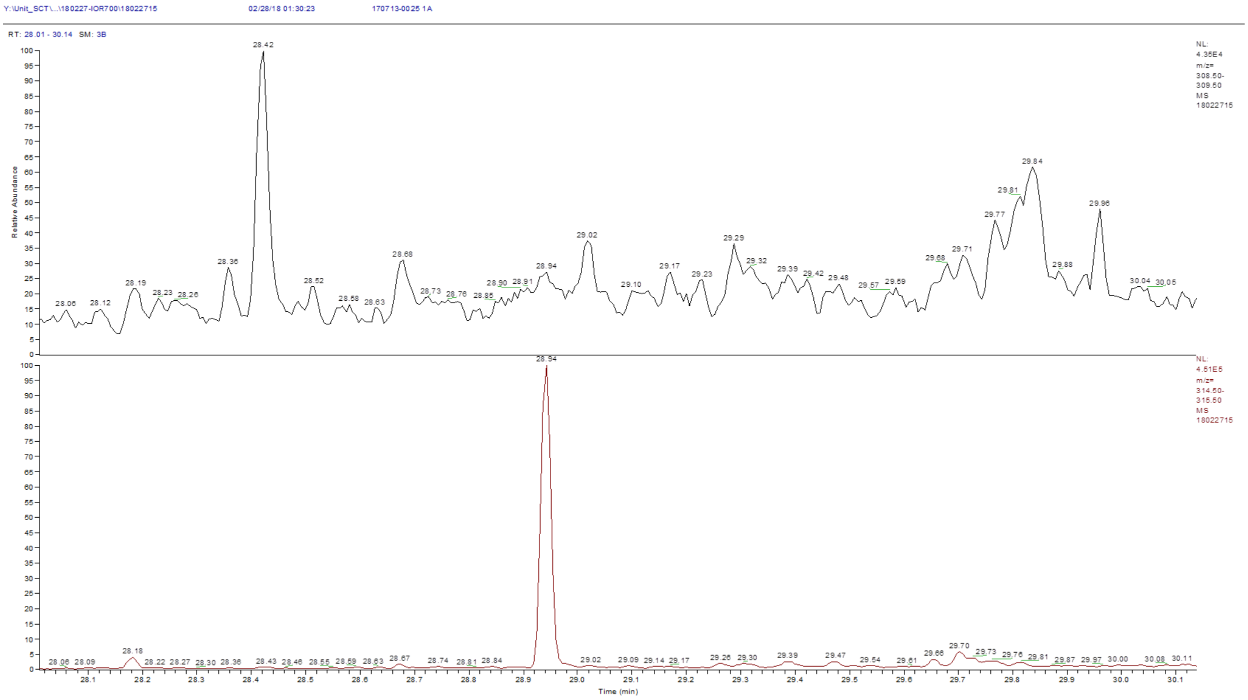
Nonylphenol and 13C-nonylphenol



NP-monoethoxylate and 13C-NP-monoethoxylate



NP-diethoxylate and 13C-NP-diethoxylate



CHAPTER 21 RECOMMENDATIONS FOR ADAPTATIONS OF STANDARDS

See next pages.

Date:	Document: **EN 14039 –** Characterization of waste – Determination of hydrocarbon contant in the range of C10 to C40 by gas chromatography	Project:

MB/NC[1]	Line number (e.g. 17)	Clause/ Subclause (e.g. 3.1)	Paragraph/ Figure/ Table/ (e.g. Table 1)	Type of comment[2]	Comments	Proposed change	Observations of the secretariat
		1	Scope		Standard describes a method for solid waste	The scope should be extended to construction products	
		10.4	Determination by gas chromatography		The recovery of the control sample was low, the correction for recovery of n-C40 as an internal standard is recommended	Add note: for the determination of mineral oil in construction materials, it is advised to apply n-C40 as an internal standard.	

Date:	Document: **FprCEN/TS 16181 –** Sludge, treated biowaste and soil – Determination of polycyclic aromatic hydrocarbons (PAH) by gas chromatography (GC) and high performance liquid chromatography (HPLC)	Project:

MB/NC[1]	**Line number** (e.g. 17)	**Clause/ Subclause** (e.g. 3.1)	**Paragraph/ Figure/ Table/** (e.g. Table 1)	**Type of comment**[2]	**Comments**	**Proposed change**	**Observations of the secretariat**
					Replace by NEN 7331 - Bitumen and bitumen containing materials – Determination of the content of polycyclic aromatic hydrocarbons (PAH) – Gas-chromatographic method with mass spectrometric detection		

Date:	Document: **NEN 7331 -** Bitumen and bitumen containing materials – determination of the content of polycyclic aromatic hydrocarbons (PAH) and of benzene, toluene, etrhylbenzene and xylene (BTEX) – gas-chromatogrphic method with mass spectrometric detection	Project:

MB/ NC[1]	**Line number** (e.g. 17)	**Clause/ Subclause** (e.g. 3.1)	**Paragraph/ Figure/ Table/** (e.g. Table 1)	**Type of comment**[2]	**Comments**	**Proposed change**	**Observations of the secretariat**
		1	Scope		Standard describes a method for bitumen, and bitumen containing materials	The scope should be extended to construction products	
		5.6	Surrogate standard		The use of more than 3 deuterated surrgogate standards for PAH will give more accurate results	Add: For construction materials it is advised to use more than 3 deuterated PAH as surrogate standards.	
		10.3	Calculation of PAH contents with correction for recovery		The correction for recovery will give more accurate results for the PAH	Add: For PAH in construction materials the correction for recovery must always be applied.	
		11	Recovery		For deuterated PAH in construction materials the recovery must be between 50% and 130%.	Add: For construction materials the recovery of the deuterated PAH surrogates must be between 50% and 130%.	

Date:	Document: **EN 16167** - Sludge, treated biowaste and soil - Determination of polychlorinated biphenyls (PCB) by gas chromatography with mass selective detection (GC-MS) and gas chromatography with electron-capture detection (GC-ECD)	Project:

MB/NC[1]	**Line number** (e.g. 17)	**Clause/ Subclause** (e.g. 3.1)	**Paragraph/ Figure/ Table/** (e.g. Table 1)	**Type of comment**[2]	**Comments**	**Proposed change**	**Observations of the secretariat**
		1	Scope		Standard describes a method for sludge, treated biowaste and soil.	The scope should be extended to construction materials	

Date:	Document: **EN ISO 22032 -** Water quality -- Determination of selected polybrominated diphenyl ethers in sediment and sewage sludge -- Method using extraction and gas chromatography/mass spectrometry	Project:

MB/NC[1]	**Line number** (e.g. 17)	**Clause/ Subclause** (e.g. 3.1)	**Paragraph/ Figure/ Table/** (e.g. Table 1)	**Type of comment**[2]	**Comments**	**Proposed change**	**Observations of the secretariat**
		1	Scope		Standard describes a method for sediment and sludge.	The scope should be extended to construction materials	
					The very low limits of application (non-deca-BDE 0.05-25 µg/kg, deca-BDE 0.3-100 µg/kg) are not relevant for construction products	For construction products increase the application range with a factor 1000.	

Date:	Document: **EN 16190** Soil, treated biowaste and sludge - Determination of dioxins and furans and dioxin-like polychlorinated biphenyls by gas chromatography with high resolution mass selective detection (HR GC-MS)	Project:

MB/NC[1]	Line number (e.g. 17)	Clause/ Subclause (e.g. 3.1)	Paragraph/ Figure/ Table/ (e.g. Table 1)	Type of comment[2]	Comments	Proposed change	Observations of the secretariat
		1	Scope		Standard describes a method for sludge, treated biowaste and soil.	The scope should be extended to construction materials	
		5	Principle			Idem	
		9.2	Extraction		The sample amount used for extraction (5-50 g) may be too large for construction materials with high organic content	Add note: “For construction materials with high organic content the intake should be reduced (e.g. to 1 g) to safeguard the chromatographic performance”. As a consequence higher limits of detection are applicable.	

Date:	Document: **CEN/TS 16183 -** Sludge, treated biowaste and soil - Determination of selected phthalates using capillary gas chromatography with mass spectrometric detection (GC-MS)	Project:

MB/NC[1]	Line number (e.g. 17)	Clause/ Subclause (e.g. 3.1)	Paragraph/ Figure/ Table/ (e.g. Table 1)	Type of comment[2]	Comments	Proposed change	Observations of the secretariat
		1	Scope	ge	Standard describes a method for sludge, treated biowaste and soil. As isomeric mixtures, e.g. DiNP, DiDP and mixed alkyl esters are frequently used we recommend to include these phthalates to the scope of the standard	The scope should be extended to construction materials and other phthalates.	
		8.3	Extraction	te	The extraction conditions appeared to be insufficiently adequate for quantitative extraction of phthalates out of polymeric materials.	For polymeric materials like PU, polyacrylate or silicone sealants longer extraction times, repeated extractions and/or the use of more appropriate solvents (e.g. THF) are recommended.	

Date:	Document: **CEN/TR 14823 –** Durability of wood and wood-based products – Quantitative determination of PCP in wood – Gas chromatographic method-	Project:

MB/NC[1]	Line number (e.g. 17)	Clause/ Subclause (e.g. 3.1)	Paragraph/ Figure/ Table/ (e.g. Table 1)	Type of comment[2]	Comments	Proposed change	Observations of the secretariat
		4	Principle	te	GC-MS should be included as detection technique	… analysed by gas chromatography with electron capture or mass selective detection	
		5.7	Reagents	te	^{13}C-PCP should be used as internal standard in case of GC-MS detection	2,4,6-tribromophenol (…) (GC-ECD) or ^{13}C-PCP (GC-MS) as internal standard	
		6.9	Apparatus	te	Add GC-MS	Gas chromatograph equipped with … electron capture (ECD) or mass selective detection (MS)	
		8	Procedure	te		Replace TBP by TBP or ^{13}C-PCP	
		8.3.2	Acetylation	te	Washing of the hexane layers with water prior to the drying step with sodium sulfate is recommended		
		8.4.3	Gas chromatographic conditions	te		Add mass spectrometric conditions and target ions	
		9	Calculation and expression of results	te		Replace TBP by TBP or ^{13}C-PCP	

Date:	**EN 15637** Foods of plant origin - Determination of pesticide residues using LC-MS/MS following methanol extraction and clean-up using diatomaceous earth	Project:

MB/NC[1]	**Line number** (e.g. 17)	**Clause/ Subclause** (e.g. 3.1)	**Paragraph/ Figure/ Table/** (e.g. Table 1)	**Type of comment[2]**	**Comments**	**Proposed change**	**Observations of the secretariat**
		1	Scope	ge	Standard describes a method for foods of plant origins	The scope of the standard should be extended to non-biological materials including construction products and eluates	
		several		ge	‘Residue’ and ‘maximum residue level (MRL)’ are typical terms for food and feed monitoring	Replace by ‘pesticide’ and ‘regulatory limit’ or …	
		2	Principle	ge	Make distinction between solid samples and eluates. Clean up will in most cases not be necessary.	Change to: ‘Solid samples are extracted … Clean up can be applied when necessary by partitioning into dichloromethane, followed by evaporation and reconstitution with methanol. Quantification … Eluates are injected directly into the LC-MS system.	
		3.7	Internal standards	te	Proposed internal standards are inappropriate	Replace by ‘Use as much as possible isotope labelled internal standards, if available and obtainable at reasonable price. The internal standard solution should be added at the extraction step and to standard solutions’.	
		3.10.2	Standard solutions with internal standard	te	Equation (1) simplifies in case no clean is applied	Add: ‘In case no clean up is applied equation(1) simplifies to $C^{sample}_{ISTD} = V_{ISTD}$ x C_{ISTD}/V_{ex}’	
		4.14	LC-MS/MS	ge	Depending on construction material, matrix		

			sytem		interferences, biocide and LOQ-requirement, it is possible that reliable results can be obtained using a less selective detection system, e.g LC-UV.		
		5.1	Preparation and storage of the samples	ge	Make distinction between solid and aqueous samples; sample preparation is typical for food samples	3.1.3 Solid samples: rewrite clauses 5.1.3, 5.1.4 and 5.1.5 (delete all text referring to food samples) 3.1.4 Eluates of solid samples: 'Make eluates according to CEN/TS 16637-2 and CEN/TS 16637-3; centrifuge the eluates, take a test portion, add internal standard and proceed to 5.4'	
		Table 2	Water content of selected foods	ge	Delete		
		6.2	Calculation of pesticide concentrations without standard addition	te	Equation (2) simplifies in case no clean up is applied and for eluates	Add: 'In case no clean up is applied equation(2) simplifies to: w_R = (A-c)/b .x V_{ex}/m_a' For eluates equation(2) becomes: w_R = (A-c)/b	
		6.3	Calculation of pesticide concentrations without standard addition	te	Idem		
		Annex A	Examples for appropriate experimental conditions	te	UHPLC example should be added. MS/MS systems are obsolete and no longer available on the market	Add UHPLC-conditions Replace MS/MS systems and conditions by recent ones	
		Annex B	Precision data	ge	Only applicable to food	Add non-food validation data	

Date:	Document: **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)	Project:

MB/NC[1]	**Line number** (e.g. 17)	**Clause/ Subclause** (e.g. 3.1)	**Paragraph/ Figure/ Table/** (e.g. Table 1)	**Type of comment[2]**	**Comments**	**Proposed change**	**Observations of the secretariat**
		1	Scope		Standard describes a method for sludge, treated biowaste and soil. The method will most probably also be applicable to chlorophenols but this should be confirmed by a validation study.	The scope should be extended to construction products	
		5.11	Internal standards		The use of branched labelled internal standards will give more accurate results	Add $^{13}C_{ring}$-4-(3,6-dimethyl-3-heptyl)phenol and corresponding mono- and diethoxylates to the internal standards list	
		7.2	Table 2			Add construction product (cfr soil)	
		8.1.4	Extraction of soil and treated biowaste			Add construction product Add remark for possible co-extraction of polymers when using acetone, which may lead to lower recoveries of nonylphenol and ethoxylates	
		8.4	Derivatisation			Add iso-octane as keeper to the hexane extract prior to evaporation and derivatisation	

Date:	Document: **EN ISO 9377-2 -** Water quality -- Determination of hydrocarbon oil index -- part 2: method using solvent extraction and gas chromatography	Project:

MB/ NC[1]	**Line number** (e.g. 17)	**Clause/ Subclause** (e.g. 3.1)	**Paragraph/ Figure/ Table/** (e.g. Table 1)	**Type of comment**[2]	**Comments**	**Proposed change**	**Observations of the secretariat**
		1	Scope		Standard describes a method for surface water, waste water and water from sewage treatment plants.	The scope should be extended to eluates of construction products	
		9.7	Calibration		The recovery of the control sample was low, the correction for recovery of n-C40 as an internal standard is recommended	Add note: for the determination of mineral oil in eluate of construction materials, it is advised to apply n-C40 as an internal standard.	

Date:	Document: **ISO 28540 -** Determination of 16 polycyclic aromatic hydrocarbons (PAH) in water - Method using gas chromatography with mass spectrometric detection	Project:

MB/ NC[1]	**Line number** (e.g. 17)	**Clause/ Subclause** (e.g. 3.1)	**Paragraph/ Figure/ Table/** (e.g. Table 1)	**Type of comment**[2]	**Comments**	**Proposed change**	**Observations of the secretariat**
		1	Scope		Standard describes a method for drinking water, ground water, surface water and waste water.	The scope should be extended to eluates of construction products	

Date:	Document: **EN 16694** - Water quality - Determination of selected polybrominated diphenly ether (PBDE) in whole water samples - Method using solid phase extraction (SPE) with SPE-disks combined with gas chromatography - mass spectrometry (GC-MS)	Project:

MB/NC[1]	**Line number** (e.g. 17)	**Clause/ Subclause** (e.g. 3.1)	**Paragraph/ Figure/ Table/** (e.g. Table 1)	**Type of comment**[2]	**Comments**	**Proposed change**	**Observations of the secretariat**
		1	Scope	ge	Standard describes a method for surface, drinking and groundwater	The scope should be extended to eluates of construction products	
					The lowest limit of application of the standard of 0.025 ng/L for each congener is in agreement with the LOQ requirement of the Water Framework Directive but not relevant for eluates of construction products	Add note with respect to the required LOQ for non-environmental water samples	
		8.4	Gas chromatography and mass spectrometry	te	The enrichment factor of 10000 is only applicable to surface, drinking and groundwater	… an enrichment factor of at least 10.000 is needed for the detection of BDE congeners at the required LOQ level for surface, drinking and groundwater; for eluates of construction products smaller intakes, higher internal standard concentrations and higher final volumes can be taken.	
		Annex B	Table B.1-B.3		Concentration units should be ng/L instead of µg/L	Replace µg/L by ng/L	

Date:	Document: **ISO 18856-** Water quality -- Determination of selected phthalates using gas chromatography/mass spectrometry	Project:

MB/NC[1]	**Line number** (e.g. 17)	**Clause/ Subclause** (e.g. 3.1)	**Paragraph/ Figure/ Table/** (e.g. Table 1)	**Type of comment[2]**	**Comments**	**Proposed change**	**Observations of the secretariat**
		1	Scope	ge	Standard describes a method for surface, drinking and groundwater	The scope should be extended to eluates of construction products	
		3	Principle/ Figure 1	te	Spiking of internal standard should be done preferably to the water sample and not to the elution solvent	Change Figure 1	
		3	Principle/ Figure 1	ge	Alternatively to SPE LLE with DCM should be allowed	Add LLE to Figure 1	
		8.2	Extraction	ge	We recommend to add LLE as alternative extraction method		

Date:	Document: **EN 12673** – Water quality – Gas chromatographic determination of some selected chlorophenols in water	Project:

MB/NC[1]	**Line number** (e.g. 17)	**Clause/ Subclause** (e.g. 3.1)	**Paragraph/ Figure/ Table/** (e.g. Table 1)	**Type of comment**[2]	**Comments**	**Proposed change**	**Observations of the secretariat**
		9.2.2	Acetylation of the sample	te	Washing of the hexane layer with water prior to the drying step with sodium sulfate is recommended		

Date:	Document: **ISO 11423-1** Water quality -- Determination of benzene and some derivatives -- Part 1: Head-space gas chromatographic method	Project:

MB/NC[1]	**Line number** (e.g. 17)	**Clause/ Subclause** (e.g. 3.1)	**Paragraph/ Figure/ Table/** (e.g. Table 1)	**Type of comment**[2]	**Comments**	**Proposed change**	**Observations of the secretariat**
					Replace by ISO 20595:2018 - Water quality -- Determination of selected highly volatile organic compounds in water -- Method using gas chromatography and mass spectrometry by static headspace technique (HS-GC-MS)		

Date:	Document: **EN ISO 14402 –** Water quality – Determination of phenol index by flow analysis	Project:

MB/NC[1]	**Line number** (e.g. 17)	**Clause/ Subclause** (e.g. 3.1)	**Paragraph/ Figure/ Table/** (e.g. Table 1)	**Type of comment**[2]	**Comments**	**Proposed change**	**Observations of the secretariat**
					N/A		

Date:	Document: **EN ISO 18857-2** Water quality -- Determination of selected alkylphenols -- part 2: gas chromatographic-mass spectrometric determination of alkylphenols, their ethoxylates and bisphenol a in non-filtered samples following solid-phase extraction and derivatisation	Project:

MB/ NC[1]	**Line number** (e.g. 17)	**Clause/ Subclause** (e.g. 3.1)	**Paragraph/ Figure/ Table/** (e.g. Table 1)	**Type of comment**[2]	**Comments**	**Proposed change**	**Observations of the secretariat**
					From the data no conclusion can be drawn about the suitability of the method for the analysis of phenols in eluates of construction materials The scope of the method should be extended to other (chloro)phenols Optimisation of the SPE extraction should be carried for recovery improvement		

Date:	Document: **EN ISO 15680** Water quality -- Gas-chromatographic determination of a number of monocyclic aromatic hydrocarbons, naphthalene and several chlorinated compounds using purge-and-trap and thermal desorption	Project:

MB/ NC[1]	**Line number** (e.g. 17)	**Clause/ Subclause** (e.g. 3.1)	**Paragraph/ Figure/ Table/** (e.g. Table 1)	**Type of comment**[2]	**Comments**	**Proposed change**	**Observations of the secretariat**
					Replace by ISO 20595:2018 - Water quality -- Determination of selected highly volatile organic compounds in water -- Method using gas chromatography and mass spectrometry by static headspace technique (HS-GC-MS))		

CHAPTER 22 GENERAL CONCLUSION

In Table 102 an overview is given of the performances of the methods which were evaluated for the determination of the content of organic substances in **construction products**. On the basis of the performance characteristics, taking the repeatabilities, LOD values and current regulatory limits in Europe as criteria, it can be concluded that for the quantitative determination of the following parameters an appropriate EN or ISO standard is in place:

- **PAH**
- **PCB**
- **PCP**
- **Hydrocarbons C10-C40**
- **PBDE**
- **BTEX**
- **PCDD/F** and **dl-PCB**

For PAH we recommend the use of NEN 7331. Within CEN/TC 351/WG 5 a new work item should be defined for the conversion of NEN 7331 to a EN standard.
For PCP GC-MS should be added to CEN/TR 14823 as alternative detection technique.

For the following parameters a method optimisation will be needed to counter issues of insufficient extraction yields in case of polymeric materials.

- **Phtalates**:
  Longer extraction times and/or repeated extractions and/or the use of other solvents (e.g. DCM or THF followed by polymer precipitation in hexane) can be evaluated in an additional robustness study
- **Nonylphenol and ethoxylates**:
  The use of a keeper (e.g. iso-octane) in the evaporation step prior to the derivatization should be checked in a first place for the improvement of the recovery; a validation study may be carried out for extension of the scope of the method to other phenols (chlorophenols) if desired.

For the determination of **biocides** the proposed analytical technique of the food standard is appropriate, but a specific and more detailed standard should be drafted for construction materials. A new work item can be defined to that prupose within CEN/TC 351/WG 5.

For **organotin** no test results are available due to absence of a suitable construction product.

In chapter 21 some changes/improvements have been proposed to the tested standards.

In Table 103 an overview is given of the performances of the methods which were evaluated for the determination of the concentration of organic substances in **eluates of construction products**. On the basis of the performance characteristics, taking the repeatabilities, LOD values and water quality criteria as basis, it can be concluded that for the quantitative determination of the following parameters an appropriate EN or ISO standard is in place:

- **PCDD/F** and **dl-PCB**
- **Hydrocarbons C10-C40**
- **BTEX**
- **Phenol index**
- **PAH**
- **PCP**

With regard to the determination of BTEX we recommend to refer to the new ISO 20595:2018 standard.

For the determination of **biocides** the proposed analytical technique of the food standard is appropriate, but a specific and more detailed standard should be drafted for water or eluates of construction materials. DIN 38407-36 could serve as base document.

For the following parameters a method optimization, with respect to extraction, is needed:

- **Phthalates:**
  Improvement of precision and bias can be realized by addition of the internal standard to the eluate sample and not to the SPE elution solvent; liquid-liquid extraction will lead to lower blank values
- **Nonylphenol, nonylphenol ethoxylates and other phenols:**
  Optimisation of the solid phase extraction and desorption steps with respect to recovery improvement of polar and non-polar phenols; a validation study may be carried out for extension of the scope of the method to other phenols

For **PBDE** no test results are available due to insufficient sample volume. It is however expected that EN 16694 will be fit for purpose.

For **organotin** no test results are available due to absence of a suitable construction product.

In chapter 21 some changes/improvements have been proposed to the tested standards.

In table and a final overview is given of all organic substances studied, the appropriate analytical standards, proposed adaptations (for inclusion in the umbrella standards) and if needed additional validation actions to be undertaken.

Table 102: Summary of method performances for the determination of the content of organic substances in construction products

Parameter / Substance group	Method (Number and short title)	Sample preparation	Method type	LOD of standard mg/kg	Construction products tested	Method applied	CV_r	LOD mg/kg	Comment	Suitabilityt
PAH	NEN 7331 (PAH in bitumen)	Cryogenic size reduction	GC-MS	0,5 - 1,5	Asphalt aggregate Roofing felt Rubber crumbs	Soxhlet with PE, transfer to ACN GC-MS	<15%	<0,5		Suitable Preferred method
	prEN 16181 (PAH in sludge, etc. – Horizontal)	Possibly: Drying Extraction with Solvent and Agitation or Soxhlet, PLE	GC-MS and HPLC	0,01	Asphalt aggregate Recycled mixed aggregates	Shaking with acetone-hexane GC-MS	<15% (except most volatile PAH)	<0,01		Suitable
PCB	EN 16167 (PCB in sludge, etc. – Horizontal)	SLE and agitation; Soxhlet; PLE	GC-MS; GC-ECD	0,001	Recycled mixed aggregates	PLE with acetone/hexane, multilayer silica, DMSO partitioning GC-MS	<15%	<0,001		Suitable
BTEX	EN ISO 16558-1 (Hydrocarbons in soil)	SLE, Headspace	GC-MS	0,1					Not in scope of project	
	NEN 7331 (BTEX in bitumen)	Cryogenic size reduction	P&T-GC-MS	0,1	Asphalt aggregate	Sonication with methanol	-	<0,1	All BTEX < LOQ Recovery	Expected to be suitable

						HS-GC-MS			and RSD internal standard OK	
Phenols	ISO 14154 (Chlorophenols in soil)	SLE,acetylation, LLE	GC-ECD	0,01 – 0,05	Water proofing sheets (PVC)				Replaced by CEN/TS 16182 (see below)	
Pentachlorophenol	CEN/TR 14823 (PCP in wood)	SLE, derivatisation	GC-ECD	0,1	Wood	Sonication with methanol, acetylation, LLE with hexane, GC-MS	<5%	<0,1	Add GC-MS to the standard	Suitable
Mineral Oil **(C10 – C40)**	EN 14039 (Hydrocarbons in waste)	SLE	GC-FID	100	Asphalt aggregate Recycled mixed aggregates	PLE acetone/hexane, florisil clean up, GC-FID	<11%	<25	IS method recommended	Suitable
Dioxins and Furanes	CEN/TS 16190 (Dioxin, Furanes and dioxin-like PCBs in Sludge, etc. - Horizontal)	Soxhlet, isotope dilution	GC-HRMS	10-6	Rubber crumbs	cfr CEN/TS 16190	PCDD/F: 4-25% dl-PCB: 18-27%	PCDD/F: <2 dl-PCBs: <7		Suitable

Phthalates	FprCEN/TS 16183 (Phthalates in sludge, etc. – Horizontal)	SLE	GC-MS	0,1 – 0,5	PUR and polyacrylate sealants	Shaking with ethylacetate GC-MS	<15% (except DMP)	<0,1	Recoveries not quantitative Interference by DiNP	Suited but method optimisation needed for sealants
PBDE	EN ISO 22032 (Water quality, sediment and sludge)	SLE Soxhlet	GC-MS EI or NCI mode	5 × 10-5 - 3 × 10-4	Polyethylene	Soxhlet with toluene	<8%	Achievable with concentration factor of 100	Relevance of required low LOQ	Suitable
Organotin: Tributyltin	ISO 23161 (Organotin in soil)	SLE, derivatization	GC-AED, GC-MS, GC-FPD, GC-AAS, GC ICP-MS	0,01					No sample available	
Nonylphenol/ Nonylphenol ethoxylate	CEN/TS 16182 (NP in sludge etc. – Horizontal)	SLE, derivatisation	GC-MS	0,02 – 0,1	Render Water proofing sheets (PVC)	Shaking with acetone and hexane, removal of acetone, derivatization with MSTFA, GC-MS	Render: CVr < 16% PVC: CVr too high	<0,01-0,1	PVC: insufficient recovery of IS	Suitable for render Not suitable for PVC

Biocides	EN 15637 (Pesticides in food)	Stirring with methanol	LC-MS/MS	not specified	Polyacrylate sealant	Sonication with methanol, LC-MS/MS	Sealant and wood: <8% Render: 9-19%	<0,01		Analytical technique is suitable, standard for construction products should be drafted

Table 103: Summary of method performances for the determination of the concentration of organic substances in eluates of construction products

Parameter / Substance group	Method (Number and short title)	Method type	LOD of standard µg/L	Construction products tested	Method applied	CV$_r$	LOD µg/L	Comment	Suitability
PAH	ISO 28540 (PAH in water)	LLE GC-MS	0,01	Asphalt aggregate Recycled mixed aggregates Rubber crumbs	LLE with hexane, GC-MS	11-23% (except low MW PAH) >> 15% low MW PAH: <8%; other <LOD	<0,01 µg/L	Higher CV$_r$ caused by low concentrations and differences in sample composition	Suitable
PCB	EN ISO 6468 (Organochlorines in water)	LLE GC-FID	$10^{-3} – 10^{-4}$					Not in scope of project	
Dioxins and dioxinlike PCBs	ISO 17858 (Dioxin-like PCB in water) ISO 18073 (Dioxins in water)	GC-HRMS	10^{-5}	Rubber crumbs Recycled mixed aggregates	LLE with toluene GC-HRMS	all congeners <LOQ		Recoveries and CV$_r$ of IS are acceptable	Suitability expected
Hydrocarbons (C10– C40)	EN ISO 9377-2 (Oil Index in water)	GC-MS	100	Recycled mixed aggregates	LLE with hexane, florisil clean up, GC-FID, internal standard method	<LOQ	<100 ug/L	Recovery IS = 100%, CVr IS = 5%	Suitable

Alkylated Benzenes (BTEX)	ISO 11423-1 (BTEX in water)	GC with FID, MS or PID	0,2		HS-GC-MS	<LOQ	<0,1-0,2	Recovery IS = 100%, CVr IS <5%	Suitable, but replace by ISO 20595:2018
	EN ISO 15680 (BTEX and chlorinated compounds in water)	Purge and Trap GC-MS	0,01					Not tested	
Nonylphenoles: 4-NP and isomers	EN ISO 18857-2 (Alkylphenoles in water)	SPE GC-MS	0,005 – 0,2	Render Waterproofing sheets (PVC)	SPE Derivatisation with MSTFA GC-MS	Render: NP<15%, NPEOs < LOQ PVC: Phenol, NP, BPA <15% other <LOQ	<0,01-0,1	NP high blank contribution	No conclusion, method optimization needed
PCP	EN 12673	Acetylation LLE GC-MS; GC-ECD	0,1	Wood	Acetylation, LLE with hexane, GC-MS	<6%	<0,1		Suitable
Phenol index	EN ISO 14402	Flow analysis	10	Water proofing sheet (PVC)	Steam distillation, colorimetry	11%	<1		Suitable
Organotin Compounds	EN ISO 17353 (Organotin in water)	Derivatisation LLE GC-MS; GC-FPD; GC-AED	0,01					No sample available	
Phthalates	EN ISO 18856 (Phthalates in water)	SPE GC-MS	0,02 – 0,15	Sealant	SPE (DCM) GC-MS	6-34%	<0,02	Interference by DiNP Contaminated eluates?	No conclusion Method optimization needed

PBDE	EN 16694 (PBDE in water)	SPE GC-MS	5×10^{-4}				Not tested, insufficient sample volume		
Biocides	EN 15637 (Pesticides in food)	LC-MS/MS	Not specified	Treated wood Sealant Render	Direct injection LC-MS/MS	Wood: <4% Sealant: 5-24% Render: 7-17%	<0,1		Analytical technique is suitable, water standard should be drafted

Table 104: Summary of methods for the determination of the content of organic substances in construction products and proposed improvement actions

Parameter / Substance group	**Method (Number and short title)**	**Method type**	**Comment, proposed adaptation or additional validation action**
PAH: Anthracen, Benzo(a)pyren, Dibenz(a,h)anthracen, Benzo(b)fluoranthen, Benzo(k)fluoranthen, Benz(g,h,i)perylen, Indeno(1,2,3-cd)pyren, Fluoranthen, Naphthaline, Acenaphten, Acenaphtylen, Phenanthren, Benzo(a)anthracen, Fluoren, Pyren, Chrysen	NEN 7331 (PAH in bitumen) (preferred method)	GC-MS	Recommended method
	prEN 16181 (PAH in sludge, etc. – Horizontal)	GC-MS and HPLC	Replace by NEN 7331
PCB PCB-28, PCB-52, PCB-101, PCB-118, PCB-138, PCB-153, PCB-180	EN 16167 (PCB in sludge, etc. – Horizontal)	GC-MS, GC-ECD	
BTEX	EN ISO 16558-1 (Hydrocarbons in soil)	GC-MS	
	NEN 7331 (BTEX in bitumen)	GC-MS	

Phenols	ISO 14154 (Chlorophenols in soil)	GC-ECD	Not tested We recommend to validate CEN/TS 16182 for chlorophenols
Pentachlorophenol (PCP)	CEN/TR 14823 (PCP in wood)	GC-ECD, GC-MS	The use of GC-MS using ^{13}C-PCP as internal standard is recommended; mass spectrometric conditions and target ion have to be added
Mineral Oil (C10 – C40)	EN 14039 (Hydrocarbons in waste)	GC-FID	
Dioxins and Furanes	CEN/TS 16190 (Dioxin, Furanes and dioxin-like PCBs in Sludge, etc. -Horizontal)	HRGC-MS	For construction materials with high organic content the intake should be reduced (e.g. to 1 g) to safeguard the chromatographic performance (9.2 Extraction). As a consequence higher limits of detection are applicable.
Phthalates	FprCEN/TS 16183 (Phthalates in sludge, etc. – Horizontal)	GC-MS	A validation study should be carried for improvement of the recoveries in case of polymeric materials like PU, polyacrylate or silicone sealants, using longer extraction times, repeated extractions and/or more appropriate solvents (e.g. THF)
PBDE	EN ISO 22032 (water quality, sediment and sludge)	GC-MS EI or NCI mode	Check relevance of LOQ requirement (very low LOQ values)
Organotin: Tributyltin	ISO 23161 (Organotin in soil)	GC-AED, GC-MS, GC-FPD, GC-AAS, GC ICP-MS	Not tested
Nonylphenol/ Nonylphenol ethoxylate	CEN/TS 16182 (NP in sludge etc. –	GC-MS	Use a keeper (e.g. iso-octane) in the evaporation step prior to the derivatization (8.4 Derivatisation)

	Horizontal)		We recommend to carry out a validation study for the extension of the scope of the method to other phenols (chlorophenols)
Biocides	EN 15637 (Pesticides in food)	LC-MS/MS	Standard for construction products should be drafted

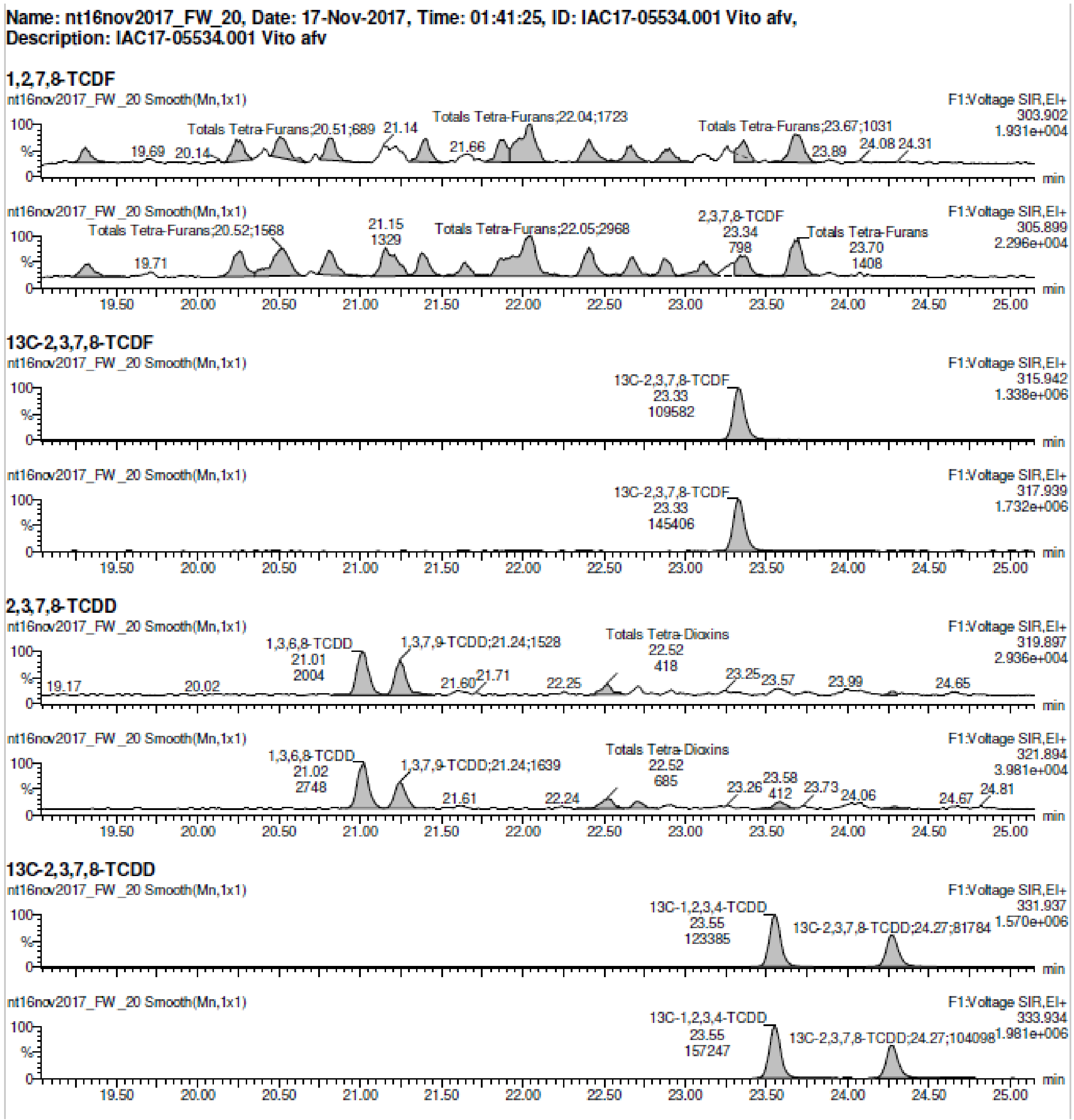
Table 105: Summary of methods for the determination of the concentration of organic substances in eluates of construction products and proposed improvement actions

Parameter / Substance group	**Method (Number and short title)**	**Method type**	**Comment, proposed adaptation or additional validation action**
PAH Anthracen, Benzo(a)pyren, Dibenz(a,h)anthracen, Benzo(b)fluoranthen, Benzo(k)fluoranthen, Benz(g,h,i)perylen, Indeno(1,2,3-cd)pyren, Fluoranthen, Naphthaline, Acenaphten, Acenaphtylen, Phenanthren, Benzo(a)anthracen, Fluoren, Pyren, Chrysen	ISO 28540 (PAH in water)	LLE GC-MS	

Dioxins and dioxinlike PCBs	ISO 17858 (Dioxin-like PCB in water) ISO 18073 (Dioxins in water)	GC-HRMS	
Hydrocarbons (C10– C40)	EN ISO 9377-2 (Oil Index in water)	GC-MS	
Alkylated Benzenes (BTEX)	ISO 11423-1 (BTEX in water)	GC with FID, MS or PID	Replace by ISO 20595:2018 - Water quality -- Determination of selected highly volatile organic compounds in water -- Method using gas chromatography and mass spectrometry by static headspace technique (HS-GC-MS)
	EN ISO 15680 (BTEX and chlorinated compounds in water)	Purge and Trap GC-MS	Idem
Nonylphenols: 4-NP and isomers	EN ISO 18857-2 (Alkylphenoles in water)	SPE GC-MS	An optimisation study should be carried out of the solid phase extraction and desorption steps with respect to recovery improvement; a validation study can be conducted to extend the scope of the method to other phenols (chlorophenols)
PCP	EN 12673	Acetylation LLE GC-MS; GC-ECD	
Phenol index	EN ISO 14402	Flow analysis	

Organotin Compounds	EN ISO 17353 (Organotin in water)	Derivatisation LLE GC-MS; GC- FPD; GC-AED	Not tested
Phthalates	EN ISO 18856 (Phthalates in water)	SPE GC-MS	Alternatively to SPE liquid-liquid extraction should be included in the standard (8.2 Extraction); internal standards should be added to the eluate and not to the SPE eluation solvent
PBDE	EN 16694 (PBDE in water)	SPE GC-MS	
Biocides	EN 15637 (Pesticides in food)	LC-MS/MS	A water standard or a standard for eluates of construction products should be drafted

ANNEX A – ION CHROMATOGRAMS FOR PCDD/F AND DL-PCB IN RUBBER CRUMBS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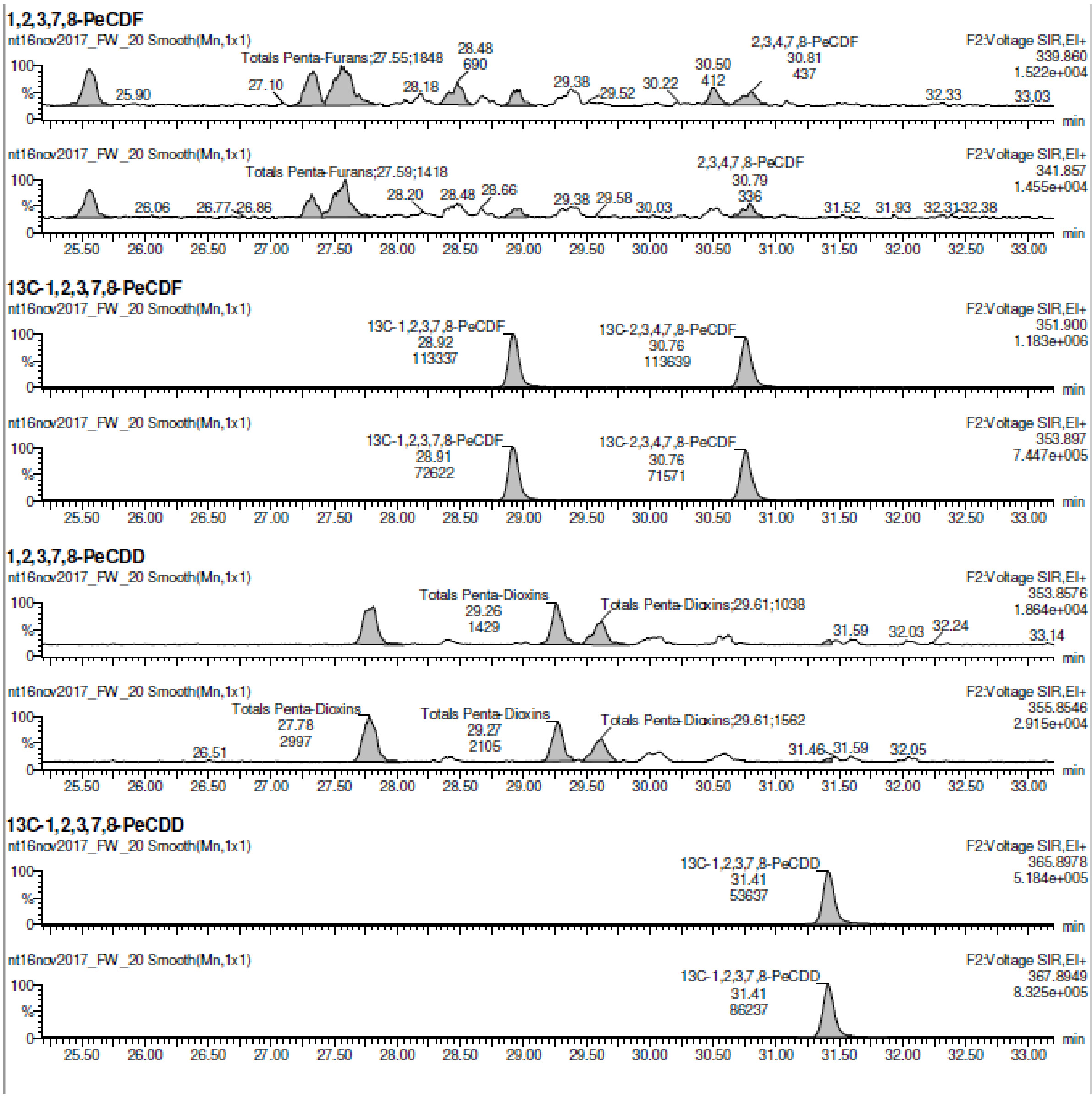
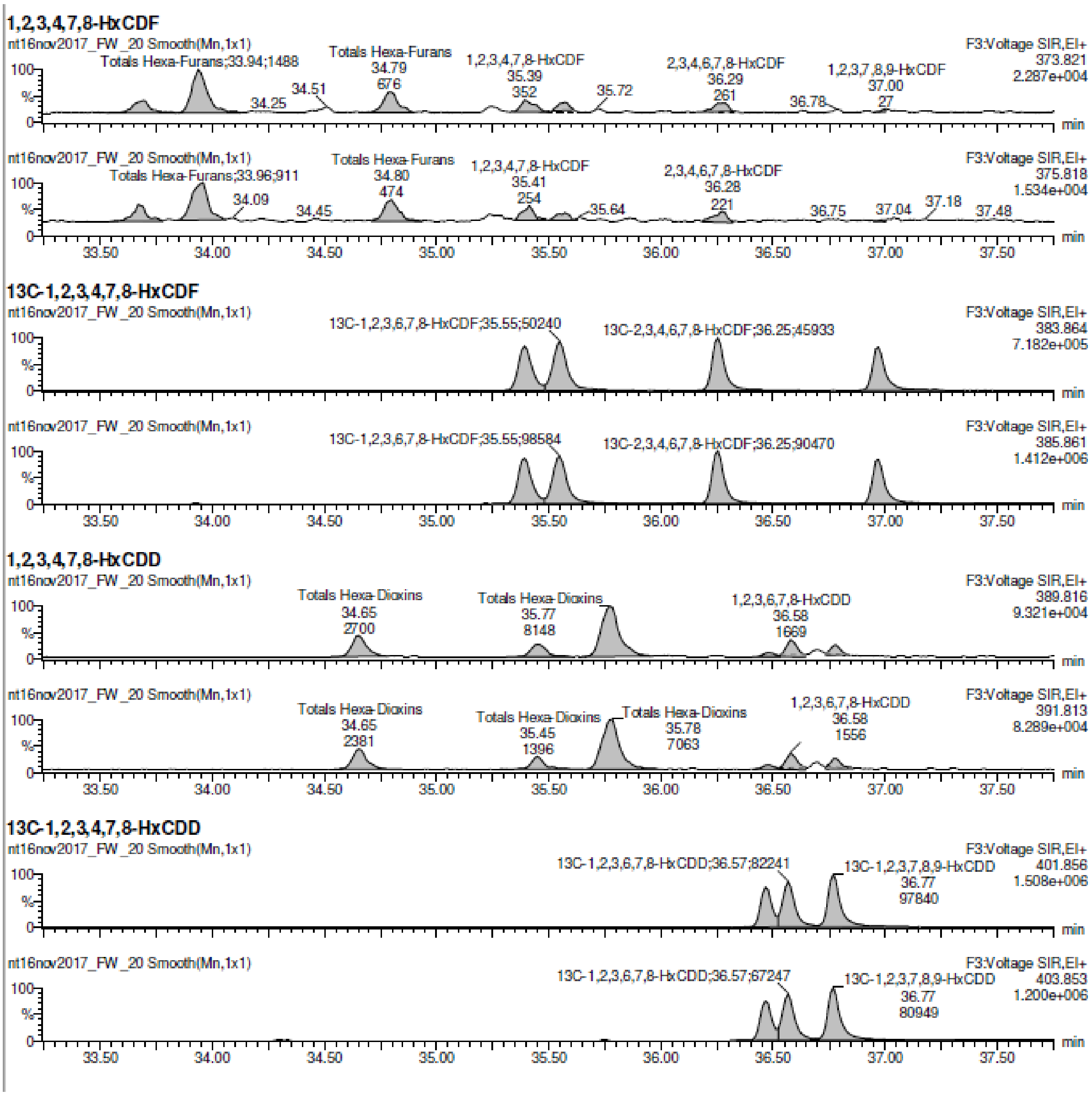
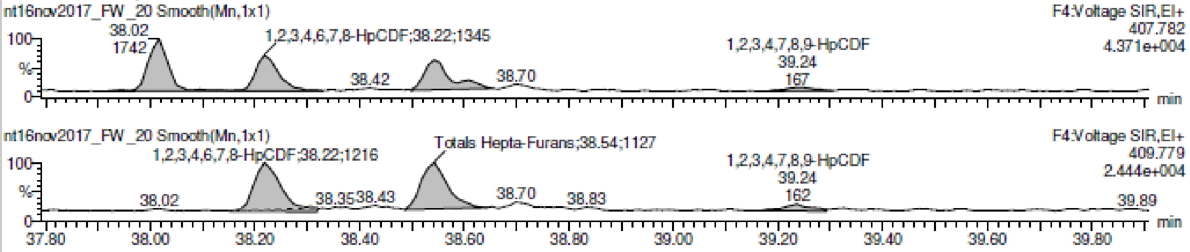
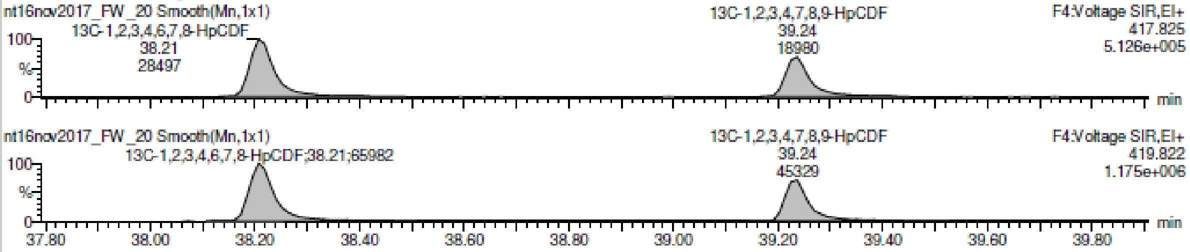

1,2,3,7,8-PeCDF
nt16nov2017_FW_20 Smooth(Mn,1x1)
F2:Voltage SIR,EI+
339.860
1.522e+004
Totals Penta-Furans;27.55;1848
28.48
690
2,3,4,7,8-PeCDF
30.81
437
25.90
27.10
28.18
29.38
29.52
30.22
30.50
412
32.33
33.03
nt16nov2017_FW_20 Smooth(Mn,1x1)
F2:Voltage SIR,EI+
341.857
1.455e+004
Totals Penta-Furans;27.59;1418
2,3,4,7,8-PeCDF
30.79
336
26.06
26.77
26.86
28.20
28.48
28.66
29.38
29.58
30.03
31.52
31.93
32.31
32.38
13C-1,2,3,7,8-PeCDF
nt16nov2017_FW_20 Smooth(Mn,1x1)
F2:Voltage SIR,EI+
351.900
1.183e+006
13C-1,2,3,7,8-PeCDF
28.92
113337
13C-2,3,4,7,8-PeCDF
30.76
113639
nt16nov2017_FW_20 Smooth(Mn,1x1)
F2:Voltage SIR,EI+
353.897
7.447e+005
13C-1,2,3,7,8-PeCDF
28.91
72622
13C-2,3,4,7,8-PeCDF
30.76
71571
1,2,3,7,8-PeCDD
nt16nov2017_FW_20 Smooth(Mn,1x1)
F2:Voltage SIR,EI+
353.8576
1.864e+004
Totals Penta-Dioxins
29.26
1429
Totals Penta-Dioxins;29.61;1038
31.59
32.03
32.24
33.14
nt16nov2017_FW_20 Smooth(Mn,1x1)
F2:Voltage SIR,EI+
355.8546
2.915e+004
Totals Penta-Dioxins
27.78
2997
Totals Penta-Dioxins
29.27
2105
Totals Penta-Dioxins;29.61;1562
26.51
31.46
31.59
32.05
13C-1,2,3,7,8-PeCDD
nt16nov2017_FW_20 Smooth(Mn,1x1)
F2:Voltage SIR,EI+
365.8978
5.184e+005
13C-1,2,3,7,8-PeCDD
31.41
53637
nt16nov2017_FW_20 Smooth(Mn,1x1)
F2:Voltage SIR,EI+
367.8949
8.325e+005
13C-1,2,3,7,8-PeCDD
31.41
86237
100
%
0
min
25.50
26.00
26.50
27.00
27.50
28.00
28.50
29.00
29.50
30.00
30.50
31.00
31.50
32.00
32.50
33.00


1,2,3,4,7,8-HxCDF
nt16nov2017_FW_20 Smooth(Mn,1x1)
Totals Hexa-Furans;33.94;1488
34.25
34.51
Totals Hexa-Furans
34.79
676
1,2,3,4,7,8-HxCDF
35.39
352
35.72
2,3,4,6,7,8-HxCDF
36.29
261
36.78
1,2,3,7,8,9-HxCDF
37.00
27
F3:Voltage SIR,EI+
373.821
2.287e+004
100
%
0
min
nt16nov2017_FW_20 Smooth(Mn,1x1)
Totals Hexa-Furans;33.96;911
34.09
34.45
Totals Hexa-Furans
34.80
474
1,2,3,4,7,8-HxCDF
35.41
254
35.64
2,3,4,6,7,8-HxCDF
36.28
221
36.75
37.04
37.18
37.48
F3:Voltage SIR,EI+
375.818
1.534e+004
100
%
0
min
33.50
34.00
34.50
35.00
35.50
36.00
36.50
37.00
37.50
13C-1,2,3,4,7,8-HxCDF
nt16nov2017_FW_20 Smooth(Mn,1x1)
13C-1,2,3,6,7,8-HxCDF;35.55;50240
13C-2,3,4,6,7,8-HxCDF;36.25;45933
F3:Voltage SIR,EI+
383.864
7.182e+005
100
%
0
min
nt16nov2017_FW_20 Smooth(Mn,1x1)
13C-1,2,3,6,7,8-HxCDF;35.55;98584
13C-2,3,4,6,7,8-HxCDF;36.25;90470
F3:Voltage SIR,EI+
385.861
1.412e+006
100
%
0
min
33.50
34.00
34.50
35.00
35.50
36.00
36.50
37.00
37.50
1,2,3,4,7,8-HxCDD
nt16nov2017_FW_20 Smooth(Mn,1x1)
Totals Hexa-Dioxins
34.65
2700
Totals Hexa-Dioxins
35.77
8148
1,2,3,6,7,8-HxCDD
36.58
1669
F3:Voltage SIR,EI+
389.816
9.321e+004
100
%
0
min
nt16nov2017_FW_20 Smooth(Mn,1x1)
Totals Hexa-Dioxins
34.65
2381
Totals Hexa-Dioxins
35.45
1396
Totals Hexa-Dioxins
35.78
7063
1,2,3,6,7,8-HxCDD
36.58
1556
F3:Voltage SIR,EI+
391.813
8.289e+004
100
%
0
min
33.50
34.00
34.50
35.00
35.50
36.00
36.50
37.00
37.50
13C-1,2,3,4,7,8-HxCDD
nt16nov2017_FW_20 Smooth(Mn,1x1)
13C-1,2,3,6,7,8-HxCDD;36.57;82241
13C-1,2,3,7,8,9-HxCDD
36.77
97840
F3:Voltage SIR,EI+
401.856
1.508e+006
100
%
0
min
nt16nov2017_FW_20 Smooth(Mn,1x1)
13C-1,2,3,6,7,8-HxCDD;36.57;67247
13C-1,2,3,7,8,9-HxCDD
36.77
80949
F3:Voltage SIR,EI+
403.853
1.200e+006
100
%
0
min
33.50
34.00
34.50
35.00
35.50
36.00
36.50
37.00
37.50

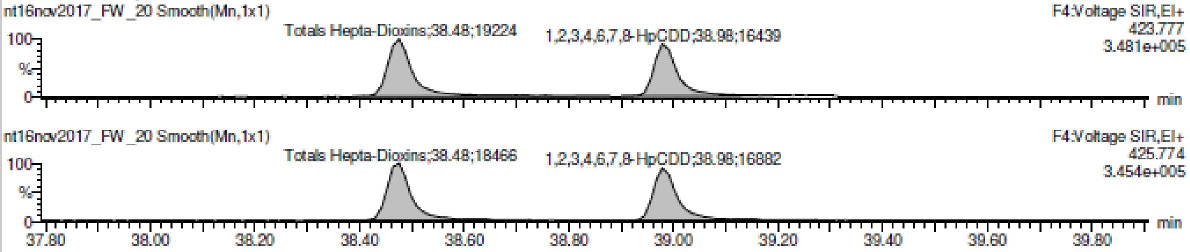
1,2,3,4,6,7,8-HpCDF



13C-1,2,3,4,6,7,8-HpCDF



1,2,3,4,6,7,8-HpCDD



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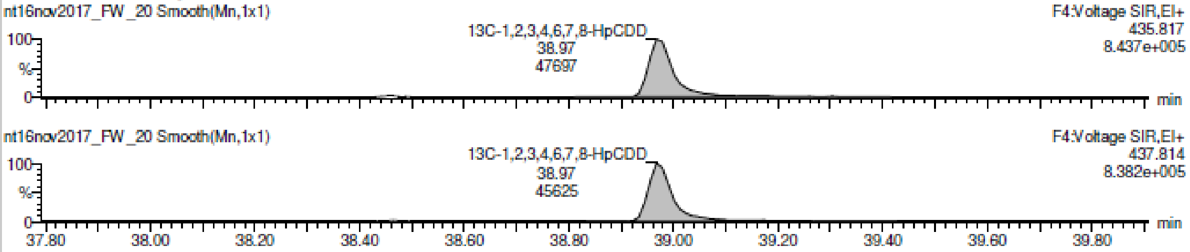
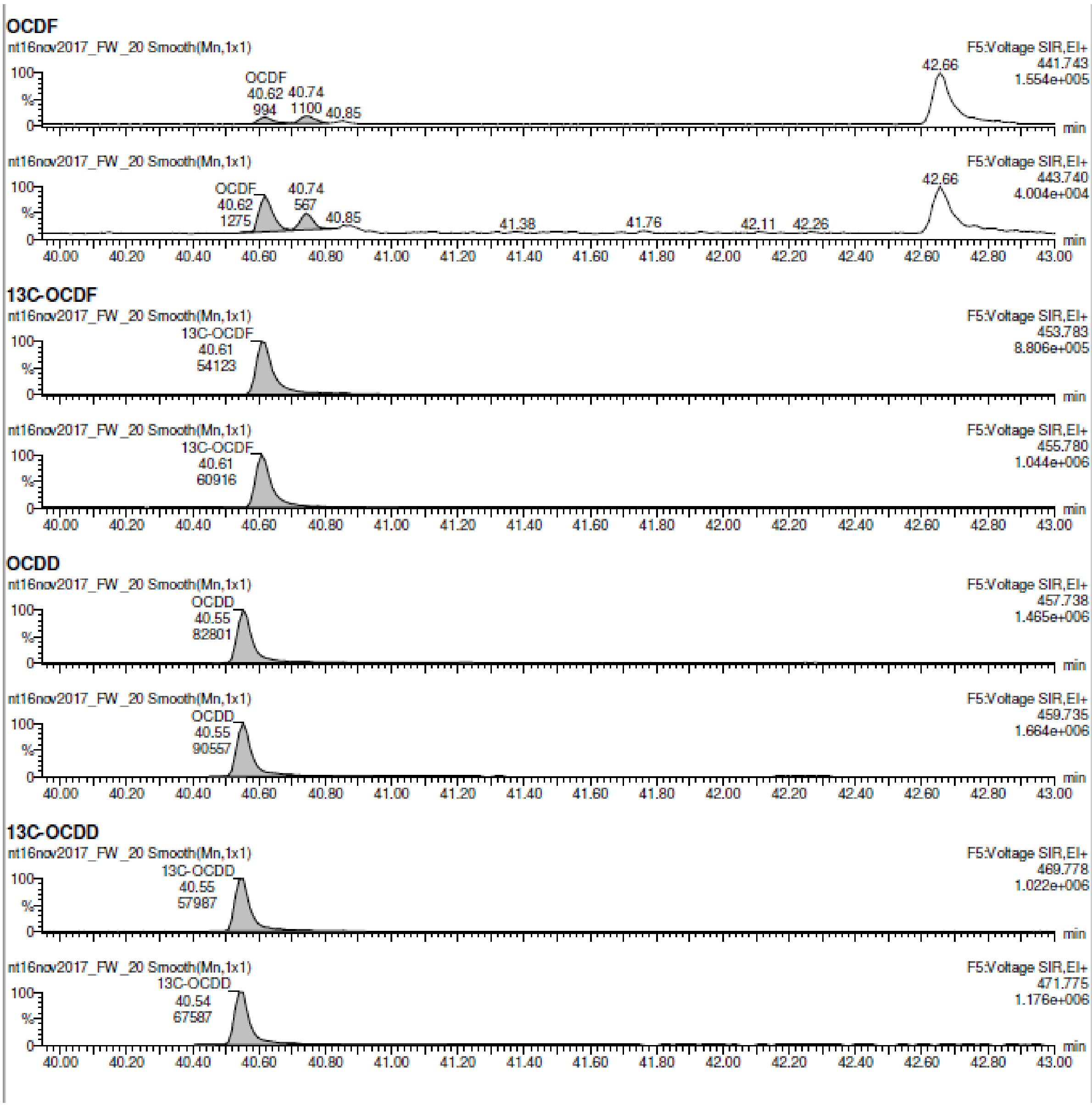
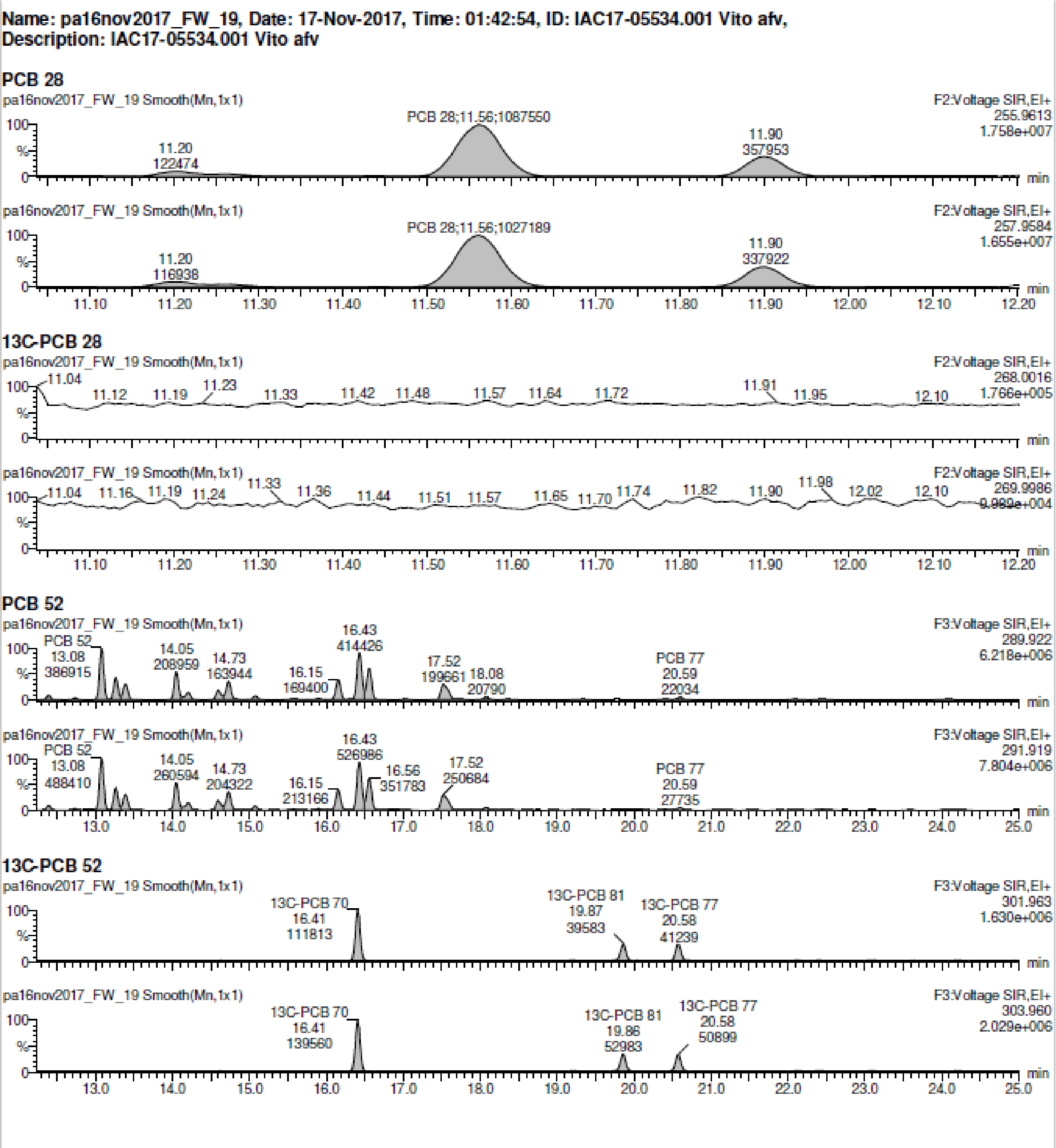



OCDF
nt16nov2017_FW_20 Smooth(Mn,1x1)
F5:Voltage SIR,EI+
441.743
1.554e+005
OCDF
40.62
994
40.74
1100
40.85
42.66
nt16nov2017_FW_20 Smooth(Mn,1x1)
F5:Voltage SIR,EI+
443.740
4.004e+004
OCDF
40.62
1275
40.74
567
40.85
41.38
41.76
42.11
42.26
42.66
13C-OCDF
nt16nov2017_FW_20 Smooth(Mn,1x1)
F5:Voltage SIR,EI+
453.783
8.806e+005
13C-OCDF
40.61
54123
nt16nov2017_FW_20 Smooth(Mn,1x1)
F5:Voltage SIR,EI+
455.780
1.044e+006
13C-OCDF
40.61
60916
OCDD
nt16nov2017_FW_20 Smooth(Mn,1x1)
F5:Voltage SIR,EI+
457.738
1.465e+006
OCDD
40.55
82801
nt16nov2017_FW_20 Smooth(Mn,1x1)
F5:Voltage SIR,EI+
459.735
1.664e+006
OCDD
40.55
90557
13C-OCDD
nt16nov2017_FW_20 Smooth(Mn,1x1)
F5:Voltage SIR,EI+
469.778
1.022e+006
13C-OCDD
40.55
57987
nt16nov2017_FW_20 Smooth(Mn,1x1)
F5:Voltage SIR,EI+
471.775
1.176e+006
13C-OCDD
40.54
67587
100
%
0
min
40.00
40.20
40.40
40.60
40.80
41.00
41.20
41.40
41.60
41.80
42.00
42.20
42.40
42.60
42.80
43.00



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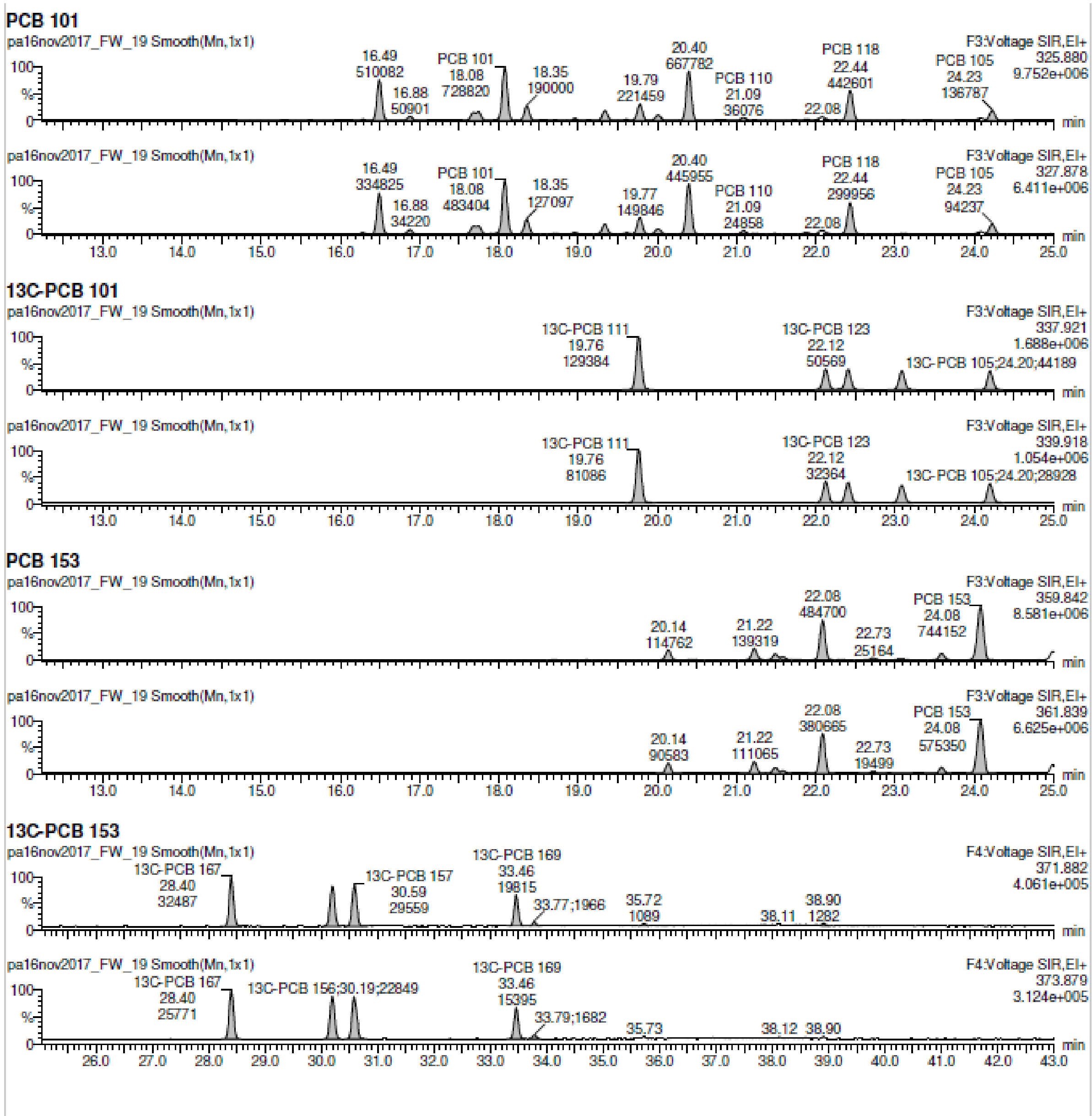
PCB 28

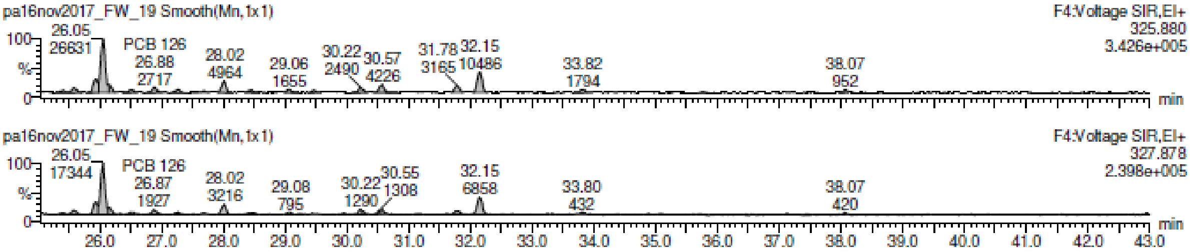
13C-PCB 28

PCB 52

13C-PCB 52


PCB 101
pa16nov2017_FW_19 Smooth(Mn,1x1)
F3:Voltage SIR,EI+
325.880
9.752e+006
16.49
510082
16.88
50901
PCB 101
18.08
728820
18.35
190000
19.79
221459
20.40
667782
PCB 110
21.09
36076
22.08
PCB 118
22.44
442601
PCB 105
24.23
136787
pa16nov2017_FW_19 Smooth(Mn,1x1)
F3:Voltage SIR,EI+
327.878
6.411e+006
16.49
334825
16.88
34220
PCB 101
18.08
483404
18.35
127097
19.77
149846
20.40
445955
PCB 110
21.09
24858
22.08
PCB 118
22.44
299956
PCB 105
24.23
94237
13C-PCB 101
pa16nov2017_FW_19 Smooth(Mn,1x1)
F3:Voltage SIR,EI+
337.921
1.688e+006
13C-PCB 111
19.76
129384
13C-PCB 123
22.12
50569
13C-PCB 105;24.20;44189
pa16nov2017_FW_19 Smooth(Mn,1x1)
F3:Voltage SIR,EI+
339.918
1.054e+006
13C-PCB 111
19.76
81086
13C-PCB 123
22.12
32364
13C-PCB 105;24.20;28928
PCB 153
pa16nov2017_FW_19 Smooth(Mn,1x1)
F3:Voltage SIR,EI+
359.842
8.581e+006
20.14
114762
21.22
139319
22.08
484700
22.73
25164
PCB 153
24.08
744152
pa16nov2017_FW_19 Smooth(Mn,1x1)
F3:Voltage SIR,EI+
361.839
6.625e+006
20.14
90583
21.22
111065
22.08
380665
22.73
19499
PCB 153
24.08
575350
13C-PCB 153
pa16nov2017_FW_19 Smooth(Mn,1x1)
F4:Voltage SIR,EI+
371.882
4.061e+005
13C-PCB 167
28.40
32487
13C-PCB 157
30.59
29559
13C-PCB 169
33.46
19815
33.77;1966
35.72
1089
38.11
38.90
1282
pa16nov2017_FW_19 Smooth(Mn,1x1)
F4:Voltage SIR,EI+
373.879
3.124e+005
13C-PCB 167
28.40
25771
13C-PCB 156;30.19;22849
13C-PCB 169
33.46
15395
33.79;1682
35.73
38.12
38.90
100
%
0
min
13.0
14.0
15.0
16.0
17.0
18.0
19.0
20.0
21.0
22.0
23.0
24.0
25.0
26.0
27.0
28.0
29.0
30.0
31.0
32.0
33.0
34.0
35.0
36.0
37.0
38.0
39.0
40.0
41.0
42.0
43.0

PCB 126



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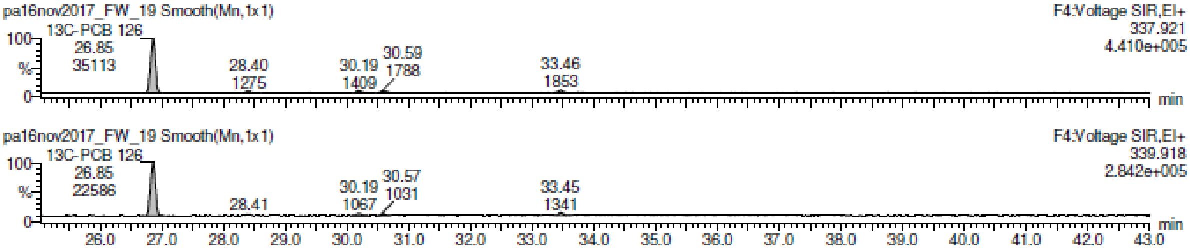
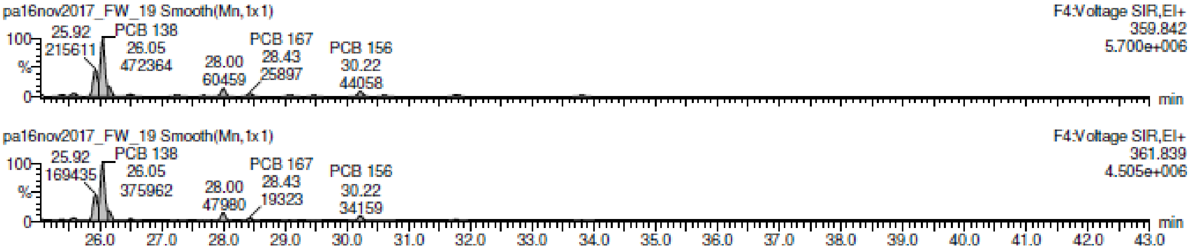
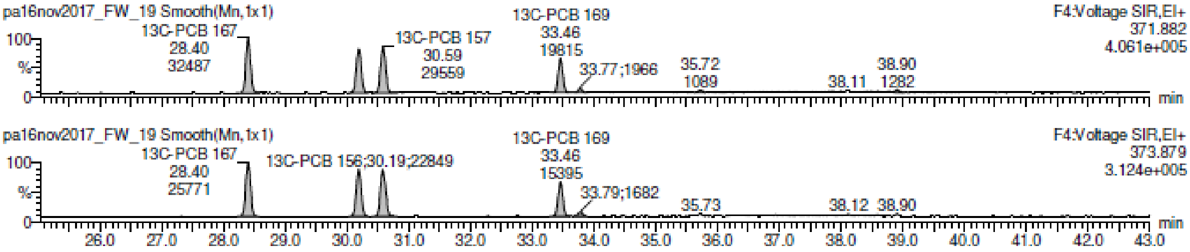
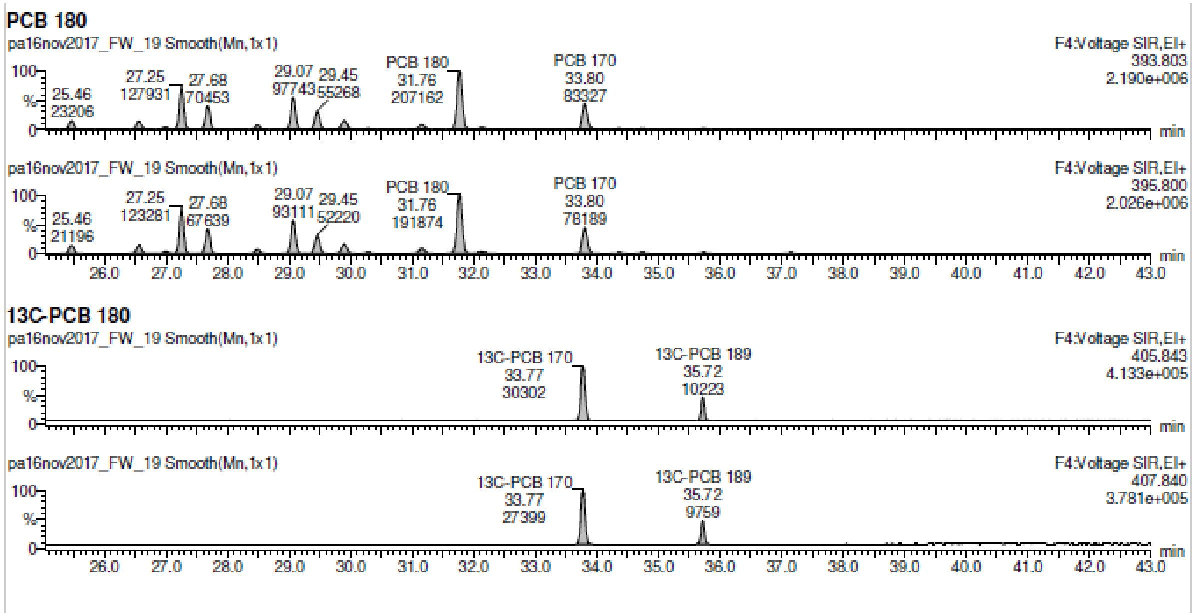


PCB 138

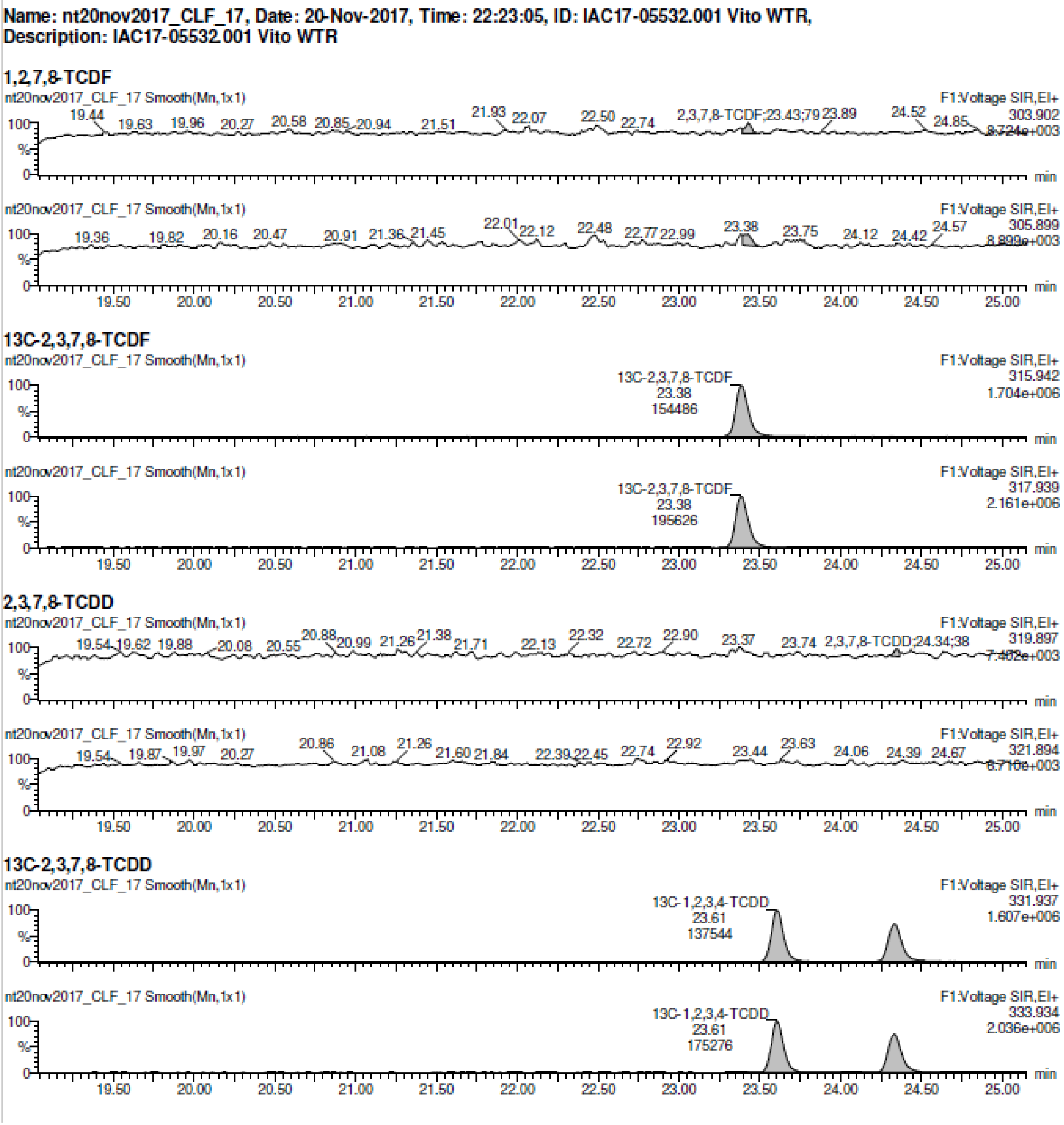


13C-PCB 138




PCB 180
pa16nov2017_FW_19 Smooth(Mn,1x1)
F4:Voltage SIR,EI+
393.803
2.190e+006
25.46
23206
27.25
127931
27.68
70453
29.07
97743
29.45
55268
PCB 180
31.76
207162
PCB 170
33.80
83327
pa16nov2017_FW_19 Smooth(Mn,1x1)
F4:Voltage SIR,EI+
395.800
2.026e+006
25.46
21196
27.25
123281
27.68
67639
29.07
93111
29.45
52220
PCB 180
31.76
191874
PCB 170
33.80
78189
100
%
0
min
26.0
27.0
28.0
29.0
30.0
31.0
32.0
33.0
34.0
35.0
36.0
37.0
38.0
39.0
40.0
41.0
42.0
43.0
13C-PCB 180
pa16nov2017_FW_19 Smooth(Mn,1x1)
F4:Voltage SIR,EI+
405.843
4.133e+005
13C-PCB 170
33.77
30302
13C-PCB 189
35.72
10223
pa16nov2017_FW_19 Smooth(Mn,1x1)
F4:Voltage SIR,EI+
407.840
3.781e+005
13C-PCB 170
33.77
27399
13C-PCB 189
35.72
9759

ANNEX B – ION CHROMATOGRAMS FOR PCDD/F AND DL-PCB IN ELUATES (L/S =1.46) OF RUBBER CRUMBS)



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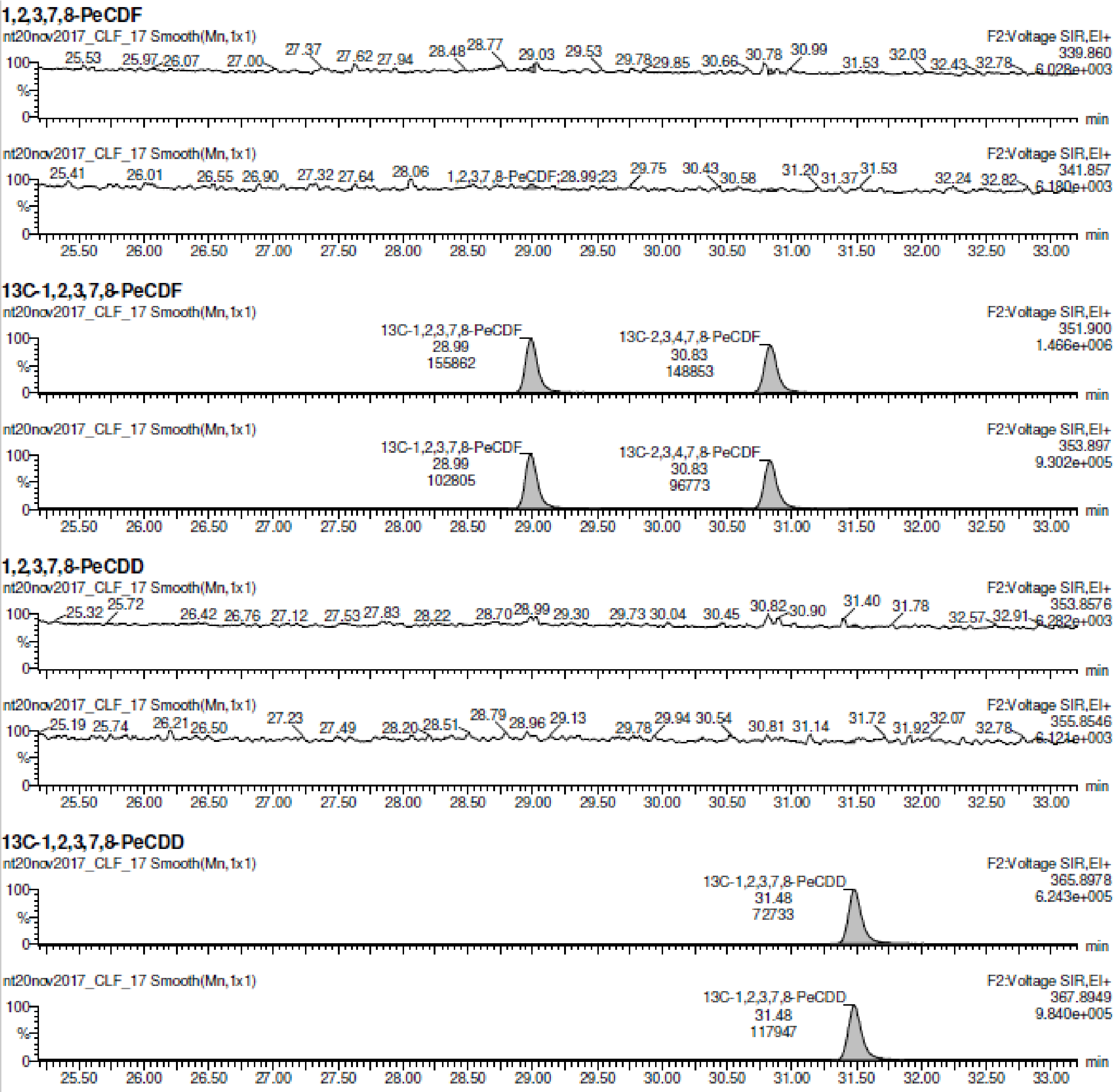
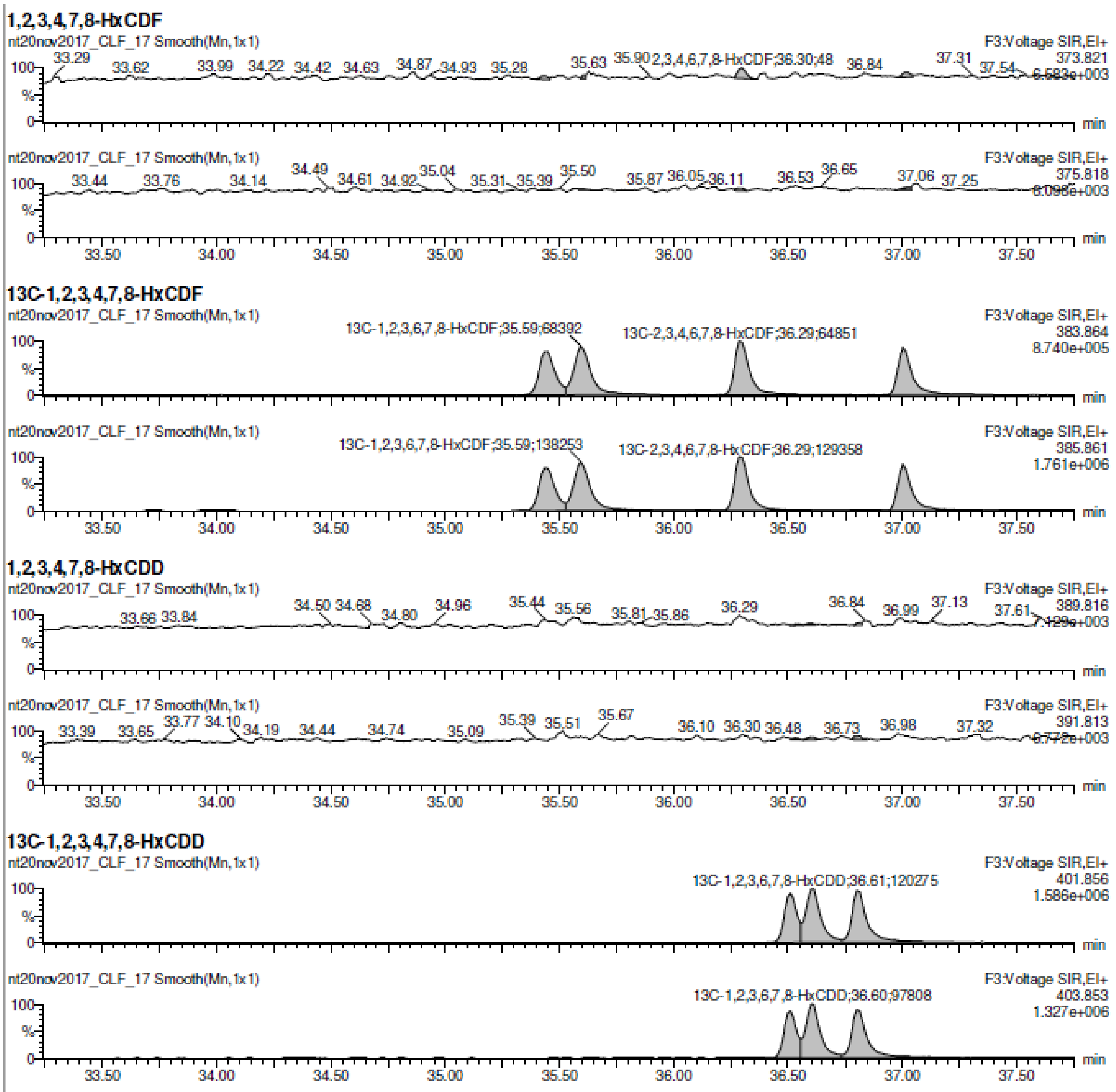
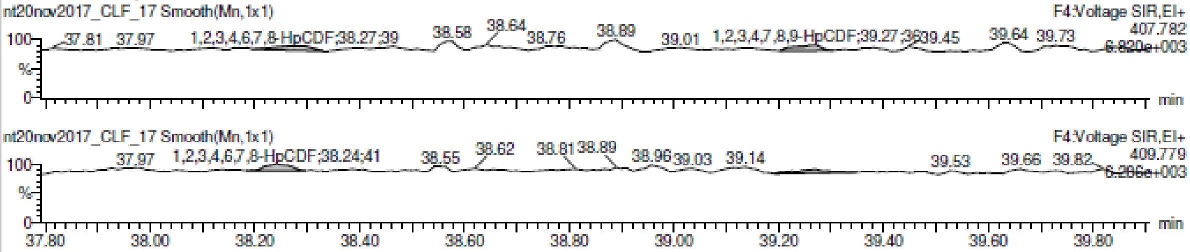
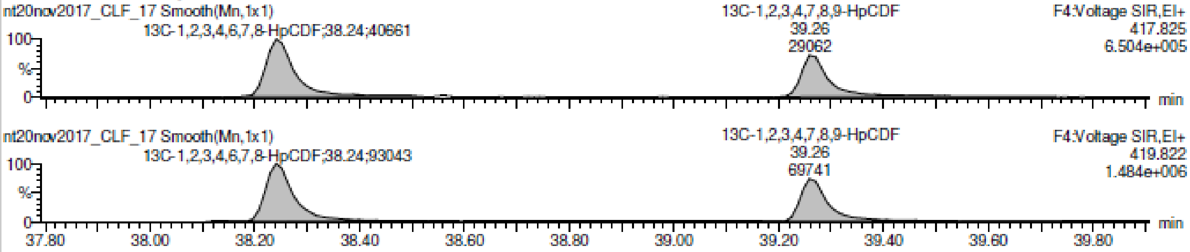
Annex B – Ion chromatograms for PCDD/F and dl-PCB in eluates (L/S =1.46) of rubber crumbs)

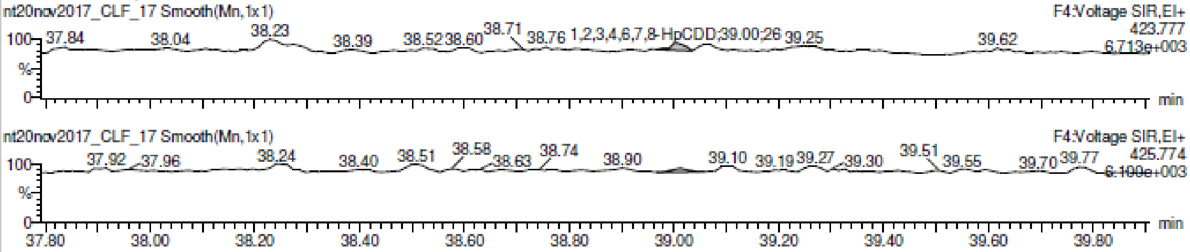


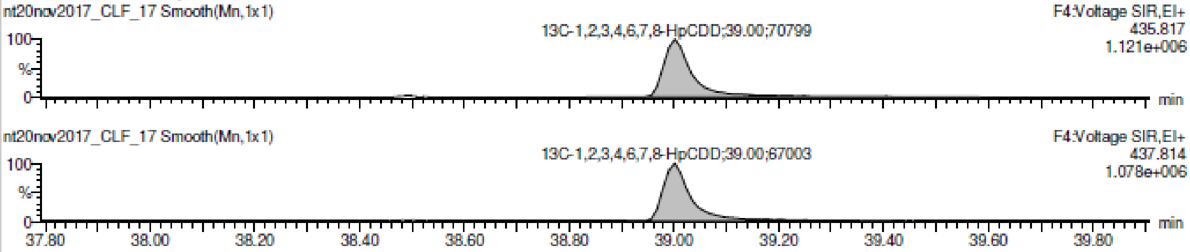

1,2,3,4,7,8-HxCDF
nt20nov2017_CLF_17 Smooth(Mn,1x1)
F3:Voltage SIR,EI+
373.821
6.583e+003
2,3,4,6,7,8-HxCDF;36.30;48
375.818
8.098e+003
13C-1,2,3,4,7,8-HxCDF
13C-1,2,3,6,7,8-HxCDF;35.59;68392
13C-2,3,4,6,7,8-HxCDF;36.29;64851
383.864
8.740e+005
13C-1,2,3,6,7,8-HxCDF;35.59;138253
13C-2,3,4,6,7,8-HxCDF;36.29;129358
385.861
1.761e+006
1,2,3,4,7,8-HxCDD
389.816
7.129e+003
391.813
8.772e+003
13C-1,2,3,4,7,8-HxCDD
13C-1,2,3,6,7,8-HxCDD;36.61;120275
401.856
1.586e+006
13C-1,2,3,6,7,8-HxCDD;36.60;97808
403.853
1.327e+006
100
%
0
33.50
34.00
34.50
35.00
35.50
36.00
36.50
37.00
37.50
min

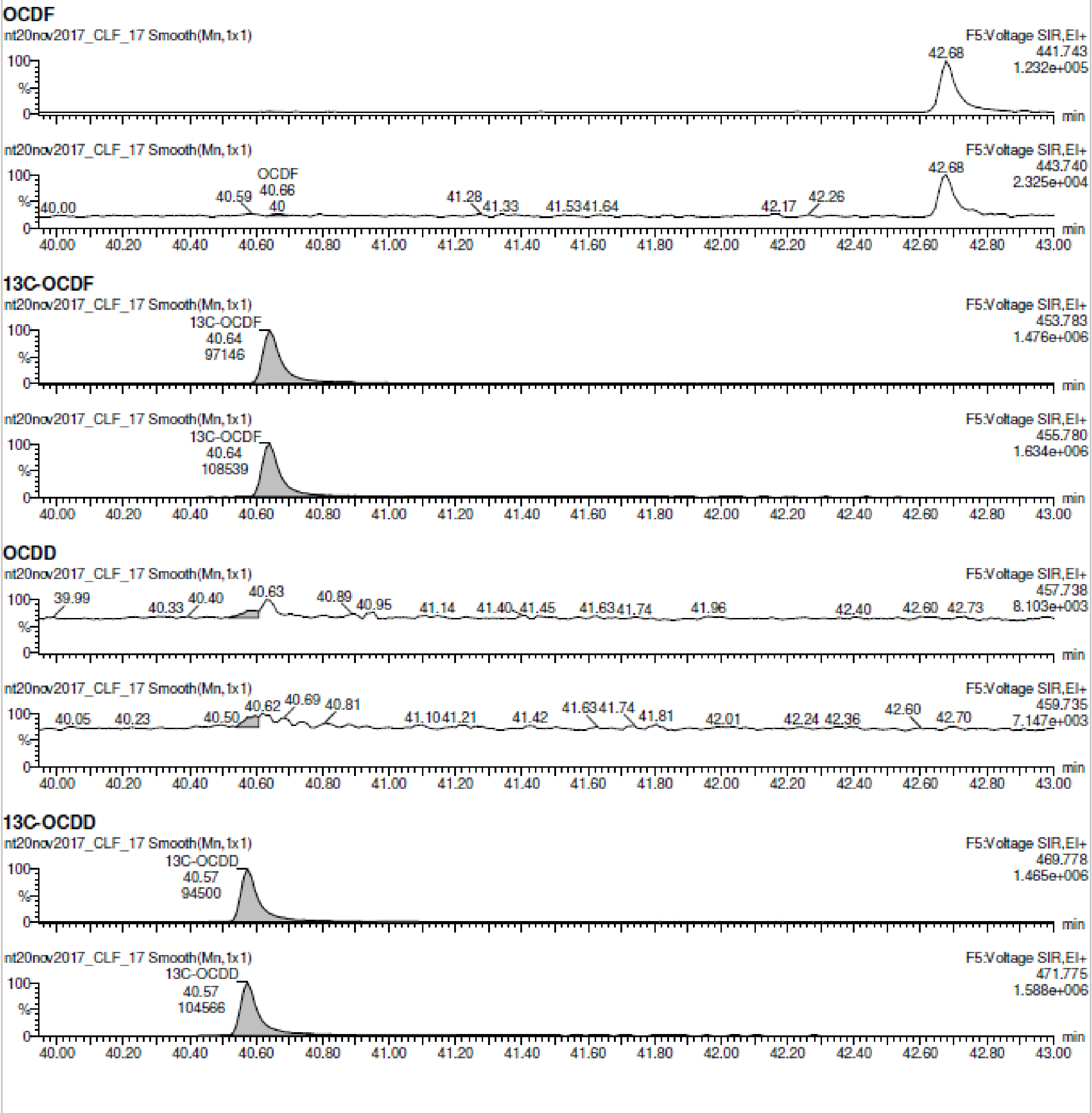
Annex B – Ion chromatograms for PCDD/F and dl-PCB in eluates (L/S =1.46) of rubber crumbs)


1,2,3,4,6,7,8-HpCDF

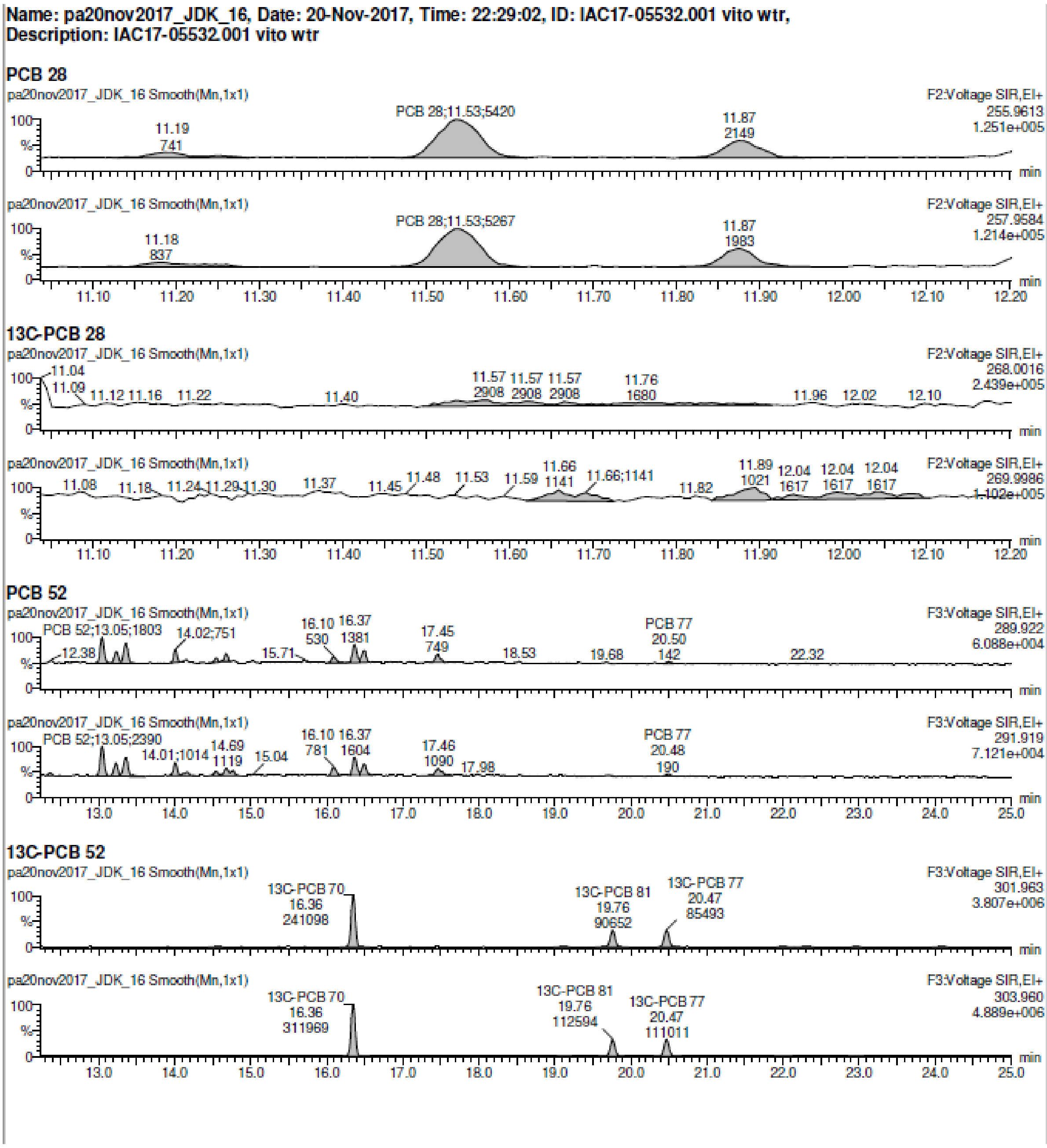

13C-1,2,3,4,6,7,8-HpCDF


1,2,3,4,6,7,8-HpCDD


13C-1,2,3,4,6,7,8-HpCDD


OCDF
nt20nov2017_CLF_17 Smooth(Mn,1x1)
F5:Voltage SIR,EI+
441.743
1.232e+005
42.68
nt20nov2017_CLF_17 Smooth(Mn,1x1)
F5:Voltage SIR,EI+
443.740
2.325e+004
OCDF
40.66
40
40.00
40.59
41.28
41.33
41.5341.64
42.17
42.26
42.68
13C-OCDF
nt20nov2017_CLF_17 Smooth(Mn,1x1)
F5:Voltage SIR,EI+
453.783
1.476e+006
13C-OCDF
40.64
97146
nt20nov2017_CLF_17 Smooth(Mn,1x1)
F5:Voltage SIR,EI+
455.780
1.634e+006
13C-OCDF
40.64
108539
OCDD
nt20nov2017_CLF_17 Smooth(Mn,1x1)
F5:Voltage SIR,EI+
457.738
8.103e+003
39.99
40.33
40.40
40.63
40.89
40.95
41.14
41.40
41.45
41.6341.74
41.96
42.40
42.60
42.73
nt20nov2017_CLF_17 Smooth(Mn,1x1)
F5:Voltage SIR,EI+
459.735
7.147e+003
40.05
40.23
40.50
40.62
40.69
40.81
41.1041.21
41.42
41.6341.74
41.81
42.01
42.24
42.36
42.60
42.70
13C-OCDD
nt20nov2017_CLF_17 Smooth(Mn,1x1)
F5:Voltage SIR,EI+
469.778
1.465e+006
13C-OCDD
40.57
94500
nt20nov2017_CLF_17 Smooth(Mn,1x1)
F5:Voltage SIR,EI+
471.775
1.588e+006
13C-OCDD
40.57
104566
100
%
0
min
40.00
40.20
40.40
40.60
40.80
41.00
41.20
41.40
41.60
41.80
42.00
42.20
42.40
42.60
42.80
43.00

Annex B – Ion chromatograms for PCDD/F and dl-PCB in eluates (L/S =1.46) of rubber crumbs)



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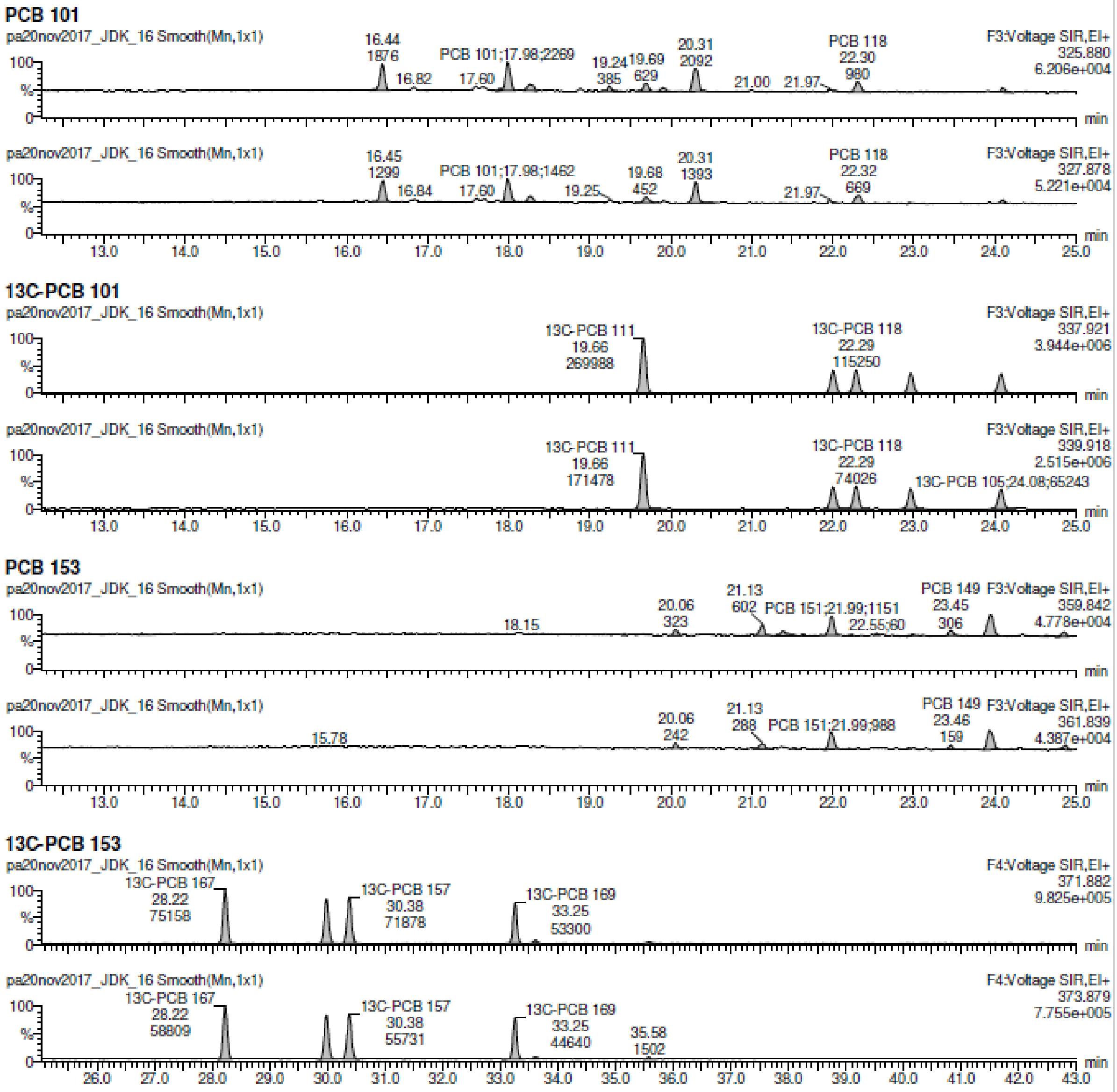
Description: IAC17-05532.001 vito wtr

PCB 28

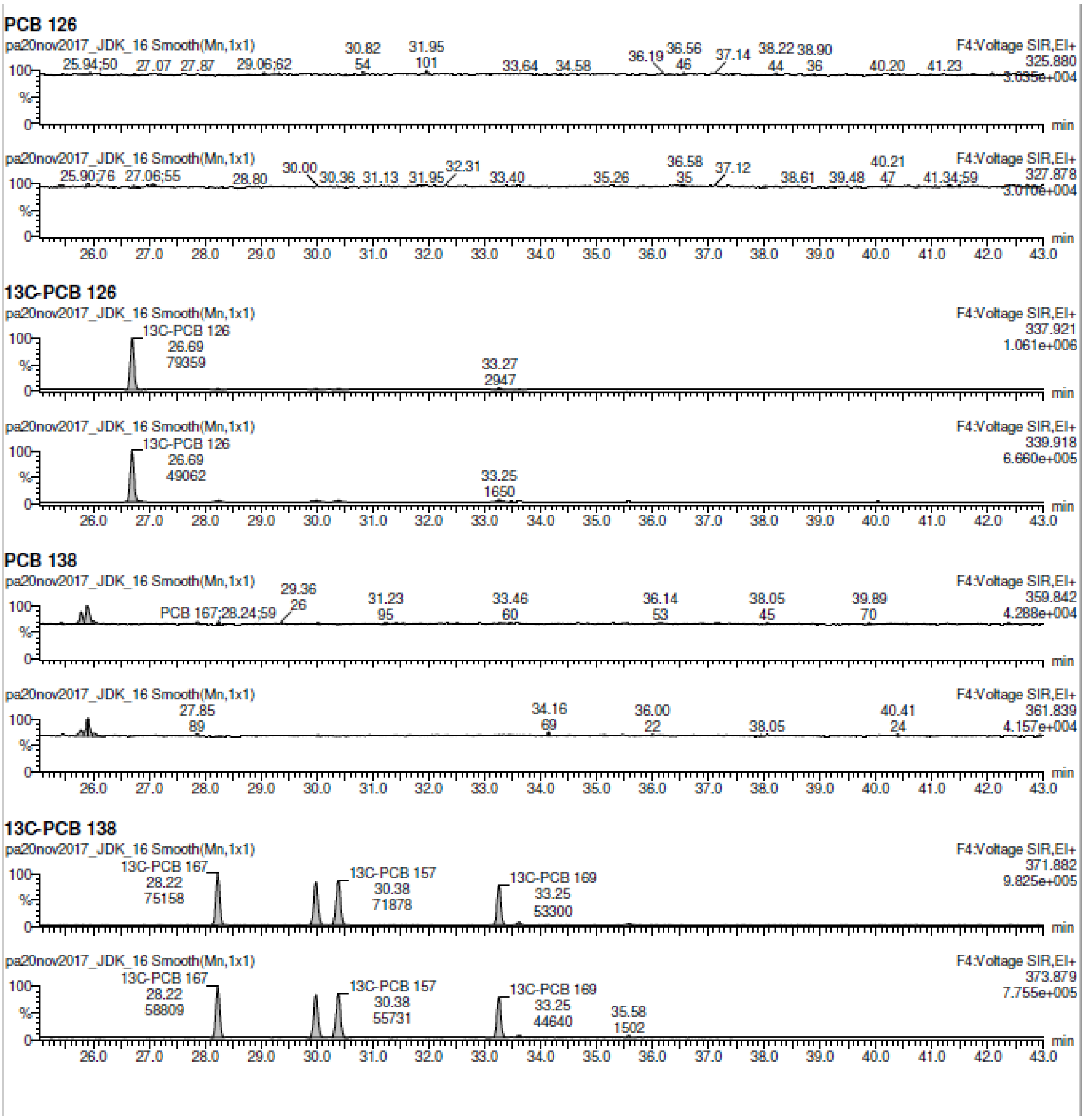
13C-PCB 28

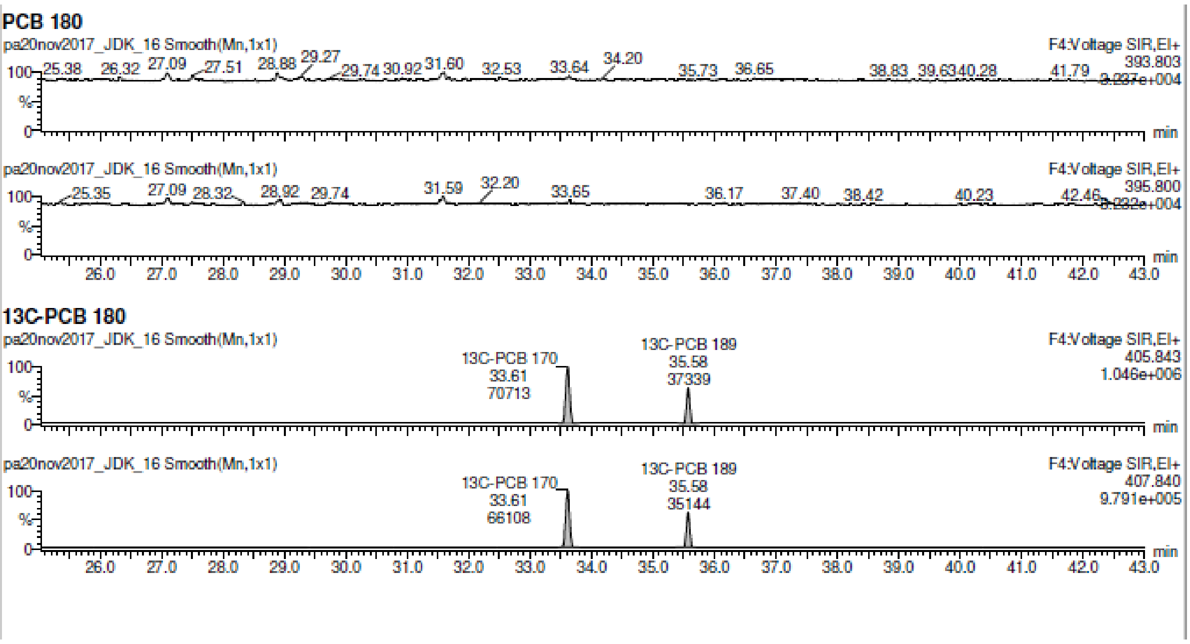
PCB 52

13C-PCB 52

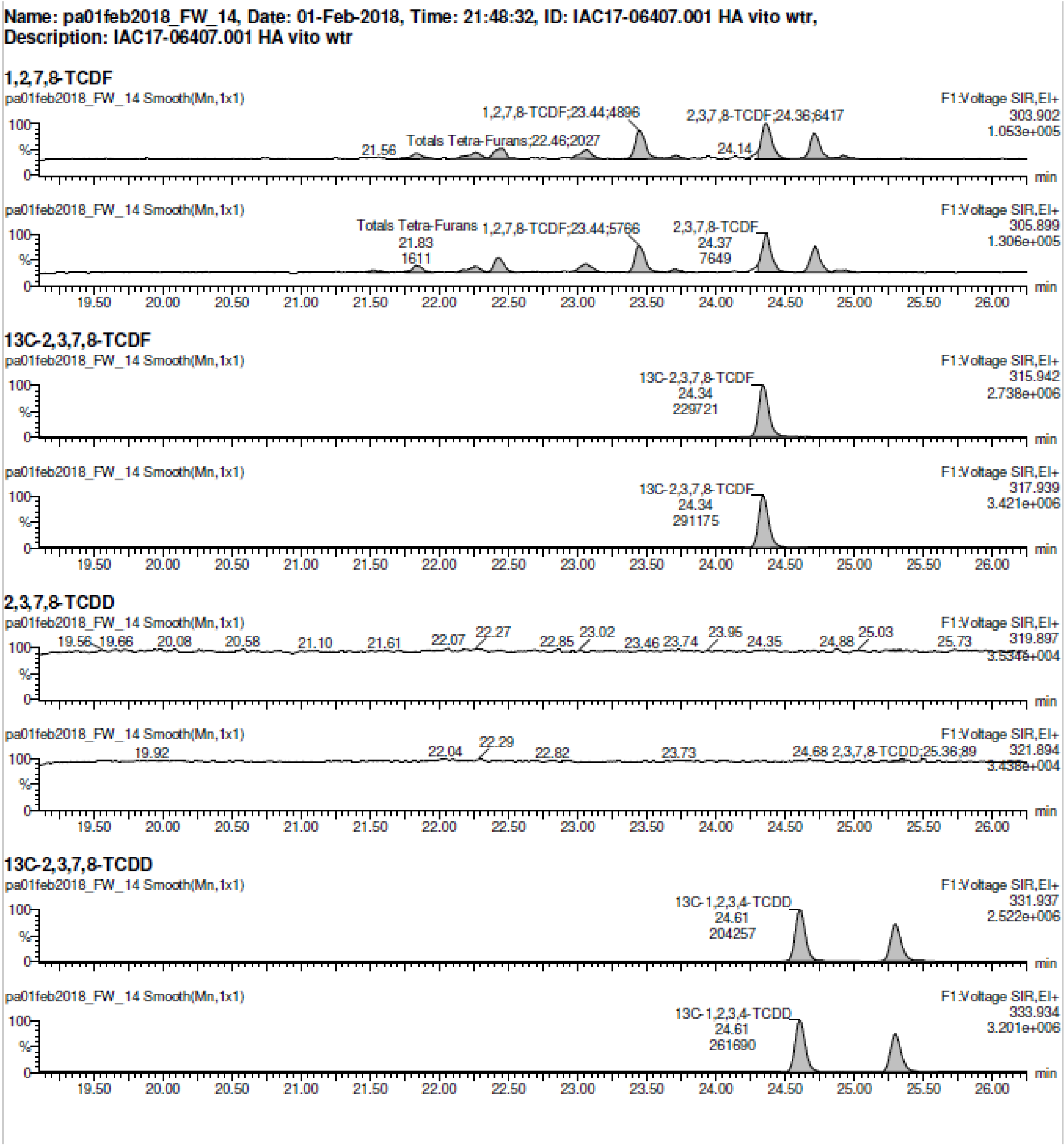

PCB 101
pa20nov2017_JDK_16 Smooth(Mn,1x1)
F3:Voltage SIR,EI+
325.880
6.206e+004
16.44
1876
16.82
17.60
PCB 101;17.98;2269
19.24
385
19.69
629
20.31
2092
21.00
21.97
PCB 118
22.30
980
pa20nov2017_JDK_16 Smooth(Mn,1x1)
F3:Voltage SIR,EI+
327.878
5.221e+004
16.45
1299
16.84
17.60
PCB 101;17.98;1462
19.25
19.68
452
20.31
1393
21.97
PCB 118
22.32
669
13C-PCB 101
pa20nov2017_JDK_16 Smooth(Mn,1x1)
F3:Voltage SIR,EI+
337.921
3.944e+006
13C-PCB 111
19.66
269988
13C-PCB 118
22.29
115250
pa20nov2017_JDK_16 Smooth(Mn,1x1)
F3:Voltage SIR,EI+
339.918
2.515e+006
13C-PCB 111
19.66
171478
13C-PCB 118
22.29
74026
13C-PCB 105;24.08;65243
PCB 153
pa20nov2017_JDK_16 Smooth(Mn,1x1)
F3:Voltage SIR,EI+
359.842
4.778e+004
18.15
20.06
323
21.13
602
PCB 151;21.99;1151
22.55;60
PCB 149
23.45
306
pa20nov2017_JDK_16 Smooth(Mn,1x1)
F3:Voltage SIR,EI+
361.839
4.387e+004
15.78
20.06
242
21.13
288
PCB 151;21.99;988
PCB 149
23.46
159
13C-PCB 153
pa20nov2017_JDK_16 Smooth(Mn,1x1)
F4:Voltage SIR,EI+
371.882
9.825e+005
13C-PCB 167
28.22
75158
13C-PCB 157
30.38
71878
13C-PCB 169
33.25
53300
pa20nov2017_JDK_16 Smooth(Mn,1x1)
F4:Voltage SIR,EI+
373.879
7.755e+005
13C-PCB 167
28.22
58809
13C-PCB 157
30.38
55731
13C-PCB 169
33.25
44640
35.58
1502
100
%
0
min
13.0
14.0
15.0
16.0
17.0
18.0
19.0
20.0
21.0
22.0
23.0
24.0
25.0
26.0
27.0
28.0
29.0
30.0
31.0
32.0
33.0
34.0
35.0
36.0
37.0
38.0
39.0
40.0
41.0
42.0
43.0

Annex B – Ion chromatograms for PCDD/F and dl-PCB in eluates (L/S =1.46) of rubber crumbs)




PCB 180
pa20nov2017_JDK_16 Smooth(Mn,1x1)
F4:Voltage SIR,EI+
393.803
3.237e+004
25.38
26.32
27.09
27.51
28.88
29.27
29.74
30.92
31.60
32.53
33.64
34.20
35.73
36.65
38.83
39.63
40.28
41.79
100
%
0
min
pa20nov2017_JDK_16 Smooth(Mn,1x1)
F4:Voltage SIR,EI+
395.800
3.232e+004
25.35
27.09
28.32
28.92
29.74
31.59
32.20
33.65
36.17
37.40
38.42
40.23
42.46
100
%
0
min
26.0
27.0
28.0
29.0
30.0
31.0
32.0
33.0
34.0
35.0
36.0
37.0
38.0
39.0
40.0
41.0
42.0
43.0
13C-PCB 180
pa20nov2017_JDK_16 Smooth(Mn,1x1)
F4:Voltage SIR,EI+
405.843
1.046e+006
13C-PCB 170
33.61
70713
13C-PCB 189
35.58
37339
100
%
0
min
pa20nov2017_JDK_16 Smooth(Mn,1x1)
F4:Voltage SIR,EI+
407.840
9.791e+005
13C-PCB 170
33.61
66108
13C-PCB 189
35.58
35144
100
%
0
min
26.0
27.0
28.0
29.0
30.0
31.0
32.0
33.0
34.0
35.0
36.0
37.0
38.0
39.0
40.0
41.0
42.0
43.0

ANNEX C – ION CHROMATOGRAMS FOR PCDD/F AND DL-PCB CONGENERS IN ELUATES (L/S = 1.21) OF RECYCLED MIXED AGGREGATES



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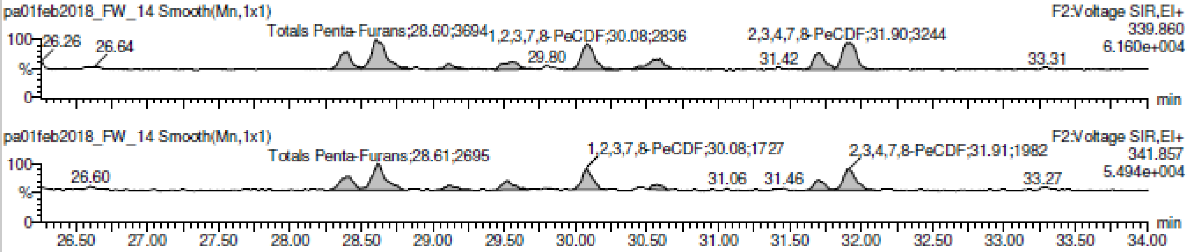
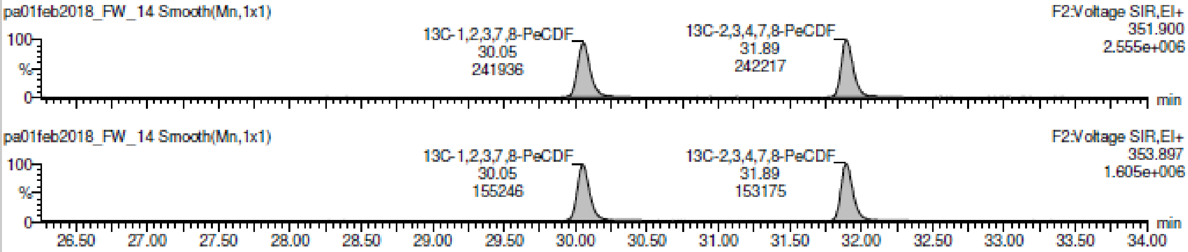
Description: IAC17-06407.001 HA vito wtr

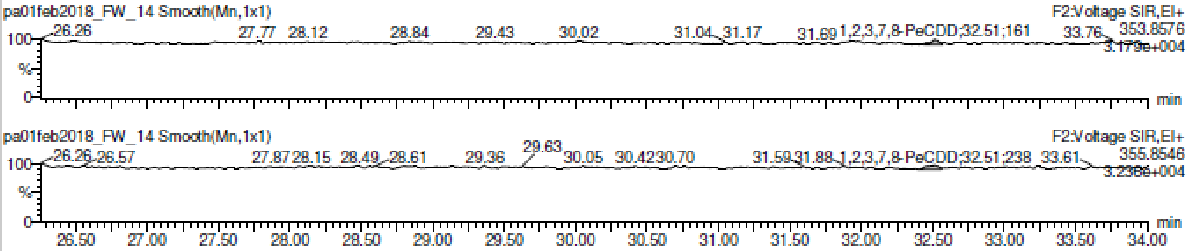
1,2,3,7,8-PeCDF



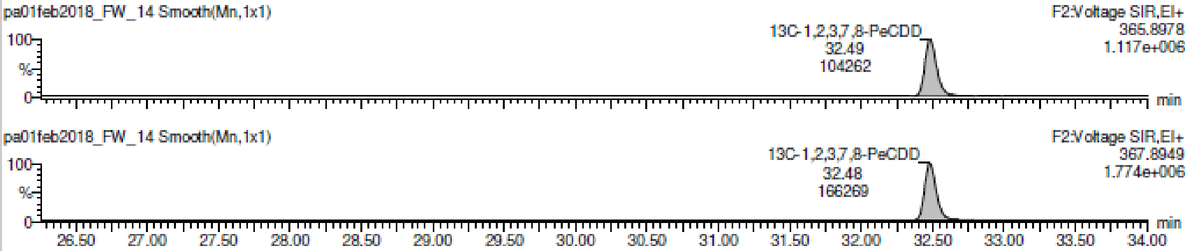
13C-1,2,3,7,8-PeCDF



1,2,3,7,8-PeCDD

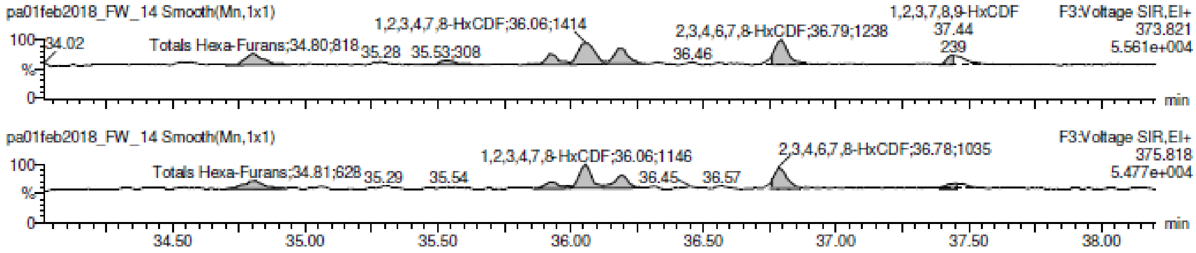


13C-1,2,3,7,8-PeCDD

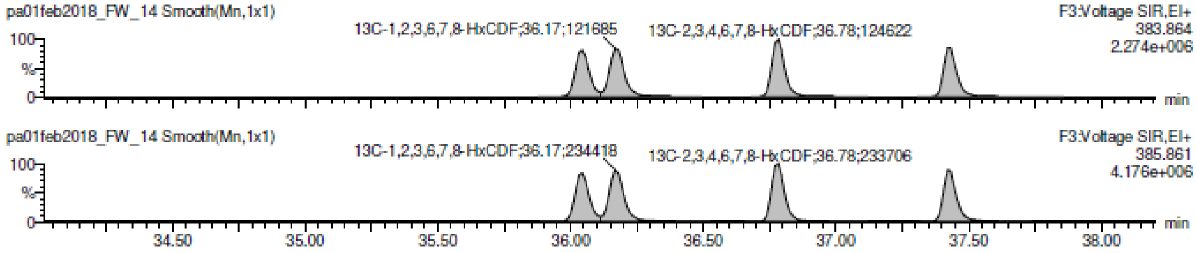


Annex C – Ion chromatograms for PCDD/F and dl-PCB congeners in eluates (L/S = 1.21) of recycled mixed aggregates

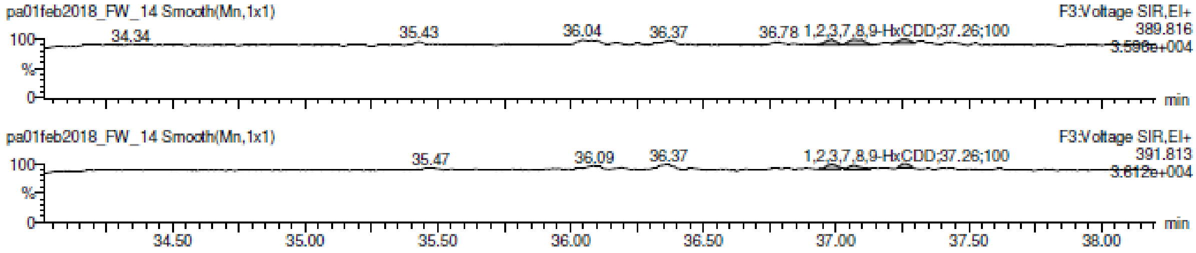
1,2,3,4,7,8-HxCDF



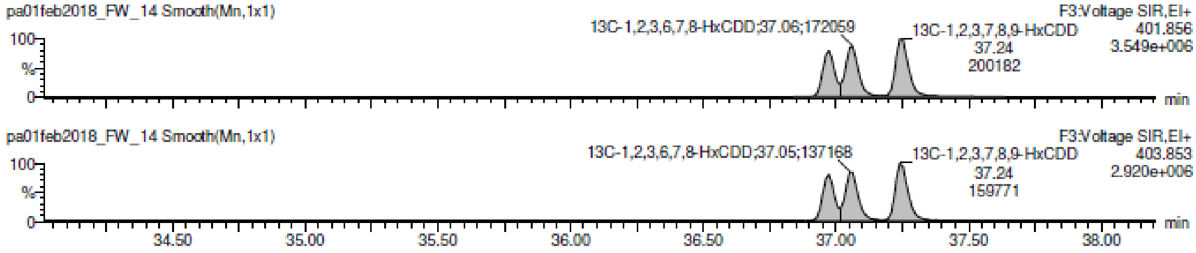
13C-1,2,3,4,7,8-HxCDF



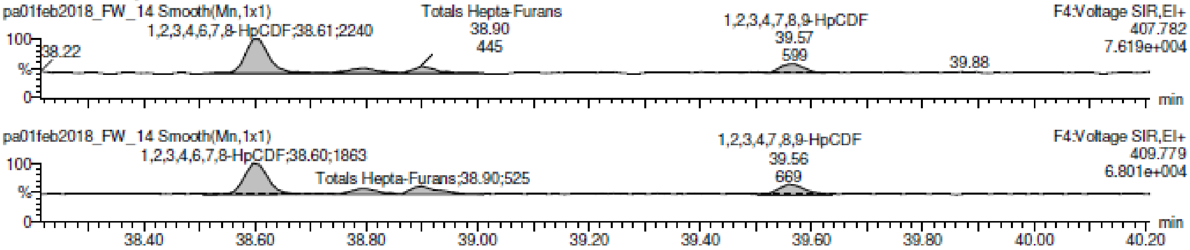
1,2,3,4,7,8-HxCDD



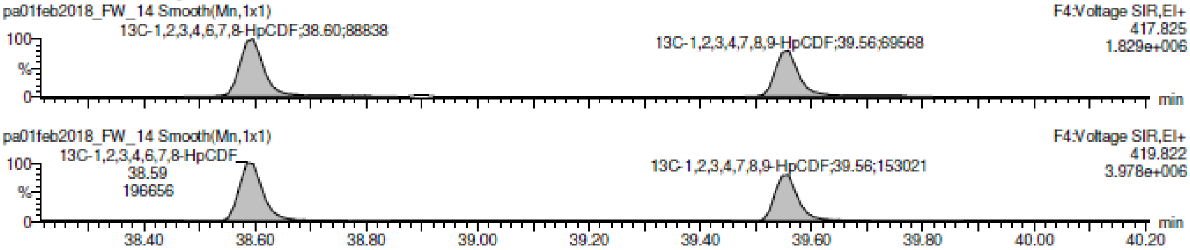
13C-1,2,3,4,7,8-HxCDD



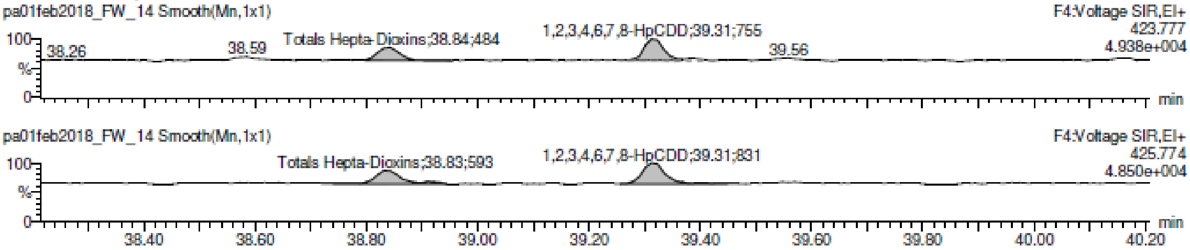
1,2,3,4,6,7,8-HpCDF



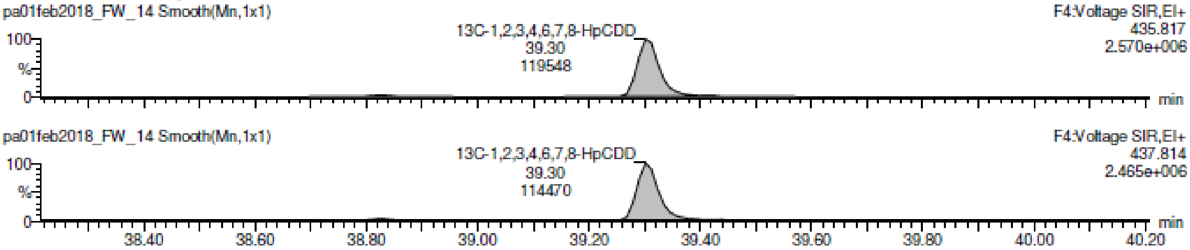
13C-1,2,3,4,6,7,8-HpCDF



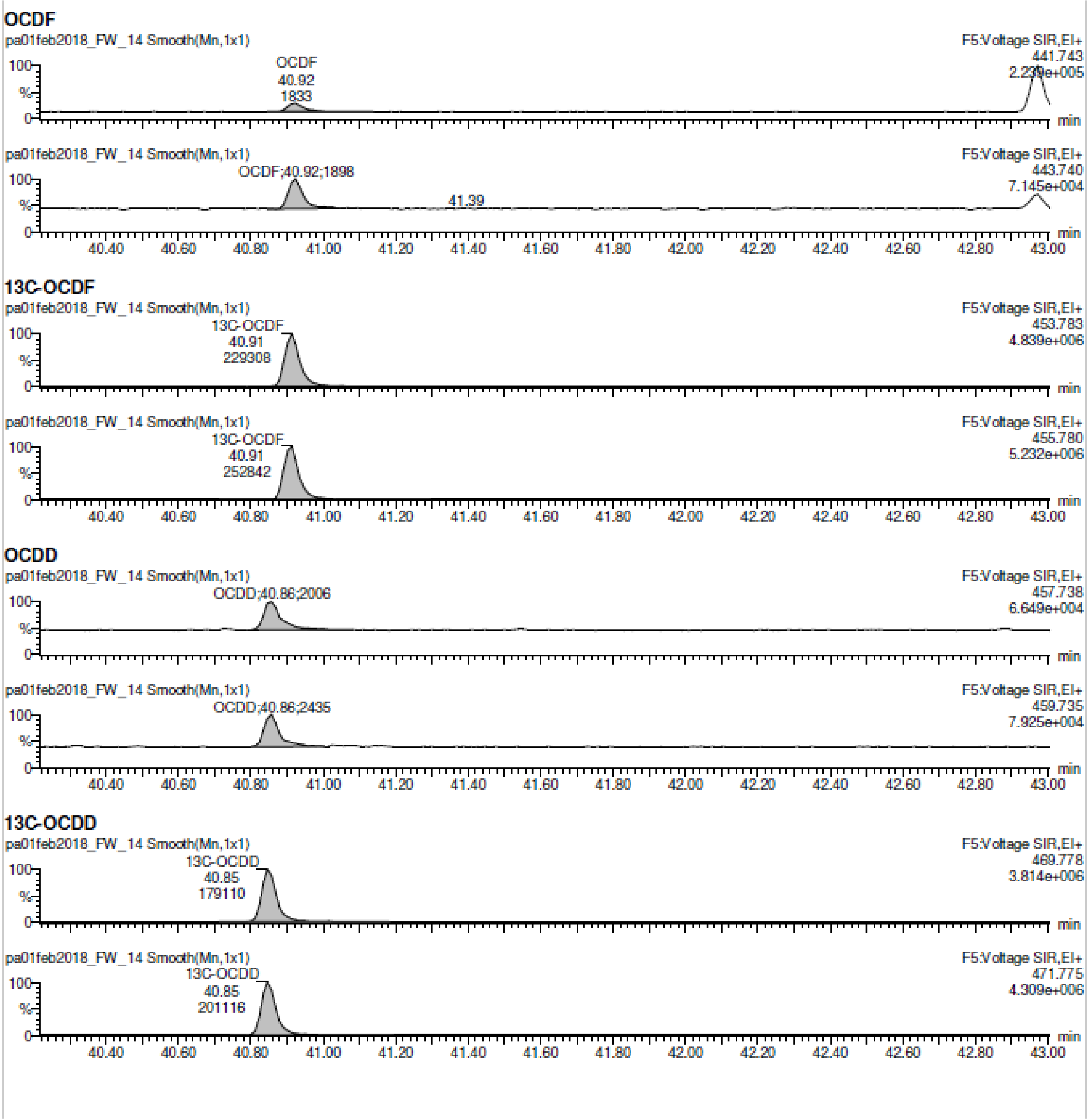
1,2,3,4,6,7,8-HpCDD



13C-1,2,3,4,6,7,8-HpCDD



Annex C – Ion chromatograms for PCDD/F and dl-PCB congeners in eluates (L/S = 1.21) of recycled mixed aggregates



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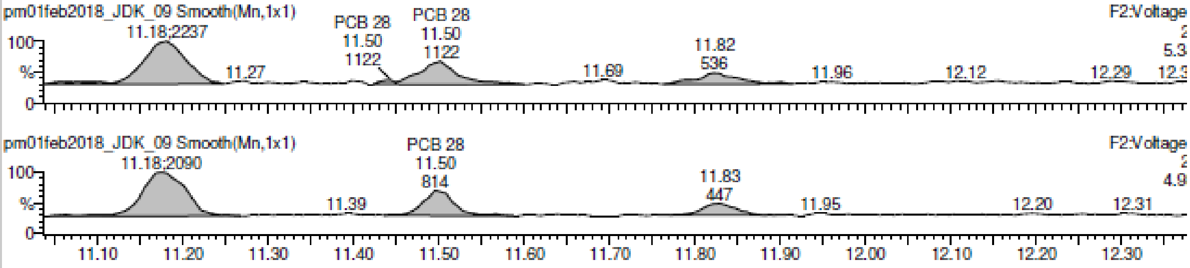
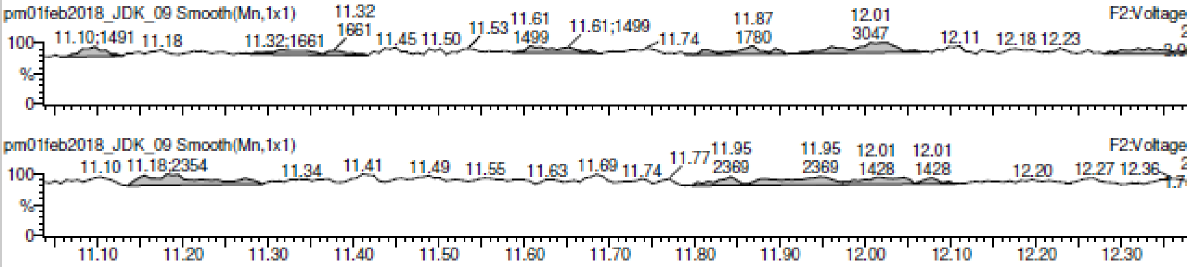
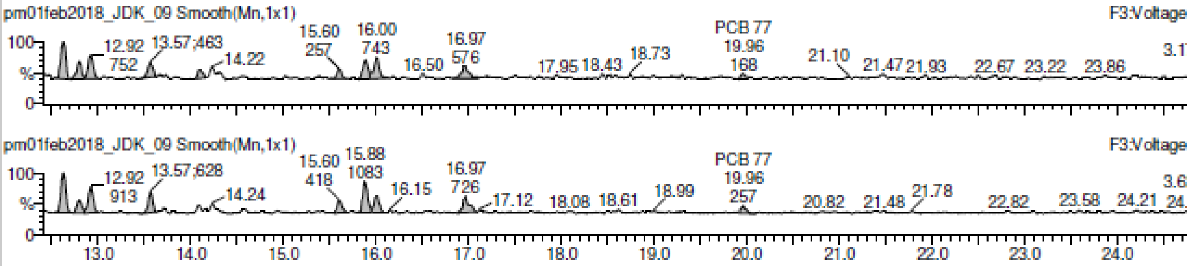
PCB 28



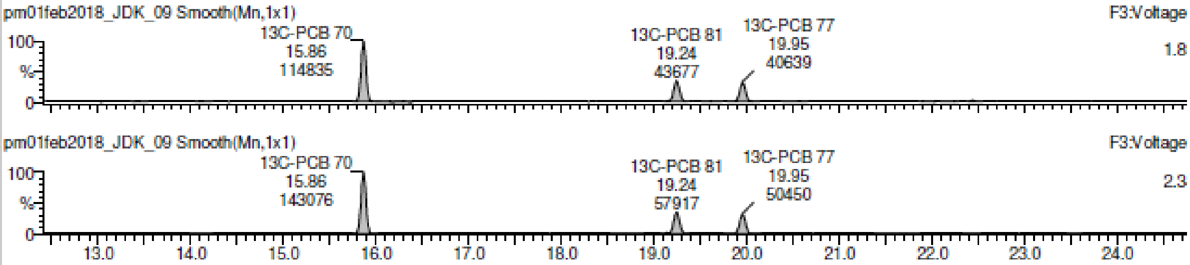
13C-PCB 28



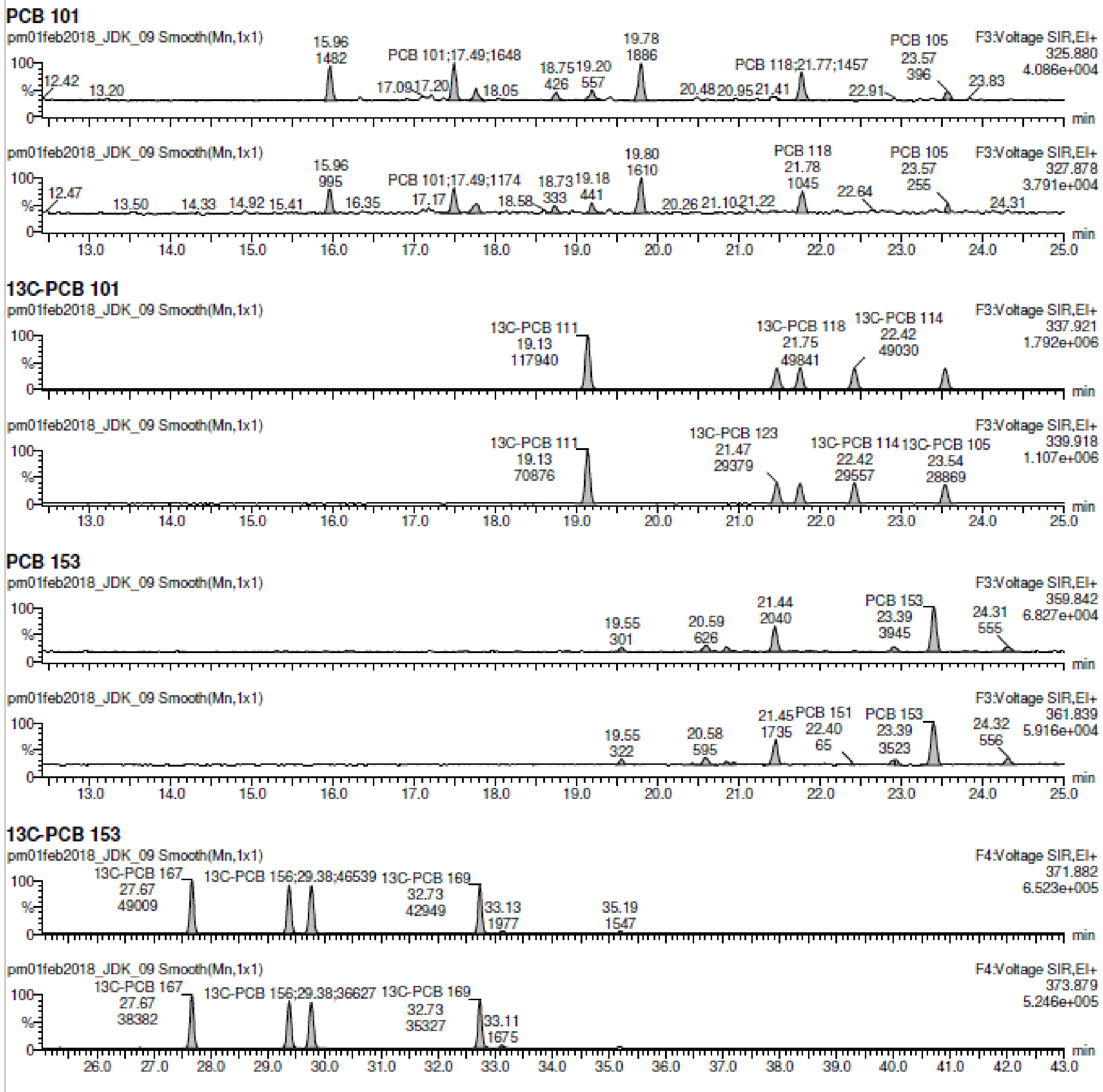
PCB 52



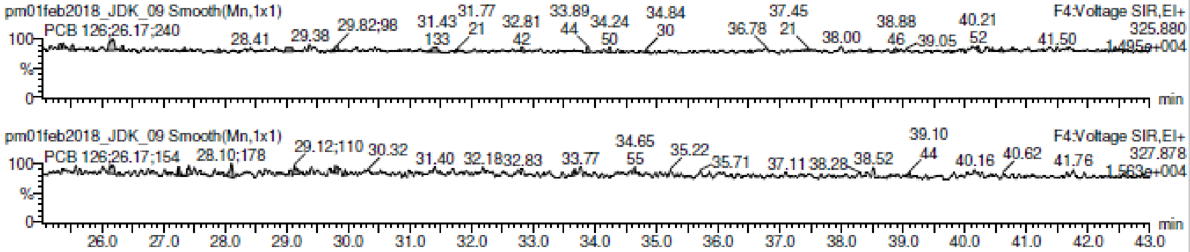
13C-PCB 52



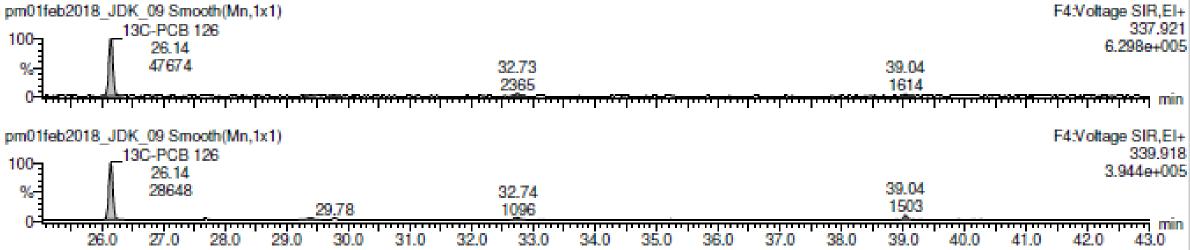
Annex C – Ion chromatograms for PCDD/F and dl-PCB congeners in eluates (L/S = 1.21) of recycled mixed aggregates



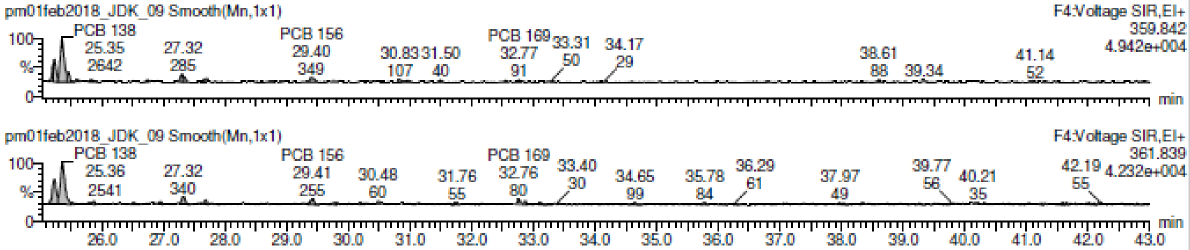
PCB 126



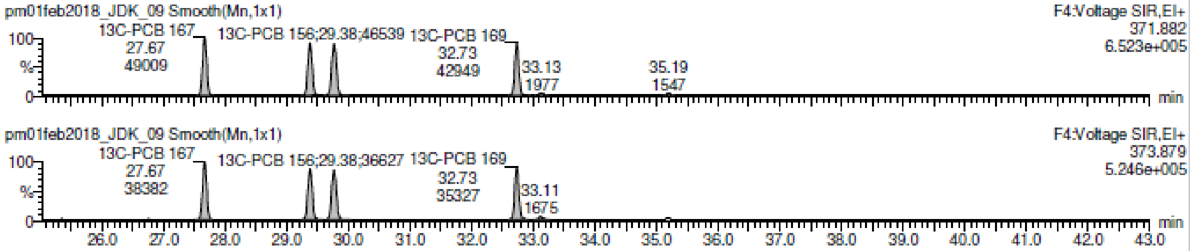
13C-PCB 126



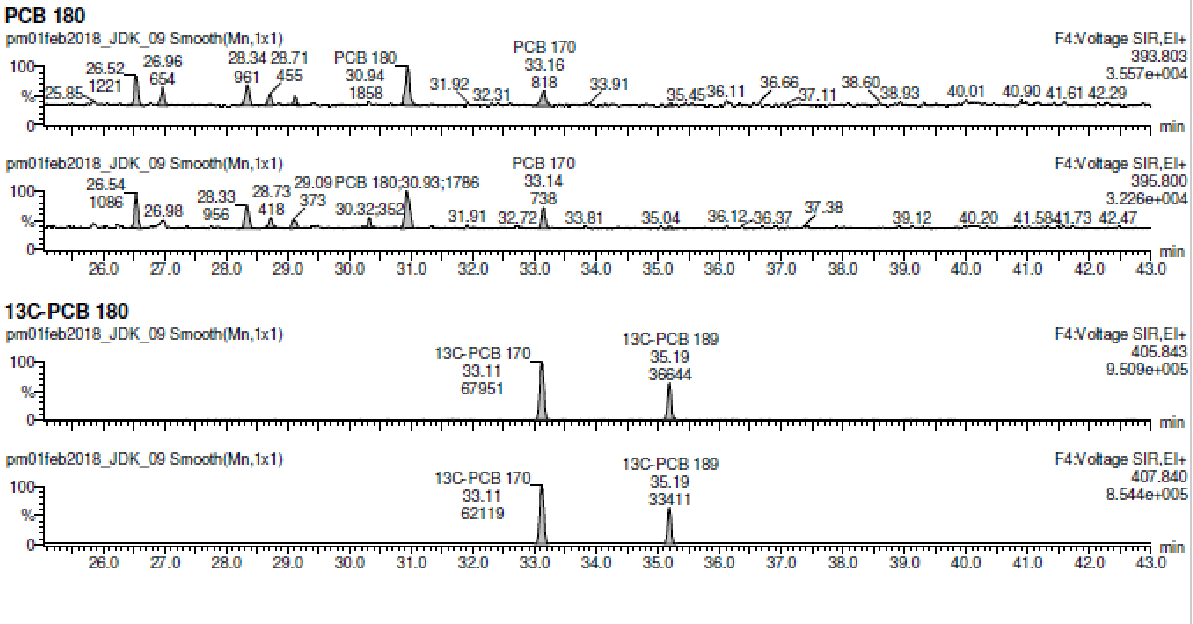
PCB 138



13C-PCB 138



Annex C – Ion chromatograms for PCDD/F and dl-PCB congeners in eluates (L/S = 1.21) of recycled mixed aggregates



ANNEX D – OVERVIEW OF RESULTS, LEACHABLE FRACTIONS AND COMPLIANCE CHECK WITH REGULATORY LIMITS

Hydrocarbons C10-C40

Parameter	Construction product		Eluate µg/L	Rel st dev %	Content product mg/kg	CEN /TS 16637-3 L/S		Cumulative amount leached mg/kg at L/S=10	Fraction of total leached %	CEN /TS 16637-2 area release mg/m^2
Mineral Oil	Asphalt aggregate	<	100		2795	1,09	<		0,004	

Polycyclic aromatic hydrocarbons

Parameter	Construction product		Eluate µg/L	Rel st dev %	Content product mg/kg	CEN /TS 16637-3 L/S		Cumulative amount leached mg/kg at L/S=10	Fraction of total leached %	CEN /TS 16637-2 area release mg/m^2
PAH	Asphalt aggregate									
Naftalene	Eluate A				4,71	1,09				
Acenaftylene			0,02	22,3	0,53	1,09			0,0041	
Acenaftene			0,05	44,4	6,2	1,09			0,0009	
Fluorene			0,03	29,9	7,92	1,09			0,0004	
Fenanthrene			0,14	16,3	95,3	1,09			0,0002	
Anthracene			0,06	12,8	17,24	1,09			0,0004	
Fluoranthene			0,68	19,1	252	1,09			0,0003	
Pyrene			0,45	17,9	151	1,09			0,0003	
Benzo(a)anthracene			0,32	15	114	1,09			0,0003	
Chrysene			0,39	14	123	1,09			0,0003	
Benzo(b)fluoranthene			0,56	11	88,5	1,09			0,0007	
Benzo(k)fluoranthene			0,27	13,4	44,1	1,09			0,0007	
Benzo(a)pyrene			0,66	14	76,5	1,09			0,0009	
Indeno(1,2,3,c,d)pyrene			0,52	12,9	41,1	1,09			0,0014	
Dibenzo(a,h)anthracene			0,08	16,9	9,27	1,09			0,0009	
Benzo(g,h,i)perylene			0,51	12,9	41,8	1,09			0,0013	
PAH 10 sum			4,74	15	810	1,09			0,0006	

Parameter	Construction product		Eluate µg/L	Rel st dev %	Content product mg/kg	CEN /TS 16637-3 L/S		Cumulative amount leached mg/kg at L/S=10	Fraction of total leached %	CEN /TS 16637-2 area release mg/m^2
PAH	Asphalt aggregate									
Naftalene	Eluate B				4,71	8,91				
Acenaftylene					0,53	8,91		0,02		
Acenaftene					6,2	8,91		0,05		
Fluorene					7,92	8,91		0,03		
Fenanthrene			0,02	17,4	95,3	8,91		0,16	0,0002	
Anthracene			0,02	10,4	17,24	8,91		0,08	0,0010	
Fluoranthene			0,13	17,8	252	8,91		0,81	0,0005	
Pyrene			0,08	18,9	151	8,91		0,53	0,0005	
Benzo(a)anthracene			0,06	17,5	114	8,91		0,38	0,0005	
Chrysene			0,08	17,7	123	8,91		0,47	0,0006	
Benzo(b)fluoranthene			0,22	19,3	88,5	8,91		0,78	0,0022	
Benzo(k)fluoranthene			0,09	20,6	44,1	8,91		0,36	0,0018	
Benzo(a)pyrene			0,24	20,4	76,5	8,91		0,9	0,0028	
Indeno(1,2,3,c,d)pyrene			0,16	22	41,1	8,91		0,68	0,0035	
Dibenzo(a,h)anthracene			0,03	20,7	9,27	8,91		0,11	0,0029	
Benzo(g,h,i)perylene			0,15	22,8	41,8	8,91		0,66	0,0032	
PAH 10 sum			1,28	19,1	810	8,91		0,00602	0,0007	

Parameter	Construction product		Eluate µg/L	Rel st dev %	Content product mg/kg	CEN /TS 16637-3 L/S		Cumulative amount leached mg/kg at L/S=10	Fraction of total leached %	CEN /TS 16637-2 area release mg/m^2
PAH	Recycled mixed									
Naftalene	aggregates		0,08	5,7	0,08	1,21			0,1210	
Acenaftylene	Eluate A		0,01	5,6		1,21				
Acenaftene			0,1	3,4		1,21				
Fluorene			0,06	3,7		1,21				
Fenanthrene			0,13	5,3	0,328	1,21			0,0480	
Anthracene			0,02	7	0,086	1,21			0,0281	
Fluoranthene			0,12	21,6	0,46	1,21			0,0316	
Pyrene			0,12	22,3	0,408	1,21			0,0356	
Benzo(a)anthracene			0,04	97,9	0,23	1,21			0,0210	
Chrysene			0,06	88,3	0,295	1,21			0,0246	
Benzo(b)fluoranthene					0,199	1,21				
Benzo(k)fluoranthene					0,109	1,21				
Benzo(a)pyrene					0,202	1,21				
Indeno(1,2,3,c,d)pyrene			0,04	95,8	0,137	1,21			0,0353	
Dibenzo(a,h)anthracene			0,05	102,4		1,21				
Benzo(g,h,i)perylene			0,05	98,1	0,145	1,21			0,0417	
PAH 10 sum			0,88	21,95	2	1,21				

Parameter	Construction product		Eluate µg/L	Rel st dev %	Content product mg/kg	CEN /TS 16637-3 L/S		Cumulative amount leached mg/kg at L/S=10	Fraction of total leached %	CEN /TS 16637-2 area release mg/m^2
PAH	Recycled mixed									
Naftalene	aggregates		0,04	10,4	0,08	8,79		0,1200	0,4395	
Acenaftylene	Eluate B			-		8,79		0,01		
Acenaftene			0,08	6,4		8,79		0,18		
Fluorene			0,04	1,9		8,79		0,1		
Fenanthrene			0,13	20,5	0,328	8,79		0,26	0,3484	
Anthracene			0,02	14,2	0,086	8,79		0,04	0,2044	
Fluoranthene			0,12	16,1	0,46	8,79		0,24	0,2293	
Pyrene			0,12	18,8	0,408	8,79		0,24	0,2585	
Benzo(a)anthracene			0,04	59,7	0,23	8,79		0,08	0,1529	
Chrysene			0,04	85,5	0,295	8,79		0,1	0,1192	
Benzo(b)fluoranthene					0,199	8,79				
Benzo(k)fluoranthene					0,109	8,79				
Benzo(a)pyrene					0,202	8,79				
Indeno(1,2,3,c,d)pyrene					0,137	8,79		0,04		
Dibenzo(a,h)anthracene						8,79		0,05		
Benzo(g,h,i)perylene					0,145	8,79		0,05		
PAH 10 sum			0,63	17,45	2	8,79		0,00151	0,0719	

Parameter	Construction product		Eluate µg/L	Rel st dev %	Content product mg/kg	CEN /TS 16637-3 L/S		Cumulative amount leached mg/kg at L/S=10	Fraction of total leached %	CEN /TS 16637-2 area release mg/m^2
PAH	Rubber crumbs									
Naftalene	Eluate A		0,11	0	0,49	1,46			0,0328	
Acenaftylene					0,84	1,46				
Acenaftene			0,04	4,1	1,12	1,46			0,0052	
Fluorene			0,02	5,1	1,24	1,46			0,0024	
Fenanthrene			0,03	3,3	7,66	1,46			0,0006	
Anthracene			0,01	7,5	1,31	1,46			0,0011	
Fluoranthene					9,69	1,46				
Pyrene			0,02	2,4	28,34	1,46			0,0001	
Benzo(a)anthracene					1,1	1,46				
Chrysene					3,19	1,46				
Benzo(b)fluoranthene					1,2	1,46				
Benzo(k)fluoranthene					0,39	1,46				
Benzo(a)pyrene					1,54	1,46				
Indeno(1,2,3,c,d)pyrene					0,74	1,46				
Dibenzo(a,h)anthracene						1,46				
Benzo(g,h,i)perylene					6,32	1,46				
PAH 10 sum			0,23	4,1	32	1,46				

Parameter	**Construction product**		**Eluate µg/L**	**Rel st dev %**	**Content product mg/kg**	**CEN /TS 16637-3 L/S**		**Cumulative amount leached mg/kg at L/S=10**	**Fraction of total leached %**	**CEN /TS 16637-2 area release mg/m^2**
PAH	Rubber crumbs									
Naftalene	Eluate B		0,11	2,5	0,49	8,48		0,22	0,19	
Acenaftylene			0,08		0,84	8,48		0,08	0,08	
Acenaftene			0,05	3,0	1,12	8,48		0,09	0,04	
Fluorene			0,04	2,3	1,24	8,48		0,06	0,03	
Fenanthrene			0,1	2,9	7,66	8,48		0,13	0,01	
Anthracene			0,02	5,4	1,31	8,48		0,03	0,01	
Fluoranthene			0,03	3,8	9,69	8,48		0,03	0,00	
Pyrene			0,06	2,3	28,34	8,48		0,08	0,00	
Benzo(a)anthracene					1,1	8,48				
Chrysene					3,19	8,48				
Benzo(b)fluoranthene					1,2	8,48				
Benzo(k)fluoranthene					0,39	8,48				
Benzo(a)pyrene					1,54	8,48				
Indeno(1,2,3,c,d)pyrene					0,74	8,48				
Dibenzo(a,h)anthracene						8,48				
Benzo(g,h,i)perylene					6,32	8,48				
PAH 10 sum	rubber crumbs		0,49	2,95	32			0,72	2,2	

Dioxins and Furans

Parameter	Construction product		Eluate ng/L	Rel st dev %	Content product ng/kg	CEN /TS 16637-3 L/S		Cumulative amount leached mg/kg at L/S=10	Fraction of total leached %	CEN /TS 16637-2 area release mg/m^2
PCDD/F	Rubber crumbs									
2378-TCDF		<	0,0022			1,46				
2378-TCDD		<	0,0011			1,46				
12378-PeCDF		<	0,0011			1,46				
23478-PeCDF		<	0,0011			1,46				
12378-PeCDD		<	0,0011			1,46				
123478-HxCDF		<	0,0018			1,46				
123678-HxCDF		<	0,0018			1,46				
234678-HxCDF		<	0,0018			1,46				
123789-HxCDF		<	0,0018			1,46				
123478-HxCDD		<	0,0018		2,3	1,46		<	0,11	
123678-HxCDD		<	0,0018		7,8	1,46		<	0,03	
123789-HxCDD		<	0,0018		4,2	1,46		<	0,06	
1234678-HpCDF		<	0,011		6,0	1,46		<	0,27	
1234789-HpCDF		<	0,011			1,46				
1234678-HpCDD		<	0,011		101	1,46		<	0,02	
OCDF *		<	0,022		9,9	1,46		<	0,32	
OCDD		<	0,022		638	1,46		<	0,01	

Parameter	Construction product		Eluate ng/L	Rel st dev %	Content product ng/kg	CEN /TS 16637-3 L/S		Cumulative amount leached mg/kg at L/S=10	Fraction of total leached %	CEN /TS 16637-2 area release mg/m^2
PCDD/F	Recycled mixed aggregate LS=1.21									
2378-TCDF			0,020	50		1,21				
2378-TCDD		<	0.0025			1,21				
12378-PeCDF			0,014			1,21				
23478-PeCDF			0,0085	50		1,21				
12378-PeCDD			0,002			1,21				
123478-HxCDF			0,005			1,21				
123678-HxCDF			0,0045			1,21				
234678-HxCDF			0,0043			1,21				
123789-HxCDF			0,003			1,21				
123478-HxCDD			0,004			1,21	<			
123678-HxCDD			0,0032			1,21	<			
123789-HxCDD			0,0033			1,21	<			
1234678-HpCDF		<	0,0025			1,21	<			
1234789-HpCDF		<	0,0025			1,21				
1234678-HpCDD		<	0,0025			1,21	<			
OCDF *		<	0,05			1,21	<			
OCDD		<	0,06			1,21	<			

Parameter	Construction product		Eluate ng/L	Rel st dev %	Content product ng/kg	CEN /TS 16637-3 L/S		Cumulative amount leached mg/kg at L/S=10	Fraction of total leached %	CEN /TS 16637-2 area release mg/m^2
PCDD/F	Recycled mixed									
2378-TCDF	aggregate		0,033	13,2		8,79				
2378-TCDD	LS=8.9	<	0,0025			8,79				
12378-PeCDF			0,0089			8,79				
23478-PeCDF			0,041	120		8,79				
12378-PeCDD			0,006	20,5		8,79				
123478-HxCDF		<	0,005			8,79				
123678-HxCDF		<	0,005			8,79				
234678-HxCDF		<	0,005			8,79				
123789-HxCDF		<	0,005			8,79				
123478-HxCDD			0,0076			8,79				
123678-HxCDD		<	0,005			8,79				
123789-HxCDD		<	0,005			8,79				
1234678-HpCDF		<	0,003			8,79				
1234789-HpCDF		<	0,003			8,79				
1234678-HpCDD		<	0,003			8,79				
OCDF *		<	0,006			8,79				
OCDD		<	0,006			8,79				

Dioxin-like PCB

Parameter	Construction product		Eluate ng/L	Rel st dev %	Content product ng/kg	CEN /TS 16637-3 L/S		Cumulative amount leached mg/kg at L/S=10	Fraction of total leached %	CEN /TS 16637-2 area release mg/m^2
dl-PCB	Rubber crumbs									
PCB-81		<	0,044		18,2	1,46		<	0,35	
PCB-77		<	0,088		370	1,46		<	0,03	
PCB-126 *		<	0,022		48,3	1,46		<	0,07	
PCB-169		<	0,022			1,46				
PCB-123		<	0,088		162	1,46		<	0,08	
PCB-118		<	0,88		7580	1,46		<	0,02	
PCB-114		<	0,088		172	1,46		<	0,07	
PCB-105		<	0,44		2780	1,46		<	0,02	
PCB-167		<	0,44		630	1,46		<	0,10	
PCB-156		<	0,44		1312	1,46		<	0,05	
PCB-157		<	0,088		202	1,46		<	0,06	
PCB-189		<	0,088		160	1,46		<	0,08	

Parameter	Construction product		Eluate ng/L	Rel st dev %	Content product ng/kg	CEN /TS 16637-3 L/S		Cumulative amount leached mg/kg at L/S=10	Fraction of total leached %	CEN /TS 16637-2 area release mg/m^2
dl-PCB	Recycled mixed aggregate LS=1.21									
PCB-81		<	0,046		18,2	1,21	<		0,31	
PCB-77		<	0,092		370	1,21	<		0,03	
PCB-126 *		<	0,023		48,3	1,21	<		0,06	
PCB-169		<	0,023			1,21	<			
PCB-123		<	0,092		162	1,21	<		0,07	
PCB-118		<	0,92		7580	1,21	<		0,01	
PCB-114		<	0,092		172	1,21	<		0,06	
PCB-105		<	0,46		2780	1,21	<		0,02	
PCB-167		<	0,46		630	1,21	<		0,09	
PCB-156		<	0,46		1312	1,21	<		0,04	
PCB-157		<	0,092		202	1,21	<		0,06	
PCB-189		<	0,092		160	1,21	<		0,07	

Parameter	Construction product		Eluate ng/L	Rel st dev %	Content product ng/kg	CEN /TS 16637-3 L/S		Cumulative amount leached mg/kg at L/S=10	Fraction of total leached %	CEN /TS 16637-2 area release mg/m^2
dl-PCB	Recycled mixed									
PCB-81	aggregate	<	< 0,10			8,79				
PCB-77	LS=8.9	<	< 0,20			8,79				
PCB-126 *		<	< 0,051			8,79				
PCB-169		<	< 0,051			8,79				
PCB-123		<	< 0,20			8,79				
PCB-118		<	< 2,0			8,79				
PCB-114		<	< 0,20			8,79				
PCB-105		<	< 1,0			8,79				
PCB-167		<	< 1,0			8,79				
PCB-156		<	< 1,0			8,79				
PCB-157		<	< 0,20			8,79				
PCB-189		<	< 0,20			8,79				

Phthalates

Parameter	Construction product		Eluate µg/L	Rel st dev %	Content product mg/kg	CEN /TS 16637-3 L/S		Cumulative amount leached mg/kg at L/S=10	Fraction of total leached %	CEN /TS 16637-2 area release mg/m^2
Phthalates	Sealant 1									
DMP	L/A = 80		0,04		0,27					0,0032
DEP	Fraction 1		0,7		0,01					0,056
DPropP		<	0,02		<0,01				<	0,0016
DIBP			2,58		0,062					0,2064
DBP			6,8		0,049					0,544
BBP			0,03		2,74					0,0024
DEHP			1,23	12	0,48					0,0984
DCHP			0,03		0,093					0,0024
DOP			0,07		-					0,0056
DDcP		<	0,02		<0,03				<	0,0016
DUP		<	0,02		<0,03				<	0,0016

Parameter	Construction product		Eluate µg/L	Rel st dev %	Content product mg/kg	CEN /TS 16637-3 L/S		Cumulative amount leached mg/kg at L/S=10	Fraction of total leached %	CEN /TS 16637-2 area release mg/m^2
Phthalates										
DMP	Sealant 1	<	0,02		0,27				<	0,0016
DEP	L/A = 80		0,36		0,01					0,0288
DPropP	Fraction 3	<	0,02		<0,01				<	0,0016
DIBP			2,4		0,062					0,192
DBP			3,18		0,049					0,2544
BBP			0,03		2,74					0,0024
DEHP			0,9	26	0,48					0,072
DCHP			0,07		0,093					0,0056
DOP			0,19		-					0,0152
DDcP		<	0,02		<0,03				<	0,0016
DUP		<	0,02		<0,03				<	0,0016

Pentachlorophenol

Parameter	Construction product		Eluate µg/L	Rel st dev %	Content product mg/kg	CEN /TS 16637-3 L/S		Cumulative amount leached mg/kg at L/S=10	Fraction of total leached %	CEN /TS 16637-2 area release mg/m^2
PCP	Wood		4,85	6,2	3,76	10		1,29		0,388

Biocides

Parameter	Construction product		Eluate µg/L	Rel st dev %	Content product mg/kg	CEN /TS 16637-3 L/S		Cumulative amount leached mg/kg at L/S=10	Fraction of total leached %	CEN /TS 16637-2 area release mg/m^2
Biocides	Wood									
propiconazole	L/A = 80		39,6		72,3					3,17
tebuconazole	Eluate A		50		71,8					4,00
propiconazole	L/A = 80		52		72,3					4,16
tebuconazole	Eluate B		68,2		71,8					5,46

Parameter	Construction product		Eluate µg/L	Rel st dev %	Content product mg/kg	CEN /TS 16637-3 L/S		Cumulative amount leached mg/kg at L/S=10	Fraction of total leached %	CEN /TS 16637-2 area release mg/m^2
Biocides	Sealant 2									
diuron	L/A = 80	<	0,1						<	0,01
terbutryn	Eluate A	<	0,1						<	0,01
MIT			290		34,6					23,20
BIT			150		32,3					12,00
OIT		<	0,1						<	0,01
CMIT		<	0,1		0,01				<	0,01
diuron	L/A = 80	<	0,1						<	0,01
terbutryn	Eluate B	<	0,1						<	0,01
MIT			509		34,6					40,72
BIT			364		32,3					29,12
OIT		<	0,1						<	0,01
CMIT		<	0,1		0,01				<	0,01

Parameter	Construction product		Eluate µg/L	Rel st dev %	Content product mg/kg	CEN /TS 16637-3 L/S		Cumulative amount leached mg/kg at L/S=10	Fraction of total leached %	CEN /TS 16637-2 area release mg/m^2
Biocides	Render 2									
diuron	L/A = 80		1,756		498					0,14
terbutryn	Eluate A		0,27		455					0,02
MIT			25,22		534					2,02
BIT			23,63		771					1,89
OIT			1,054		555					0,08
carbendazim			0,375		318					0,03
diuron	L/A = 80		1,746		498					0,14
terbutryn	Eluate B		0,373		455					0,03
MIT			3,519		534					0,28
BIT			3,788		771					0,30
OIT			1,231		555					0,10
carbendazim			0,615		318					0,05

Phenols

Parameter	Construction product		Eluate µg/L	Rel st dev %	Content product mg/kg	CEN /TS 16637-3 L/S		Cumulative amount leached mg/kg at L/S=10	Fraction of total leached %	CEN /TS 16637-2 area release mg/m^2
Phenols	Water proofing									
phenol	sheets		1181		180					94,5
bisphenol A	L/A = 80		1,2		0,11					0,10
								(remark: blank contribution)		
nonylphenol	Eluate A		2,11		1,69					0,17
NP monoethoxylate		<	0,1		<0,005				<	0,01
NP diethoxylate		<	0,1		0,018				<	0,01
phenol	L/A = 80		1333		180					106,6
bisphenol A	Eluate B		0,65		0,11					0,05
								(remark: blank contribution)		
nonylphenol			2,02		1,69					0,16
NP monoethoxylate		<	0,1		<0,005				<	0,01
NP diethoxylate		<	0,1		0,018				<	0,01

Parameter	Construction product		Eluate µg/L	Rel st dev %	Content product mg/kg	CEN /TS 16637-3 L/S		Cumulative amount leached mg/kg at L/S=10	Fraction of total leached %	CEN /TS 16637-2 area release mg/m^2
Phenols	Render 1									
nonylphenol	L/A = 80		2,76					(remark: blank contribution)		0,22
NP monoethoxylate	Eluate A	<	0,1						<	0,01
NP diethoxylate		<	0,1						<	0,01
nonylphenol	L/A = 80		2,56					(remark: blank contribution)		0,20
NP monoethoxylate	Eluate B	<	0,1						<	0,01
NP diethoxylate		<	0,1						<	0,01

Compliance check of results of content determinations

Parameter	Construction product	Content mg/kg*	St dev mg/kg	Rel st dev %	Regulatory criteria on content mg/kg NL	Ratio Product/ Reg Limit - NL	Regulatory criteria on content mg/kg DE	Ratio Product/ Reg Limit - DE
Mineral oil	asphalt aggregate	2795	182	6,5	500	5,6		
Mineral oil	recycled mixed aggregates	709	76	10,7	500	1,4		
PAH 10 sum	asphalt aggregate	810	87,5	10,8	50	16,2	25	32,4
PAH 10 sum	recycled mixed aggregates	2,1	0,2	13,4	50	0,041	25	0,08
PAH 10 sum	Roofing felt	19,8	2,1	5,0	50	0,40	25	0,79
PAH 10 sum	rubber crumbs	32,4	3,5	2,0	50	0,65	25	1,30
Dioxin sum (corrected with TEF)*	rubber crumbs	2,69	0,4	14,6			100	0,03
sum PCB's	recycled mixed aggregate	82,6	9,2	11,1	500	0,17		

**dioxins in ng TEQ/kg*

Compliance check of results of eluate determinations

Parameter	Construction product	Eluate µg/L	Rel st dev %	Content product mg/kg	CEN/TS 16637-3 L/S	Cumulative amount leached mg/kg at L/S=10	Fraction of total leached %	CEN/TS 16637-2area release mg/m^2	Regulatory criteria on water quality WHO µg/L NL	Ratio Product/ Reg Limit
PAH 10 sum	asphalt aggregate	4,74	15	810	1,09				0,7	6,8
PAH 10 sum	asphalt aggregate	1,28	19,1		8,91	0,006	0,0007		0,7	1,8
PAH 10 sum	recycled mixed aggregates	0,88	21,95	2,1	1,21				0,7	1,3
PAH 10 sum	recycled mixed aggregates	0,63	17,45		8,79	0,00151	0,073		0,7	0,9
PAH 10 sum	rubber crumbs	0,23	4,1	32	1,46				0,7	0,3
PAH 10 sum	rubber crumbs	0,49	2,95		8,48	0,00072	0,0022		0,7	0,70
DEHP	sealant 1	1,23	12	0,48	Fraction 1			0,098	8	0,15
DEHP	sealant 1	0,9	26	0,48	Fraction 3			0,072	8	0,11
PCP	wood	4,85	6,2	3,76	10	1,29	34	0,388	9	0,54