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Emission of Flame Retardants from Consumer Products and Building Materials

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16. Abstract

Various insulating boards, assembly foams, PC-systems, upholstery and a mattress were examined for possible emissions of polybrominated and organophosphorus flame retardants. 0.02 m^3- and $1m^3$- emission test chambers and 1Llitre cells were used to perform the investigations. The substances of interest are mainly classified as SVOC. A sampling technique using polyurethane foam plugs and special analytical methods was developed. The PUF-plugs were extracted by ultrasonic and soxhlet extraction and the extracts were concentrated. The analyses were performed by GC/MS and HPLC/DAD. Chamber measurements were generally taken over 28 days, but in the case of SVOC, a test period of a minimum of 100 days was necessary to achieve equilibrium. The determination of most of OPCs was successful using emission test chambers. Due to sink effects the determination of low volatile OPC such as RDP and BDP needs to be improved. Brominated flame retardants are quantifiable up to hexabrominated compounds using emission test chambers as a reference method. The emission of lower volatile compounds, e.g. HBCD, was strongly affected by sink effects. Emission of decaBDE was not quantifiable at all. Based on the results presented further investigations are required for an adequate risk assessment of flame retarded products and their contribution to the contamination of the indoor air environment. TCPP was found to be one of the most commonly used organophosphorus flame retardants in polyurethane foam applications. Depending on the sample type 0.012 to 140 $\mu g\ m^{-2}\ h^{-1}$ was obtained for area-specific emission rates (SER_a) for TCPP. PBDEs, for example, exhibited product-specific emission rates (SER_u) between 0.1 and

14.2 $ng\ unit^{-1}\ h^{-1}$ and SER_a between 0.2 and 6.6 $ng\ m^{-2}\ h^{-1}$. More data about the emission behaviour of FR are required with special regard to substance migration, aging and long-term emission in particular.

17. Keywords

Emission, Semi Volatile Organic Compounds (SVOC), polybrominated flame retardants, organophosphorus flame retardants, emission test chamber, emission test cell, particulate organic matter (POM), insulating boards, assembly foams, printed circuit board, upholstery, mattress, PC-system, printer, monitor.

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Symbols, Abbreviations

1-C-PUR	One-component-polyurethane
a	Product loading factor
A	Area
ABS	Acrylnitrilbutadienestyrene
A_{Em}	Emission area of the sample
A_t	Insulation area in the model
A_{IS}	Peak area of internal standard
$Al(OH)_3$	Aluminium hydroxide
AMAP	Arctic Monitoring and Assessment Programme
ARR	Analyte recovery rate
ASA	Acrylnitrilstyreneacrylester copolymers
AU, a.u.	Response (in arbitrary units)
BB101	2,2’,4,5,5’-Pentabromobiphenyl
BB153	2,2’,4,4’,5,5’-Hexabromobiphenyl
BB209	2,2’,3,3’,4,4’,5,5’,6,6’-Decabromobiphenyl
BB31	2,4’,5-Tribromobiphenyl
BB4	2,2’-Dibromobiphenyl
BB52	2,2’,5,5’-Tetrabromobiphenyl
BDE100	2,2’,4,4’,6-Pentabromodiphenylether
BDE138	2,2’4,4’,5,5’-Hexabromodiphenylether
BDE153	2,2’,4,4’,5,5’-Hexabromodiphenylether
BDE154	2,2’4,4’,5,6’-Hexabromodiphenylether
BDE190	2,3,3’,4,4’,5,6-Heptabromodiphenylether
BDE209	2,2’,3,3’,4,4’,5,5’,6,6’-Decabromodiphenylether
BDE3	4-Monobromodiphenylether
BDE32	2,4,6-Tribromodiphenylether
BDE47	2,2’,4,4’-Tetrabromodiphenylether
BDE66	2,3’,4,4’-Tetrabromodiphenylether
BDE8	2,4’-Dibromodiphenylether
BDE85	2,2’,3,4,4’-Pentabromodiphenylether
BDE99	2,2’,4,4’,5-Pentabromodiphenylether
BDP	Bisphenol-A-bis(diphenyl-)phosphate
BRITE-EURAM III	Specific research and technological development programme in the field of industrial and materials technologies
BROC	Biological reference materials for organic contaminants
BSEF	Bromine Science and Environmental Forum
BV	Blank value
c	Concentration

CEM	Composite Epoxy Material
CEN TC	European Committee for Standardization Technical Committee
c_{eq}	Equilibrium concentration
CMHR	Combustion modified High-Resilience
COMPREHEND	Community Programme of Research on Environmental Hormones and Endocrines Disrupters
DEEP	Diethylethanephosphonate
DeBB	Decabromobiphenyl
DecaBDE	Decabromodiphenylether
DrL	Determination limit
d_F	Film thickness of the effective phase
DMMP	Dimethylmethylphosphonate
DOPO	9,10-Dihydro-9-oxa-10-phospha-phenanthrene-10-oxide
DPC	Diphenylcresylphosphate
DS^2	Difference of variances
EFRA	European Flame Retardants Association
EG	European Community (Europäische Gemeinschaft)
EI	Electron Impact Ionization
EPS	Expanded polystyrene
ER	Emission rate
f	Degree of freedom
FLEC	Field and Laboratory Emission Cell
FR	Flame retardant
GC	Gas chromatography
GLOBAL-SOC	Global mass balance of persistent semivolatile organic compounds: an approach with PCB as an indicator
H_3PO_4	Phosphoric acid
HARP-HAZ	Harmonized Quantification and Reporting Procedures for Hazardous Substances
HB	Hexabromobenzene
HBCD	Hexabromocyclododecane
HELCOM	Helsinki Commission
HeptaBDE	Heptabromodiphenylether
HexaBDE	Hexabromodiphenylether
HIPS	High Impact Polystyrene
HPLC	High Performance Liquid Chromatography
HR	High-Resilience

ICES	International Council for the Exploration of the Sea
ID	Internal diameter
IM1, IM2	Ion mass for better securing peak attribution
IPCS	International Programme on Chemical Safety
IS	Internal Standard
IT	Information technology
IVPU	Polyurethane Hard Foam Industrial Association (Industrieverband Polyurethan-Hartschaum e.V.)
L	Length
m_{tot}	Overall mass of emitted organophosphate compounds
m_{PU}	Emitted mass from insulation foam
MS	Mass spectrometry
MSD	Mass selective detector
$m_{w.gl}$	Emitted mass on watch glass surface (convex glass piece)
n	Air exchange rate
NCI	Negative Chemical Ionisation
DcL	Detection limit
NMR	Nuclear magnetic resonance spectroscopy
NonaBDE	Nonabromodiphenylether
OctaBDE	Octabromodiphenylether
OECD	Organisation for Economic Co-operation and Development
OPC	Organophosphorus compound
OSPAR DIFFCHEM	Oslo and Paris Working Group on Diffuse Sources
OSPARCOM	Oslo and Paris Commission
PA	Polyamide
PBB	Polybrominated biphenyls
PBDE	Polybrominated diphenylether
PBFR	Polybrominated flame retardant
PBT	Poly-butyleneglycol-terephthalate
PC	Personal Computer
PC	Polycarbonate
PE	Polyethylene
PentaBDE	Pentabromodiphenylether
PIR	Polyisocyanurate
POM	Particulate organic matter
POP	Persistent organic pollutants
PP	Polypropylene

PPE	Polyphenylene ether
PPO	Polyphenylene oxide
PS	Polystyrene
PSE	Phosphoric acid ester
PU	Polyurethane
PUR	Polyurethane
q	Area-specific air flow rate
QM	Ion mass for quantification
R.H.	Relative air humidity
RDP	Recorcinol-bis-(diphenyl-)phosphate
RDS	Relative standard deviation
s_1^2	standard deviation of first-degree function
s_2^2	standard deviation of second-degree function
SCOW	Supercritical fluids to extract and/or degrade organic waste
Ser. No.	Consecutive, sequential, serial number
SER_a	Area-specific emission rate
SER_u	Unit-specific emission rate
SIM	Single Ion Monitoring
SNR	Signal to noise ratio
SVOC	Semi Volatile Organic Compounds
T	Temperature
TBBPA	Tetrabromophenol A
TBEP	Tris(2-butoxyethyl)phosphate
TBP	Tributylphosphate
TCEP	Tris(2-chlorethyl)phosphate
TCO	Tjänstemännens Central Organisation
TCPP	Tris(2-chloroisopropyl)-phosphate
TDCP	Tris(1,3-dichloroisopropyl)phosphate
TEGEWA	Association of Textile Auxiliary, Leather Auxiliary, Tanning Agent and Washing Raw Material Industry (Verband der Textilhilfsmittel-, Lederhilfsmittel-, Gerbstoff- und Waschrohstoff-Industrie)
TEHP	Tris(2-ethylhexyl)phosphate
TEP	Triethylphosphate
TetraBDE	Tetrabromodiphenylether
t_{total}	Overall test duration
TMTP	Tris(meta-tolyl)phosphate
TOTP	Tris(ortho-tolyl)phosphate

TPTP	Tris(para-tolyl)phosphate
TPP	Triphenylphosphate
Trevira CS	permanent fireproof textile
TRGS	Technical Regulations to the Provision on Hazardous Substances (Technische Regeln zur Verordnung über gefährliche Arbeitsstoffe)
TriBDE	Tribromodiphenylether
TV	Test value
UFOPLAN	Environmental Research Programme (Umweltforschungsplan)
UNECE	United Nations Economic Commission for Europe
UNEP	United Nations Environment Programme
UV	Ultraviolet
V	Volume
V°	Air volumetric flow rate
VCI	Association of Chemical Industries (Verband der chemischen Industrie
CD (VE)	Complete desalination (Vollentsalzung)
V_{total}	Total volume of model room
VKE	Association of Plastics Manufacturing Industry (Verband der kunststofferzeugenden Industrie)
VOC	Volatile Organic Compounds
V_{xo}	Relative process standard deviation
WEEE	Waste Electrical and Electronic Equipment
WG	Working Group
WHO	World Health Organisation
$\bar{x}$	Mean value
XPS	Extruded polystyrene
XRF	X-ray fluorescence analysis
ρ	Density

Abstract

Introduction

Since the interior atmosphere represents a major part of the built environment, determining emissions from those sources which influence indoor air quality is of great importance. Recently, interest has been focussed on flame retardants (FR) which have been increasingly used in consumer and building products in combination with a rapid increase in the use of plastics. The aim of the research project initiated by the Federal Environmental Agency (Germany) is the investigation of the emission behaviour of selected FRs from interior-relevant products.

Flame retardant emission has been tested on a number of consumer goods and building products within this project. The products tested (insulation and assembly foams, IT devices, upholstered furniture, upholstery foams, mattresses and circuit boards) represent a cross-section of products relevant for use indoors.

Analytical methods and materials

The tests were performed in emission test chambers and cells of various sizes in combination with suitable sampling and analysis methods. Emission test chambers with volumes of 0.02 m³ (per DIN 55666) and 1 m³ were used within this project as well as 0.001m³ BAM emission test cells for the investigations and all operated under the same standard climatic conditions at T = 23 °C and R.H. = 50 %. The principle of mantle tempering was used for all emission test chambers and cells. The documents from CEN TC 264, WG 7 (Air properties, emissions from building materials) and CEN TC 112, WG 5 (Wooden materials, formaldehyde) set the relevant technical basis for the execution of emission tests and the design of emission test chambers. The standard DIN V ENV 13419, Part 1 - 3 compiled in connection with CEN TC 264, WG 7 contains the determination of emissions of volatile organic compounds (VOC) by emission test chambers and cells and the production, treatment and preparation of emission samples.

The product loading factor was calculated depending on product type and 17.4 m^3 of model room volume and 7 m^2 of floor area was used (DIN V ENV 13419-1). A unit-specific air flow rate was introduced instead of a surface-specific air flow rate for products with a non-specific surface (for example PC systems). Test parameters (volumetric air flow rate, air flow rate, sampling volume etc.) are adjusted to the product properties accordingly.

The following flame retardants were analysed: polybrominated diphenylethers (PBDE), polybrominated biphenyls (PBB), hexabromocyclododecane (HBCD), tetrabromo-bisphenol A (TBBPA), chloroparaffins, and halogenated and non-halogenated organophosphate compounds (OPC). The physicochemical characteristics of the analysed emitters, which mainly belong to the semivolatile organic compounds (SVOC), require air sampling by adsorption on polyurethane foam (PUR foam). The testing time is usually at least 100 days, in some cases 200 days, in order to ensure development of a steady state which is necessary for the measurement. Sample preparation of the PUR foam takes place by soxhlet or ultrasonic bath extraction using suitable organic solvents. Identification and quantitative determination are performed by gas chromatography/mass spectrometry (GC/MS) or High Performance Liquid Chromatography (HPLC) and following UV detection.

Results

Experiments carried out in emission test chambers of different sizes reflect the substantial problem of SVOC analysis: it is to be expected that sink effects would strongly influence the analytical results due the physicochemical properties of the tested organophosphate and bromine containing compounds. Experimental results showing that about 25 % to 100 % of the emitted flame retardants are adsorbed by the chamber walls, confirm this expectation. Qualitative tests are carried out on flame retardants by direct extraction and GC/MS analysis as well as x-ray fluorescence analysis for preparation and check of emission tests.

The results described in the following are summarised according to the individual product groups.

Insulation foams

Chlorinated organophosphates are extensively used in building products. TCPP is especially important in this respect which, as this study shows, is mainly used in insulation foams and also in assembly and upholstery foams.

One group of the insulation foams tested within the project was polyisocyanurate foams (PIR), which was directly delivered by the manufacturer from current production. Two different PIR foams were used for the tests, which differ in their density and accordingly in their flame retardant content. These foams were also tested in different emission chambers and cells (0.02 m^3 / 0.001 m^3) to determine the influence of different test chamber sizes and the resulting sink effects. Area-specific emission rates in the range of 0.3 to 0.7 $\mu g\ m^{-2}\ h^{-1}$ can be estimated from the equilibrium concentrations and total emitted masses during the test period. The comparison of both test chamber systems shows that a more favourable source to sink ratio, as in the 0.001 m^3 emission cell, leads to slightly increased measured values.

HBCD is used almost exclusively for flame retarding purposes in polystyrenes. Expanded polystyrene (EPS) was used for the determination of the HBCD emission - specifically manufactured for the tests' purposes. HBCD content was between 1-2% according to the manufacturers' data. Comparative measurements were also performed in different test chambers in this instant. Apart from traces, no HBCD emission could be detected above the detection limit of the procedure of 0.33 $ng\ m^{-3}$ in any of the test chambers under the appropriate test conditions during a testing time of 105 days. Rinsing the chamber and cell walls with organic solvents resulted in a value between 1-3 $\mu g\ m^{-2}$ HBCD at the chamber walls. Comparative emission tests of HBCD were accomplished on extruded polystyrene (XPS). The HBCD content was under 1% according to manufacture data. No emission could be detected under the appropriate test conditions for XPS in the 0.02m^3 emission test chamber. On the other hand the 0.001m^3 emission test cell provided trace concentrations of up to 1.79 $ng\ m^{-3}$ from a testing time of 105 days. However, the values fell again under the detection limit after 150 days and no HBCD could be measured in the later part of the test. The chamber and cell walls were also rinsed with organic solvents after the end of the test. Area-specific emission rates of 1-4 $ng\ m^{-2}\ h^{-1}$ for EPS and 0.1 - 29 $ng\ m^{-2}\ h^{-1}$ for XPS were calculated from the HBCD contents determined at the wall surfaces. It cannot be excluded that the measurement values obtained are too small due to possible decomposition and lack of HBCD solubility.

The determination of decaBDE emission from vulcanised rubber took place in a $0.02m^3$ emission test chamber with a testing time of up to 277 days. Neither air sampling nor chamber wall rinsing was able to reveal any decaBDE emission considering the determination limit of 6 ng m^{-3}. The possibility also exists in this case that the compound cannot be analytically detected due to insolubility, possible decomposition or strong adsorption on the chamber walls. A material analysis accomplished at the end of the test failed to provide any indication on the presence of further PBDEs in the material. In addition to brominated flame retardants the synthetic rubber also contains organophosphorus compounds in a technical mixture of DPC, containing about 20 % TPP. Emission rates of approx. 85 ng m^{-2} h^{-1} were calculated for DPC and about 50 ng m^{-2} h^{-1} for TPP from the equilibrium concentrations using the concentration profiles, which reflect the steady-state conditions of the system after about 100 days.

The determination of chloroparaffin emission (according to the manufacturer’s data: 70 % chlorine content, chain length C_{16-20}) from closed-cell polyethylene insulation foam took place in a $0.02m^3$ emission test chamber under standard conditions. No emission was detected during a test period of up to 203 days.

Assembly foams

Assembly foams used in this study were closed-cell polyuretane foams (PUR), which are produced from in situ pressurised vessels. B2 assembly foams manufactured for the tests contained either preparations with a flame retardant content of 14 to 18 % of TCPP or a preparation without additive halogenated flame retardants; a mixture of technical DPC and TEP. No TCEP could be found in any of the tested insulation and assembly foams in view of the detection limits. A multiple of the emission rates is expected due to a strongly increased flame retardant content in assembly foams (compared with insulating materials). The experiments gave emission rates of between 40 and 70 µg m^{-2} h^{-1} for TCPP.

Halogen free OPC from an assembly foam exhibited emission rates of 125 ng m^{-2} h^{-1} for DPC and 130 ng m^{-2} h^{-1} for TPP, which was determined from the equilibrium concentrations. Since the DPC preparation is a technical mixture, which contains up to 20 % of TPP, the almost identical emission rates can be explained by comparable physicochemical data.

IT devices

Two PC workplaces were tested in $1m^3$ emission test chambers under operational conditions to investigate the emission behaviour of polybrominated and organophosphate flame retardants from IT devices. Potential sources for flame retardant emission are the plastics used in the cases. Which FR is actually used, depends on the respective polymer type. The printed circuit boards used may represent another source of emission. The base material, component parts and solder stop are sometimes treated with different flame retardants. In addition, there are flame retarded cables and small components. Therefore all guide substances of PBDE, PBB and OPC plus TBBPA and HB were tested in the emission samples.

Workplace A consisted of a monitor, a computer, a keyboard, a mouse and a printer of different manufacturers. The case plastic of the monitor is PC/ABS as per manufacturer data, with a TCO99 conform FR on phosphorus basis. ABS, PC-PS FR 40, HIPS and PC were determined as plastics of the printer case. The computer inclusive mouse and keyboard is a system unit with ABS as the case plastic. Since the model is TCO labelled and no halogen free flame retardant is available for ABS because of material properties, it has to be assumed that no flame retardant was used for this case.

Work place A was tested for 93 days altogether to determine the emission of polybrominated and organophosphate FR. Traces of a tetrabromodiphenylether (BDE47) and three pentabromodiphenylethers (BDE100, BDE99 and BDE85) were detected among polybrominated FRs and the concentrations were below 0.27 ng m^{-3}. These values were below the detection limit at the end of the test. Hexabromobenzene (HB) was found in concentrations of around 1 ng m^{-3}. Due to the physicochemical characteristics of these substances it has to be assumed that a large part of the emitted components are adsorbed on the walls of the $1m^3$ emission test chamber. The tested product surfaces themselves make a contribution of their own, which can exert a sink effect on the emitted components. Since polybrominated flame retardants are not contained in the case plastics, the PBDEs trace concentrations are very probably due to small components and flat units. The x-ray fluorescence analysis supports this assumption. The cause behind the occurrence of hexabromobenzene is difficult to explain based on available data.

Work place B consisted of a monitor, a computer, a keyboard and a mouse from the same manufacturer. The plastic case of the monitor is marked with the TCO99 and the German "Blue Angel" environmental label and is treated with halogen free FR based on phosphorus. The computer front panel and the keyboard do not contain any flame retardants according to the manufacturers' data.

Emission tests on polybrominated flame retardants were performed over a period of 152 days. The work place tested exhibited no emission of polybrominated flame retardants. The only exception was hexabromobenzene, which was found here too in trace concentrations around 1 ng m^{-3} which dropped below the detection limit in the following part of the test. In order to achieve a more effective and sensitive sampling of the components adsorbed on the chamber walls, the empty $1m^3$ emission test chamber was fired after the end of the test at 80 °C for 6 hours and a $0.54m^3$-volume sample was taken. 150 ng m^{-3} of a tetraBDE (BDE47) and 28 and 61 ng m^{-3} of two pentaBDEs (BDE100, BDE99) were detected. In addition, traces of an unknown heptaBDE isomer and hexaBDE BDE153 were found. A number of circuit board components, the mainboard and various small components may be considered as possible sources for PBDEs detected. The results of x-ray fluorescence analysis support this theory. The results on the PC work places tested suggest that very low emission of polybrominated flame retardants in particular can be expected.

TPP, RDP and BDP emission was found in both PC work places tested. The printer case tested also showed the same qualitative findings. Therefore the experiments reflect the trend to use triaryl and bisphosphates as flame retardants. The unit-specific emission rate of TPP is common to all three product groups tested and is between 30 and 50 ng $unit^{-1}$ h^{-1}. These calculations were based on equilibrium indoor air concentrations of c_{eq} = 85 ng m^{-3} (PC work place A) and c_{eq} < 50 ng m^{-3} (PC work place B). Emission concentrations under steady-state conditions and a comparison of the unit-specific emission rates for the two other organophosphates reveal significant differences. RDP dominates the emission (SER_{RDP} ~ 13 - 49 ng $unit^{-1}$ h^{-1}) for PC work place A, while BDP with emission rates of SER_{BDP} = 40 - 50 ng $unit^{-1}$ h^{-1} and 12 ng $unit^{-1}$ h^{-1} dominates the measurements for PC work place B and the additional printer case tested. However, further data are missing to interpret the measurements in detail. The clearly positive proof of a halogenated phosphoric acid ester (TCPP), which first contradicted manufacturer data, is possibly due to a unidentified contamination.

As a comparison the emission of polybrominated FR was tested additionally on two old cases. One of them (date of manufacture 1995) was flame retarded with TBBPA. No TBBPA emission was found during a test period of 153 days taking into account a determination limit of 0.3 ng m^{-3} for diacetyl TBBPA. A TBBPA content of 356 ng m^{-2}

was determined on the chamber walls after the end of the test, from which an area-specific emission rate of 369 pg m^{-2} h^{-1} was obtained.

The second old case (manufactured in 1979 or earlier) was a part (0.07 m^{-2}) of a television rear wall which, according to the data of the University of Erlangen-Nuremberg, contains the flame retardant octaBDE. A triBDE (BDE28: max. 0.5 ng m^{-3}), two tetraBDE (BDE47: max. 8 ng m^{-3}; BDE66: max. 0.24 ng m^{-3}) and two pentaBDE isomers (BDE100: max. 0.27 ng m^{-3}, BDE99: max. 0.84 ng m^{-3}) were found in measurable concentrations in the emission samples. After the end of the test the flame retardant contents 568 ng m^{-2} of tetraBDE (BDE47) and 514 ng m^{-2} of pentaBDE (BDE99) were found in the rinsed fractions. In addition, clearly detectable contents of two hexaBDE isomers (BDE154: 95 ng m^{-2} and BDE153: 460 ng m^{-2}) were determined, of which only traces were found in the emission samples. Furthermore the complete octaBDE product was detected on the chamber walls. Since the sample tested was over 20 years old, it cannot be decided any longer whether the PBDEs with moderate degree of bromination resulted from decomposition during the long storage time, or were already present as impurities in the product. The following emission rates were obtained from the FR contents determined at the wall surfaces (in ng m^{-2} h^{-1}): 4.5 (heptaBDE), 1.5 (octaBDE), 0.83 (nonaBDE) and 0.28 (decaBDE).

Circuit boards

Emission of additives from materials is affected considerably by temperature. A flame retarded circuit board was examined in two test periods first at 23 °C and then at 60 °C to investigate the influence of temperature on possible emissions. The circuit board was of type CEM3, whose base material was flame retarded by a reactive organophosphate component. The circuit board is additionally encased by a plastic case and this case contains < 12 % of TPP according to manufacturer data.

The investigations at 23 °C supplied values between 1-3 ng m^{-3} for a triBDE (BDE28) and a tetraBDE (BDE47). The emission chamber test at 60 °C showed a clear concentration increase of the proven PBDE and further PBDEs were identified. Thus an increase of up to 500 ng m^{-3} was found for BDE47. Furthermore three pentaBDE (BDE85, BDE99 and BDE100), another triBDE (BDE17) and a hexaBDE (BDE154) were identified. Unit-specific emission rates were calculated from the data obtained after the analysis of the rinse fraction and the overall emission of the single PBDEs. So an emission rate of 0.6 (BDE17) and 1.9 ng $unit^{-1}$ h^{-1} (BDE28) was calculated for the two tribromodiphenylether. Tetrabromodiphenylether BDE47 supplied the highest value with 14 ng unit^{-1} h^{-1}. Further emission rates obtained were (in ng unit^{-1} h^{-1}): 0.4 (tetraBDE 66); 1.3 (BDE100), 2.6 (BDE99), 0.1 (BDE 85), 0.1 (BDE154) and 0.04 (BDE153). Qualitative analyses on materials, which were accomplished by direct extraction and GC/MS analysis as well as with x-ray fluorescence analysis, confirmed the emission measurements and provided hints on to the sources of emission for the polybrominated components.

The influence of temperature is also clearly visible in connection with organophosphorus compounds. Under normal conditions no RDP and BDP emission can be detected by air sampling. TPP concentration approaches an equilibrium value of approx. 40 ng m^{-3}, which corresponds to an emission rate of 5 ng unit^{-1} h^{-1}. Tempering of the experimental setup at 60 °C results in a clear change of the concentration profiles. Concentration of TPP, determined by air sampling, rises to a maximum; the equilibrium concentration of 2 µg m^{-3} determined from the experiment, leads to an emission rate of 250 ng unit^{-1} h^{-1}. The two other OPCs also show characteristic concentration profiles at 60 °C, which can be determined by air sampling. Unit-specific emission rates 25 ng unit^{-1} h^{-1} for RDP (c_{eq} = 200 ng m^{-3}) and 250 ng unit^{-1} h^{-1} for BDP (c_{eq} = 2 µg m^{-3}) can be calculated from the steady-state equilibrium concentrations.

Upholstered furniture and mattresses

The products investigated in this study were a mattress (Germany), an upholstery foam (European Market, England) and an upholstered stool (English market). A PUR soft foam was used in all cases as a polymer matrix which was flame retarded by TCPP (3-7 % mattress; 5-10 % upholstery foam). The following emission rates were obtained: 75 µg m^{-2} h^{-1} (upholstery foam), 36 µg m^{-2} h^{-1} (upholstered stool covered with upholstery fabric) and 12 ng m^{-2} h^{-1} (mattress). A emission rate of TCPP from the upholstered stool, decreased by a factor 2 in comparison with the foam, can be explained by the fact that the foam is coated by an upholstery fabric (see also PBFR). The determined room air concentrations and emission rates of TCPP belong to the highest values determined in this study. The reduced emission from the mattress cannot be explained by test results available.

Since according to manufacturer data the upholstery fabric is flame retarded by polybrominated flame retardants in contrast to soft foam, the upholstered stool was also tested for possible PBFR emissions. However no emission of brominated organic compounds could be detected up to a testing time of 168 days. Subsequently, the material was qualitatively tested by direct extraction. This showed the following flame retardants: decabromodiphenylether, various nonabromodiphenylether isomers, hexabromocyclododecane and further moderately brominated cyclododecanes and a row of unidentified brominated compounds. HBCD and decaBDE are used as standard compounds for back finishing of upholstery materials. The results of the emission tests confirm the results of the investigations on HBCD and decaBDE described for insulating materials. Also there is no emission of decaBDE and only a low emission of HBCD could be detected.

Discussion

The procedures used are well suited to detect the emission of organophosphorus compounds both qualitatively and quantitatively, in particular tris(1-chloro-2-propyl) phosphate (TCPP), triphenylphosphate (TPP) and diphenylcresilphosphate (DPC). Exceptions are recorcinol-bis-(diphenylphosphate) (RDP) and bisphenol-A-bis(diphenyl-phosphate) (BDP), for which the emission tests by air sampling are dominated by sink effects. The analysis methods are well suited to be applied for brominated flame retardants with up to six bromine atoms. With decreasing volatility the influence of sink effects becomes stronger and hampers the determination of emission. Thus hexabromocyclododecane (HBCD) was detected on the wall surfaces of emission test chambers, but, apart from traces, not in emission test chamber air. The results are not sufficient for a comprehensive representation of the emission behaviour and exposition assessment of flame retardants. There are further gaps in our knowledge, for example, concerning the explanation of high flame retardant contents in house dust. Nevertheless, the study provides a substantial basis for follow-up investigations. It appears desirable to extend the investigations, for example, to long-term measurements for test periods over 1 year and to determine the influence of material aging and various flame retardant concentrations on the emission.

1 Introduction and objectives

In principle, almost all materials used indoors are capable of emitting different types of substances into the interior atmosphere. Since this atmosphere represents a major part of the built environment, determining emissions from those sources which influence indoor air quality is of great importance.

Recently, interest has been focussed on flame retardants (FR) which have been increasingly used in consumer and building products in combination with a rapid increase in the use of plastics.

FR are added to a variety of polymers in the form of additives, or bound using a macromolecular reaction to reduce their flammability. In doing so the potential risk to human health and the environment must be weighed against the reduction of fire hazard. FR can be released into the environment during manufacture and processing, gas release from products (which commonly occurs in open systems) and through industrial sewage and waste disposal.

Certain compounds are lipophilic and bioaccumulative and exhibit a high persistence. Analytical studies show that FR are increasingly found in the biosphere (e.g. in sediments, marine organisms etc.) and in the built environment (e.g. house dust) [1, 2, 3, 4, 5, 6].

There has not yet been any systematic examination of potential contamination pathways which lead to this impairment, and little is known of the emission behaviour of FR, however this information is crucial for a comprehensive evaluation of this class of substances.

To make statements on the emission behaviour of different FR, a test method is required which can be used under standard conditions to determine the extent of FR release from various materials. Emission data obtained in this way can be extrapolated to estimate indoor exposure to products protected by flame retardants.
For this purpose the Federal Environmental Agency in Germany (Umweltbundesamt, UBA) has commissioned a research project aimed at investigating the emission behaviour of selected FR from indoor products.

The group of polybrominated flame retardants, halogenated and halogen-free phosphoric acid esters and chloroparaffins has been primarily investigated. Representatives of polybrominated diphenylethers (PBDE) and polybrominated biphenyls (PBB), hexabromocyclododecane (HBCD), tetrabromobisphenol A (TBBPA), hexabromobenzene (HB), diphenylcresylphosphate (DPC), tris(3-chloropropyl)-phosphate (TCPP), triphenylphosphate (TPP) and further aryl/alkyl organophosphorus compounds (OPC) have been selected as guide substances.

The examination concentrated on the following product groups:

- Upholstered furniture
- PUR/PIR/PS insulation materials and others
- PUR One-component assembly foam
- Mattresses
- Computers

In accordance with the objectives of the project, the test procedure to be developed should be based on determining the concentration in the air by using various test chambers.

The testing of potential emissions of FR from the individual products was performed under standard conditions: at 23 °C temperature (T) and 50 % relative air humidity (R.H.). Certain samples were tested during operation or at elevated temperatures to simulate operational conditions.

0.5 h^{-1} was set for the air exchange rate in the model room and test objects were placed in the emission test chambers depending on product type (e.g. insulation plates, pipe insulation etc.). Since no reference data were available, the available indoor area estimated at 17.4 m^3 of model room volume and 7 m^2 of floor area was used as a basis for the calculation of the product loading factor (DIN V ENV 13419-1 [21]).

If possible, the sampling and analysis method to be used should apply to a wide range of FR and must be sufficiently sensitive to make sure it can detect all contaminants. Emissions were measured in 0.001 m^3, 0.02 m^3 or 1 m^3 emission test chambers depending on the size of the products. The measurements were carried out in a constant air flow or at a constant air exchange rate, and the emittents were enriched by adsorption on suitable materials (here: polyurethane foam (PUR foam) or polyphenylene oxide (Tenax)).

Sampling time depends on the emission behaviour of the flame retardant to be tested and is at least 28 days. Some of the FR products chosen exhibited high boiling or decomposition points (> 300 °C) and correspondingly low steam pressure, so required considerably longer sampling times. Sample volumes were determined in accordance with the detection limit of the analytical method of the FR to be tested. Since no reference data were available on the concentrations to be expected, sample volumes were as big as possible (~ 2 - 40 m^3) depending on the test chamber volume.

The samples were processed by means of soxhlet extractor or ultrasonic extraction using suitable organic solvents. The identification and quantitative determination was performed by gas chromatography-mass spectrometry (GC/MS) or by high performance liquid chromatography with UV detection (HPLC-UV).

1.1 Search and selection of products, state of the art in flame retardant usage

It was a special challenge within the project's preparatory work to identify the FRs used in the products and select the products to be tested in the project.
Our ideas were initially based on the project 'Development of assessment fundamentals for the substitution of environmentally relevant flame retardants' carried out by the Federal Environmental Agency [36, 59, 60]. The following extracts illustrate and summarise the final report according to the product groups whose emission was to be tested.

Information on polybrominated FR revealed that a total of 1,000-1,500 tonnes of PBDE, 3,500-4,500 tonnes of TBBPA and 2,000-2,500 tonnes of HBCD was used in Germany in 1997. The overall consumption of chlorinated compounds including chloroparaffins was 4,000 – 5,000 tonnes [36] and that of organophosphorus FR was given as 13,500-16,000 tonnes in 1997 of which 5,500-7,000 tonnes was halogen-containing FR . The main emphasis was on TCPP (partly used as a mixture) followed by TCEP, but based on current information the TCEP proportion was actively decreasing within the EU. The proportion of halogen-free organophosphorus FR was 8,000-9,000 tonnes. The data on overall consumption refer to the amount used or processed in the Federal Republic of Germany.

1.1.1 Insulation materials

When scrutinising the overall area of insulation materials used in the construction industry, it was determined that PUR insulation materials make up 6 per cent, mineral insulation materials with practically no flame retardant approx. 50 per cent and polystyrene-insulation materials 40 per cent. PUR insulation and one-component assembly foams as inflammable building materials generally fall into building material class B. With a high proportion of isocyanurate structures in PUR foam (PIR foam), a part of the halogenated or halogen-free flame retardants do not fall into the same fire protection class. Considering a standard formula, PUR foams make up approx. 13% of flame retardants (5% additive (TCPP), 8% reactive (polybrominated polyol)) and PIR foams approx. 1.5-4 % (TCPP and/or TEP etc., in general without a reactive component) depending on the fire protection class. PUR foam 'B3' contains for example 0-4 % FR, PIR foam 'B1' however contains 8%. More than 95% of PUR insulation foams belong to building material class 2 (normal inflammable).

The proportion of TCPP in PIR foams can be reduced to under 1% in combination with TEP. Polybrominated (chlorinated) polyols have been used as further flame retardants for the PUR area, but are more cost-intensive compared to OPCs. On the other hand there is a range of goods for PUR hard foam offered by FR manufacturers. In addition, pentabromodiphenyl ether (pentaBDE), tetrabromophthalate and its derivatives, and various brominated neopentylglycole are on the market. The variety of supplied halogenated OPCs range from TDCP, oligomer chloroalkyl phosphate, chlorinated phosphonate ester to oligomeric chloroalkyl phosphonates.

Furthermore, DMMP, DPC, TPP, various phosphonates, phosphorus polyols and phosphonate esters are offered as halogen-free OPCs, Although one should assume that all flame retardants on the market for PUR hard foams have been used, the manufacturers say that only a small number of products are of importance as far quantities are concerned. Of all additive flame retardants used by German users today, approx. 90% is TCPP.

Where quantity is concerned, the single most important market of PUR hard foam is insulation sandwich elements (40%) used in industrial halls and buildings. Plate products form the second most important market (28%) with an approx. 40% PUR and 60% PIR quality. One-component assembly foams represent the third most important market, about 20%, generally with B2 classification. The PIR fraction with 80% in block foams (market proportion 7%) is even bigger than that of extruded foams.

While plate products, sandwich elements and continuously produced block foam are manufactured industrially under strict control, local foam and one-component assembly foam are building-site products which are produced under less well controlled conditions.

Polystyrene insulation materials can be divided into foam polystyrene (expanded polystyrene, EPS) and compact polystyrene (extruded polystyrene hard foam, XPS). Polystyrene used as a building material must satisfy B1 fire class conditions, this classification is however restricted to the German-speaking countries. For certain applications fireproof polystyrene meets the B1 classification. In 1997, 87% of the polystyrene raw material on the German market went for insulation materials, while 13% went for packaging materials (not flame-proof).

EPS (80%: 0.7-1.2 % FR; 20%: 2-3 % FR) and XPS (2-3 % FR) are made fire resistant using HBCD. 85% of HBCD production is used as flame retardant in EPS and XPS foams, 5% in high-impact polystyrene (HIPS) and about 10% in textile secondary backing coatings.

In polystyrene production about 20% of flame retardants hydrolyses.

1.1.2 Assembly foam

The conventional term ‘assembly foam’ usually means closed-cell PUR foam which is produced in situ from pressurised vessels.

80% is used to seal joints, approx. 10% to fasten door frames and approx. 10% to seal pipe sleeves. 95% of assembly foams are aerosol driven of which 80% are one-component foams (1 C assembly foams) and 15% two-component foams (2 C assembly foams). The remaining 5% are CO_2 driven two-component foams in cartridges. The average raw density of the one-component assembly foam is 27 kg/m³ (pistol foams 15-20, standard one-component assembly foam 25-30, 2 C aerosol foam 35-40, cartridge foam approx. 50 kg/m³). In addition to PUR one-component assembly foam, PIR one-component assembly foam is also offered on the market, particularly by the firm Rathor and Henkel. PIR one-component assembly foam, analogously to insulation foams, is produced with reduced flame retardant content (without halogenated polyol components). As a rule, PUR one-component assembly foams are made fireproof by adding brominated polyols in compounds with halogenated OPCs. The flame retardant content of a standard composition PUR one-component assembly foam based on a standard formula is approx. 20-25 % FR (halogenated polyol with approx. 8%; TCPP with approx. 14 %) and between 8-11 % in new developments without brominated polyols (DPC etc.). The average flame retardant content of B2 one-component assembly foams is between 20% (approx. 4% brominated polyol, 16% TCPP) and 25% (without brominated component), depending on type. B3 foams (export) manage with half the flame retardant content and expensive brominated polyols can be omitted completely.

Flame retardants such as TCEP, TBBPA or pentaBDE, previously used in one-component assembly foams, are no longer used according to an opinion poll among German manufacturers, however TCEP cannot be excluded in foreign products. This survey also revealed that neither brominated polyols nor halogenated OPCs are contained in newly developed one-component assembly foams. The following substances have been used as flame retardant additives with no halogen content: DPC (commercial products always used as a mix), DEEP (diethylethanephosphonate; classified as hazardous for the environment and poisonous for aquatic organisms and no longer used by IVPU members in Germany), TEP (small-scale use in 1 C foams) or TPP. In addition, reactive flame retardants (phosphorus polyols) are also applied.

1.1.3 Upholstered furniture and mattresses

Contrary to general opinion, it is not entirely compulsory for upholstered furniture and mattresses marketed in the area covered in the study to be treated with flame retardants. In the Federal Republic of Germany no fire protection regulations exist in the private sector for furnishings such as upholstered furniture or mattresses. Indeed this is handled in the same way all over Europe with the exception of Great Britain and Ireland where flame retardants have been required even in the private sector since 1988. However, there have been discussions at European level to generalise the British standards for upholstered furniture and mattresses in the private sector by harmonising legal principles all over Europe. On the other hand, only the area covered in the study has always been under discussion concerning other textiles (e.g. curtains).

PUR flexible foam is dominant among upholstery foams. International PUR production comprises 40% of the overall soft foam fraction and PUR foams produced by the block foam method are used almost exclusively. In principle, three PUR types are used in upholstered furniture (status 1999): 45% standard foam (25 - 30 kg/m^3); 40% high resilience foam (HR) (32 - 35 kg/m^3); 15% combustion modified high resilience foam (CMHR) with the same bulk density as HR foam but with addition of a special flame retardant. Upholstered furniture manufacturers report that fire-resistant upholstered furniture sold in Germany is mainly manufactured using a blend of HR foam (without FR) and covering material in such a combination that no flame retardant addition to the fabric is necessary. On the British market CMHR foams are on sale (addition > 10% concerning foam weight: e.g. a mixture of melamine, expanded graphite and halogenated OPCs (TCPP/TDCP)).

A large number of various fabrics and knitted goods are used for upholstered furniture covers, while the choice of fabrics for mattresses is not so big. The addition of flame retardant generally depends on the relevant burning properties of the material and on the extent to which the regulations and norms are adhered to. Cotton materials with flame retardant additives as well as polyester/viscose, polyester/polypropylene or polypropylene/viscose fabrics are used. Concerning quantity, this is dominated by Trevira CS, a synthetic, inherent/permanent fireproof fabric. In principle, furniture coverings can be made fireproof by using two methods: 1) backing method: a polymer or binder compound containing FR is applied together with a FR additive; 2) full bath (padding process): textiles are pulled through the bath so that the FR adheres to the fibres. The particular method used depends on the actual fabric and fibre. For blended fabrics for the English market, backing with antimony halogen compounds can be considered state of the art. A standard compound for the backing is a combination of halogen and antimony compounds with polymerdispersions (hexabromocyclododecane as a halogen component, outside Gremany PBDE (deca) as well). The FR fraction in the wet goods is around 20% and about 40% after having dried on the product. Ammonium polyphosphate is another FR. A halogen-free phosphorus nitrogen compound is used in the padding process for fabrics containing cellulose (cotton etc.).

As a rule, mattresses consist of PUR foam, latex or feather core covered with a combination of drill (cotton and synthetic fibres) as well as fleece and non-woven fabric (wool and synthetic fibres). Fireproof mattresses are generally made of PUR full foam. 90% of the fireproof mattresses are produced from ’cold foam’ or high-resilience foam with a higher bulk weight. Depending on the fire test carried out (cigarette test, match test etc.) this foam does not need the addition of a flame retardant. The remaining 10% is soft foam with lower bulk weight, which requires addition of FR composed of toluenediisocyanate (100 parts of polyol, 40 parts of TDI) with 3 - 7 parts liquid FR (TCPP, TDCP, TCEP and DMMP) per 100 parts of polyol. In drill the ratio inherent/permanent fireproof cover materials is 70% to 30%, mainly wool covers additionally treated with FR (phosphorus compounds with nitrogen content).

Furniture and mattresses represent the single largest PUR market in Germany – ahead of the construction industry and automobile sector. Due to special regulations in Britain, the upholstered furniture/mattresses sector ranks second, after insulation materials and fireproof PUR foams used within the construction industry.

1.1.4 Circuit boards

Circuit boards in principle are treated with flame retardant. It is the main field of application for halogenated (brominated) FR. Epoxy resins are used in FR 2, FR 3, FR 4 and FR 5 laminates and as CEM 1 and CEM 3 composites. Reactive TBBPA entirely dominates the standard epoxy resin circuit boards, in addition DPC can be contained in FR 2 and FR 3 laminates. Phenol resins provide the FR 1 and FR 2 types. Triarylphosphates such as TPP and DPC (8% FR in each or in a mix with TPP) are used for phenol resin circuit boards, although with only marginal importance. PBDEs may occasionally occur in older products, possibly contained in

FR 2 materials as traditionally, PBDEs, brominated OPCs or mixes of PBDE and aromatic OPCs were added to phenol resin circuit boards.

Brominated (here: brominated epoxy) and bromine-free flame retardants co-exist in phenol resins today.

Efforts have been made for at least 10 years to replace flame retardants containing halogens by halogen-free FRs (e.g. organophosphorus FR additives in combination with nitrogen carriers). Epoxy resins made fireproof using resorcinol-bis-(diphenyl)phosphate (RDP), reactive 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) and other substances are however currently only test products or have only achieved a marginal market proportion yet with various degree of maturity. In addition to circuit boards, other flat module components, particularly component cases (casting compounds) and coatings (solder resists) also contain FRs. Besides, solder resists are not necessarily halogen and bromine-free because some bromine and chlorine remains in the material from the epoxy resin synthesis (the catalysts contain bromine; see epichlorohydrin synthesis). Bromine reacted into the oligomer is another halogen source, it is used to make the varnish more temperature-resistant.

Moulding and casting compounds in the components are usually made fireproof using TBBPA, OPC etc. In addition, halogen-free moulding compounds are also available. The overall halogen content therefore results from the chlorine and bromine content of the base material, the solder resist and the casting and moulding compounds.

In 1999 a company almost exclusively listed brominated FRs (TBBPA) for duroplastics (epoxy resins: circuit boards, moulding compounds) and 25% of halogenated FR (no P halogens), 25% of halogen-free OPCs and 50% of mineral flame retardants for thermoplastic case materials (ABS, PC/ABS, PS, PPO/HIPS, PBT, PA). 50% of engineering thermoplastics (small parts, outsourced items from ABS, HIPS, PA, PE, PPE, PBT, PC, PP, PS) are made fireproof by brominated systems (decaBB, decaBDE and TBBPA derivatives), 25% by red phosphorus and 25% by mineral flame retardants. Small components currently represent the main sector where PBDEs are used. Since PBDEs are freely available at low prises in Germany, in spite of a voluntary waiver by the big synthetics manufacturers, it can be assumed that they are used by certain manufacturers and large quantities are imported via outsourced items.

Insertion of electronic components into circuit boards, including encapsulation and moulding is carried out partly by large electronics companies using insertion plants of their own, partly by circuit board manufacturers or outsourced to insertion firms. All in all, strong division of labour and inherent supplier competition characterise this interrelated area of manufacturing and processing. Therefore pre-products are subject to strong international trade within Europe. Resin production, bromination and processing into laminates/prepegs may take place in different EU countries, thus it is difficult to attribute FR consumption to individual countries.

Telecommunication, computer technology, industrial control systems and car electronics are the four most important fields of application for FR 4 materials. Paper laminates (FR1, FR 2) find their markets in consumer electronics (TV, audio, video), simple car electronics (control electronics, fittings) and household equipment (fittings). The importance of CEM 3 as a cost-efficient FR 4 substitute may increase in fields where there are less stringent requirements on mechanical stability.

1.1.5 Synthetics for product cases

When considering flame retardants used in synthetics for cases, the polymer type must be first taken into account. No halogen-free flame retardant is currently available for ABS (monitors, printers, computers etc.), so TBBPA and octaBDE as well as bis(tribromophenoxyethane) are preferentially used, otherwise flame retardant is omitted completely. PC/ABS is used as an alternative to ABS which can be made fire-resistant without using halogens.

Flame retardants with halogen content (brominated polycarbonate in combination with OPCs and others; TBBPA additive and hexabromobenzene) or without halogen content (approx. 10 % by weight of DPC, TPP, RDP and BDP) can be considered for PC/ABS. Bayer and GE Plastics have patents on PC/ABS with RDP. BDP, used as an alternative to RDP, is still in its introductory phase (status: 2000). Flame retardant systems used for Bayblend FR types consist of a combination of TPP (8-12 %) and PTFE, or RDP approx.10 %/PTFE as an alternative. Equipment labelled with the ‘Blue Angel’ (printers, PC) contain corresponding triaryl and bisphosphates as flame retardants.

In high impact polystyrene (HIPS), decaBDE (10-12 %), TBBPA etc. was used in the past. Current recommendations of FR manufacturers are bis(pentabromophenyl) ethane (12%) or TBBPA (17%). In old equipment one can also still find octabromobiphenyl. Flame-retardant properties can also be achieved using organophosphorus compounds such as TPP, RDP or butylated triarylphosphate. HIPS has proved particularly successful for the rear section of television cases.

Another polymer in the field of case materials is PPO/HIPS. In the past polybrominated aromatic systems were also used, but currently only triaryl and bisphosphates (TPP, RDP, BDP) are offered by FR manufacturers as flame retardants. Whereas at the beginning of the 1990s brominated flame retardants were used in approx. 50% of the cases, at the end of the 1990s the proportion of halogenated FRs was considerably lower in all case types.

Cases may consist of various plastics depending on country of origin and manufacturer and may contain different flame retardants (high imports). Exact figures on the proportions of plastics are not available. Halogenated plastics in European products are almost exclusively used in printers (laser printers), while they can be found in all equipment classes of non-European (import) products.

European PC monitors and computers (20%) contain no FR in general or are provided with halogen-free flame retardants. Approx. 80% represent imports from Eastern Asia also manufactured from halogen containing materials. Dominant materials are ABS and PC/ABS. Compaq, a world-wide leader in PC delivery (status 2000), states that ABS is the material for cases for the German market, all models being TCO-labelled which suggests that the outer cases are free of FR. Laser printers primarily use fireproof ABS and PC/ABS, and halogen-free PC/ABS (made fireproof by organophosphorus compounds) is used in 'Blues Angel' devices.

In 1998 the halogen content of 20 computer cases was tested and a bromine content of 4.1 - 11 % was found in 7 cases and 0.018 - 0.64 % in 13 cases. If the bromine content is > 1%, it can be assumed that the plastic contains brominated FR. The same test showed 0.002 - 0.057 % of chlorine in 25% of the cases, 0.75 - 1.3 % in four cases and 34% in one case (a PVC case). Chlorine content does not indicate chlorinated flame retardants, but with the exception of the PVC case, can always be explained by other additives or as impurities.

The project 'Brominated Flame Retardants in Plastic and Textile Products' (Bromierte Flammschutzmittel in Kunststoff- und Textilprodukten) of the Austrian Federal Environmental Agency, completed in 2001, tested brominated FR content in 64 consumer products from E & E accessories, textiles, engineering textiles and building materials. Insulation plates showed the highest decaBDE and HBCD content. Less than 1 mg/kg^{-1} (0.0001%) of TBBPA was occasionally found in circuit boards and cases. With circuit boards in particular, it must be taken into account that TBBPA is present in a reactively bound form. With one exception (cotton material, 0.0035%), PBBs were never found above the detection limit.

Less than 1 mg/kg^{-1} (0.0001%) of pentaBDE (proved by means of the BDE99 isomer) was found only in three cases. A content of less than 100 mg/kg^{-1} (0.01 %) of octaBDE was found in electronics products and less than 300 mg/kg^{-1} (0.03 %) in textiles. 1.26 - 1.57 % of decaBDE (BDE209) and 1.15% of HBCD was measured in various insulation plates. In addition, 0.12% of BDE209 was found in wall-to-wall carpets and finally, a cotton material contained 0.37% of HBCD.

To gain detailed information on the products to be tested, a meeting of experts was organised at the beginning of the project, attended in particular by manufacturers of the key product groups, with the aim of providing samples and specialist information. The talks at this meeting indicated that information available on IT equipment is often unreliable due to the export and import market. In particular circuit boards may still contain undesirable flame retardants such as PBDE without the necessary information being available to the manufacturer or user. Furthermore FR 4 circuit boards containing TBBPA as reactive flame retardant are still standard in the field of IT technology.

Information from PC manufacturers revealed that plastics used for monitor cases internationally, if they do contain flame retardants agents, are exclusively halogen-free. No current data were available on flame retardants in printers, nor was the printer manufacturer involved in the course of the project able to make a statement on flame retardants used in their products.

A representative of household appliance manufacturers stated that the change from FR 4 circuit boards containing halogens to halogen-free CEM 3 circuit boards will take place in the future and recyclates with halogen-free flame retardants have been used for cases for electronic parts.

It has been found that PBDEs are not in use any more in the production of insulation materials in Germany, unlike in most foreign countries. However, deca-bromodiphenylethane is a polybrominated flame retardant which is increasingly being used.

It has been found that flame retardant has not been used in Germany for the mattress product group, with the exception of the area covered in the study. This situation may change in the future, since British flame retardant guidelines on mattresses may prevail in other parts of Europe, including Germany, due to European legal harmonisation. This means that flame retardants should again be used in flame retardant free products such as mattresses and upholstered furniture.

German mattress and upholstered furniture manufacturers do not consider this necessary and therefore refuse to use flame retardants.

Some information on the flame retardant type tested in the project was provided by the manufacturers. Where this was not the case, bromine, phosphorus and chlorine analyses were performed in addition to using micro radiograph fluorescence to obtain basic information. In individual cases, qualitative materials analysis was carried out to verify the results obtained.

Sample history and available information on the sample material is listed in Chapter 5 in the relevant experiment series.

2 General part

2.1 Flame retardants (FR)

The use of FRs, according to the existing fire protection regulations, extends over a wide range. They are used among other things in insulation and foam materials, electronics components, fire protection coatings, textiles, leisure accessories, furniture and in airplanes and cars.

Flame retardants can be divided into several groups with different chemical basis and effect. The most important groups are inorganic FRs (for example $Al(OH)_3$), halogenated organic FRs (for example polybrominated diphenylether) and organophosphorus FRs (for example tris(2 chloroisopropyl phosphate), TCPP).
Features common to all of them are that they reduce flammability of plastics in the case of a fire and prevent the propagation of flames. The flame retarding effect is based on different mechanisms. Halogen-containing FRs inhibit the radical chain mechanism of the burning process in the gaseous phase, phosphor-containing FRs promote flame-retardance by decomposing the FR at given temperatures and forming phosphoric acid and/or glasslike polyphosphoric acids, which leads to dehydration and/or charring of the plastic surface, which in turn results in snuffs the flame.

2.2 Polybrominated flame retardants (PBFR)

This study concentrates on polybrominated diphenylethers (PBDE) and polybrominated biphenyls (PBB), tetrabromobisphenol A (TBBPA), hexabromocyclododecane (HBCD) as well as hexabromobenzene (HB) (Figures 1-5) from among approx. 30 brominated compounds which the OECD considers relevant for the industry [8].

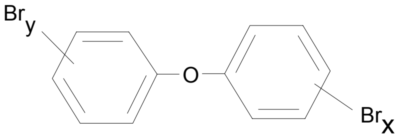


Figure 1: Basic structure of PBDEs; $\Sigma x,y$: 1-10

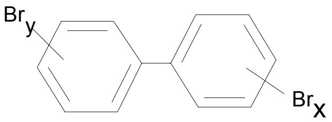


Figure 2: Basic structure of PBBs; $\Sigma x,y$: 1-10

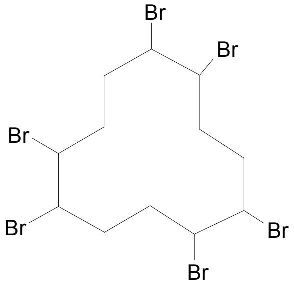


Figure 3: Basic structure of HBCD

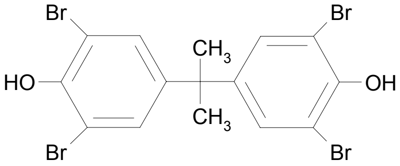


Figure 4: Basic structure of TBBPA

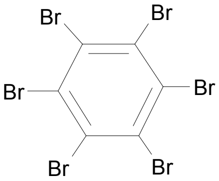


Figure 5: Basic structure of HB

Commercially used PBDE and PBB are not individual compounds, but – due to the production process - bromine-homologous preparations, consisting of different isomers and congeners (up to 209 as a maximum). Products based on pentabromodiphenylether (pentaBDE), octabromodiphenylether (octaBDE), decabromodiphenylether (decaBDE), hexabromobiphenyl (hexaBB), octabromobiphenyl (octaBB) and decabromobiphenyl (decaBB) are of commercial interest (Tables 1 and 2).

Table 1: Composition of commercially available PBDEs (13).

Product	Composition							
	TriBDE	TetraBDE	PentaBDE	HexaBDE	Hepta BDE	OctaBDE	NonaBDE	DecaBDE
DecaBDE							0.3-3%	97-98%
OctaBDE				10-12%	43-44%	31-35%	9-11%	0-1%
PentaBDE	0-1 %	24-38%	50-62%	4-8%				

Table 2: Composition of commercially available PBBs (14).

Product	Composition						
	TetraBB	PentaBB	HexaBB	HeptaBB	OctaBB	NonaBB	DecaBB
DecaBB					0.3%	3%	97%
OctaBB				1%	31%	49%	8%
HexaBB	2 %	11%	63%	14%			

Hexabromocyclododecane is used as a technical product, which contains the three isomer forms α-HBCD, β-HBCD and γ-HBCD.

The world-wide consumption of PBFRs is estimated to exceed 300,000 t/a. TBBPA and its derivatives are currently the most frequently used PBFRs totalling 150,000 t/a. TBBPA serves as a reactive flame retardant in epoxy and vinyl ester resins, which is used for example as a circuit board base material.

The consumption of polybrominated biphenyls, diphenylethers and diphenylethane is nearly 100,000 t/a, with decaBDE having the largest share. *The Bromine Science and Environmental Forum* (BSEF) calculated a total quantity of 54,800 t for decaBDE in 1999. It is used in plastics, textiles and in formulations for protective coatings.

BSEF found that the quantity of octaBDE used was 3,825 t in 1999. OctaBDE is mainly used as an additive flame retardant in ABS applications.

The output of pentaBDE according to BSEF was about 9,500 t in 1999. It is used mainly by the upholster and furniture industry (textiles, polyurethane foam). The annual consumption of alicyclic PBFRs such as HBCD is estimated at 20,000 t, with HBCD having the main share. HBCD is used predominantly as an additive in expanded (EPS) and extruded (XPS) polystyrene [9].

The FRs mentioned have high boiling and decomposition points (300 - 400 °C) depending on the number of the bromine atoms and their chemical structure, low steam pressures, for example HBCD: 1.6×10^{-5} Pa (20 °C) [10], high adsorption capacity and are chemically extremely stable. These are the required properties for flame retardants, but they also have an undesirable effect if these compounds get into the environment through any of the common pathways (production and application processes, emission during usage, waste disposal etc.). Certain members of these groups of chemicals are difficult to biodegrade, exhibit a high bioaccumulation potential due to their lipophilic properties and, finally, pose a high risk to humans being at the top of the food chain. Numerous studies have proved the spread of certain polybrominated flame retardants in various environmental media such as sewage sludge, sediments, cow and mother's milk, fish, air etc. It has been found that increasing concentrations of certain isomers, in particular PBDE (BDE47, BDE99 and BDE100 being the main components of the technical pentaBDE) have been present in the environment since 1970 [1, 9]. PBDE contents in bird’s eggs and in eels in the Baltic Sea indicate that this trend seems to have been on the reverse since 1990. Results for mother's milk, in which PBDE increased exponentially and doubled every five years, show a different trend. Based on these differences it can be assumed that different exposure paths play a role here [11, 12].

The use of PBFRs mentioned here seems to be currently on the decline. Research and development carried out by the manufacturers is being focussed on both halogen-free FRs and halogen-containing alternatives [9].

Production of hexaBB has been forbidden in the USA since 1976 due to considerable health risks and as the consequence of an accident where hexaBB was inadvertently mixed into animal food, and in Europe since 1980. In addition the use of PBBs in textiles which get into contact with human skin, has been forbidden since 1983. In France, a temporally limited exception had been in force until 2000 for the production of decaBB.

Degradation behaviour in the environment and ecological and human toxicology is currently not well understood so potential long-term effects for humans and the environment cannot be estimated. Interest is focused on PBDEs due to their great commercial importance. Since they belong to old materials, they must be evaluated in accordance with the EEC Old Materials Provision (793/93/EEC). The most important commercial substances (pentaBDE, octaDE, decaBDE) have been put on the first and second EU priority lists on grounds of their annual tonnage. PBDEs have likewise been attributed a high priority by the *Oslo and Paris Commission* for the Protection of the Marine Environment of the Northeast Atlantic (OSPARCOM), the HARP HAZ project (*Harmonised Quantification and Reporting Procedures for Hazardous Substances)*, the *Helsinki Commission* (HELCOM, Baltic Marine Environment Protection Commission) and the European Union Water Framework Guideline *(2000/60/EC)*.

The OECD has investigated PBFRs within the framework of its *Risk Reduction Programme* under the aspects of Quantities and Fields of Use, Environmental Impact and Potential Measures for Risk Reduction [8].

Intensive discussions on PBDEs within the framework of old materials evaluation of the European Union and OECD have been going on since 1997. In order to be able to better estimate and evaluate the consequences for humans and the environment, so-called *Risk Assessment Reports* have been compiled by the member states. *Risk Assessment Reports* have been available so far or are being drafted for HBCD, decaBDE, octaBDE, pentaBDE and TBBPA [91, 92, 73]. Based on existing toxicology data, ecotoxicology and the results of environmental monitoring studies, the evaluation has identified the need for action for the containment of the environment hazard due to pentaBDE. Risk reduction strategies are currently in the planning phase. The draft to Amendment 24 of the No. 76/769 Guideline (EEC) suggests the prohibition of the sale and use of pentabromodiphenylether as a substance or in mixtures and products with a limiting value of 0.1 % by weight of pentaBDE. A prohibition within this guideline comes into force on 15.08.2004 for octaBDE and pentaBDE. This guideline has to be implemented into German national legislation within the Chemicals Prohibition Provision.

A large number of instruments exist on the national and international level, which are concerned with risk assessment of PBFR and potential and/or necessary reduction measures. PBFRs have been evaluated on the basis the existing database within the International Programme on Chemical Safety (IPCS) with the participation of the *United Nations Environment Programme* (UNEP), the *International Labour Organisation* and the *World Health Organization* (WHO) [13, 14, 15, 16]. *The UNEP POP Convention* and the POP Minutes of the *UNECE Convention on Long-Range Transboundary Air Pollution* are concerned with the prohibition and/or reduction of production and release of persistent organic pollutants (POP). If a substance is classified as POP, it must meet appropriate criteria (atmospheric long-distance transport, persistence in water, soil and sediments, bioaccumulation, toxicity and ecotoxicity). The PentaBDE formulation seems to fulfil the criteria for the admission to the POP list based on current level of knowledge and was discussed as a further POP candidate on the third meeting of the UNECE in June 2002.

The ROHS (DIRECTIVE 2002/95/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 27 January 2003 on the restriction of the use of certain hazardous substances in electrical and electronic equipment) plans a prohibition for PBB and PBDE in electrical and electronic devices from 1 July 2006. Within the European Community, in addition to the WEEE guideline (Waste Electrical and Electronic Equipment), plastics which contain brominated flame retardants must be segregated from electrical and old electronic devices bound for recycling (DIRECTIVE

2002/96/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 27 January 2003 on waste electrical and electronic equipment (WEEE)) [17].

In order to improve the data situation for the evaluation of PBFRs, a large number of national and international studies and projects have been initiated in the last years under the name and/or within the framework of *UFOPLAN*, *COMPREHEND*, *HARP-HAZ*, *BROC, AMAP*, *OSPAR, DIFFCHEM, BRITE-EURAM III, GLOBAL-SOC, SCOW, ICES,* etc. which are concerned with various aspects of alternative FRs such as toxicology, environmental monitoring, development etc.

On the national level, the FR problem is treated in a different way. Sweden plans a prohibition for PBDE as such, whereas the USA and Great Britain for example endorse the continued use of PBFRs because of existing fire protection requirements. In Germany there has been a voluntary waiver for the use and production of PBDEs on the part of the Association of the Chemical Industry (VCI), the Association of the Plastic-Producing Industry (VKE) and the Association of Textile Auxiliary, Leather Auxiliary, Tanning Agent and Washing Raw Material Industry (TEGEWA) since 1986 [18, 36]. After the EU-wide prohibition guideline on PBDE failed to be implemented, sale of these substances was indirectly regulated on the national level over the Chemicals Prohibition Provision in 1993. This guideline has specified limiting values for dioxins and furanes in materials, products and preparations, which indirectly excludes the use of PBDE.

Various national and international environmental protection symbols promote the production and sale of products with no or reduced flame retardant content paying special attention to PBFRs (for example *Blue Angel*, *Nordic Swan*, *EU Flower*, *TCO*, *Environmental Protection Label, Stichting Milieukeur*).

2.3 Organophosphorus flame retardants (OPC)

Organophosphorus compunds (OPC) are extensively used in products, which appear in the interior of buildings [47, 48]. In the literature there are about 70 different phosphorus-based flame retardants mentioned, the largest group of them being phosphoric acid esters (alkylated, arylated and chlorinated).

The following pattern gives an overview of the different classes of organophosphorus compounds which are the subject of this investigation. A detailed characterisation of the individual substances will be given in Appendix 3.

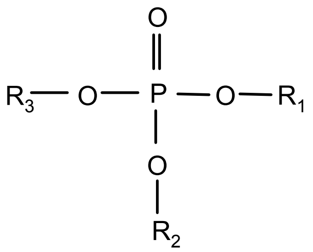


Figure 6: Basic structure of alkylated and arylated phosphoric acid ester (s. Table 3)

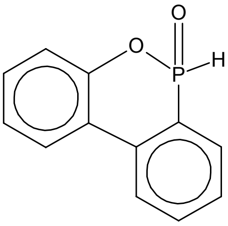


Figure7: Structure of 9,10-dihydro-9-oxa-10-phospha-phenanthrene-10-oxide (DOPO)

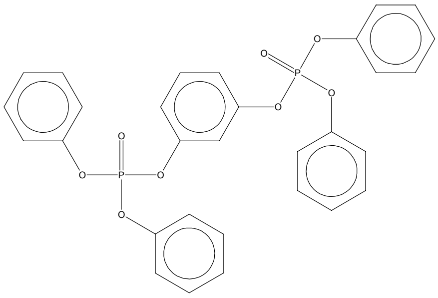


Figure 8: Structure of recorcinol-bis-(diphenyl-) phosphate (RDP)

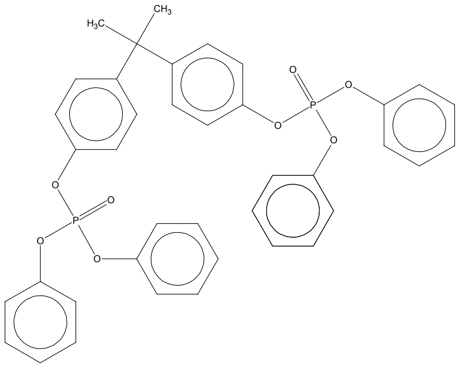


Figure 9: Structure of bisphenol-A-bis-(diphenyl-)phosphate (BDP)

Table 3: Alkylated and arylated phosphoric acid esters

$-R_{1,2,3}$	*Name*	*Abbreviation*
$-C_2H_5$	*Triethyl phosphate*	*TEP*
$-C_4H_9$	*Tributyl phosphate*	*TBP*
$-C_6H_{13}O$	*Tris(2-butoxyethyl) phosphate*	*TBEP*
$-C_8H_{17}$	*Tris(2-ethylhexyl) phosphate*	*TEHP*
$-C_2H_4Cl$	*Tris(2-chloroethyl) phosphate*	*TCEP*
$-C_3H_6Cl$	*Tris(2-chlorisopropyl) phosphate*	*TCPP*
$-C_3H_5Cl_2$	*Tris(1,3-dichloroisopropyl) phosphate*	*TDCP*
$-C_6H_5$	*Triphenyl phosphate*	*TPP*
$-C_6H_5$, $-C_7H_7$	*Diphenylcresyl phosphate*	*DPC*
$-C_7H_7$	*Tris(m-tolyl) phosphaet*	*TMTP*
$-C_7H_7$	*Tris(p-tolyl) phosphate*	*TPTP*

Material characteristics of these compounds permit their use both as softeners and flame retardants in various plastic products. They are used as a flame retardant in noise control and heat insulating boards, upholstery and assembly foams as well as in plastic materials for device components (PCs, printers, monitors). The main field of application for chlorinated phosphoric acid esters (for example TCPP) are polyurethane (PUR) foams. Arylated phosphoric acid esters (for example TPP) are used in the plastic parts of electrical and electronic devices. In addition, OPCs are also used in floor treating agents (for example TBP, TBEP). The annual consumption of the most frequently used chlorinated OPC, i.e. TCPP amounts to about 38,000 t in the European Union.

The physical and physicochemical characteristics of these compounds (e.g. polarity; boiling point of 330 °C for TCEP) suggest that these materials appear in considerable quantities in the internal atmospheric transport media (dust and air).

Widely differing OPC concentrations can occur in certain internal atmospheres due to different usage [49]. Indoor air concentrations of < 10 ng m^{-3} to 10 μg m^{-3} are described in the literature [51, 52], which can be contributed to the use of insulation materials. Another study has examined the emission behaviour of TPP from PC monitors under operating conditions [53]. In this instance the indoor air of a work place equipped with a new device was tested and a concentration of 100 ng m^{-3} of TPP was measured after one day, while the concentration decreased to < 10 ng m^{-3} in 183 days.

The different use of OPCs as flame retarding or softening substances is reflected by their OPC content:

- OPC as a flame retardant: content in the product approx. 5 – 20 %.
- OPC as a softener: content in the product < 5 %.

Public interest has been recently concentrated on a group of OPCs. An EU risk assessment has been available or is being drafted [93] for some of the tested organophosphorus compounds (TCEP, TCPP, TDCP). Further substances such as arylated phosphoric acid esters are being dealt with in other programmes (ICCA) [94].

Classification of TCEP as a substance took place in the autumn of 1998 because a carcinogenic effect [54] and impairment of reproduction ability was suspected [55] [per TRGS 905 Cat. 3]. It has now been classified as a substance damaging to health and posing a risk to the environment based on the latest studies and has been marked with R21, R40, R51/53 (25th ATP 98/98EG). It should be regarded as K2 and R_F2 in accordance with AGS (TRGS 905, status May 2002).

The neurotoxic potential of certain OPCs has been extensively reported in the literature of environmental medicine. Some of the compounds inhibit hydrolase enzymes (trypsin, chemotrypsin, cholinesterase, etc.) [56]. Two clinical pictures can be distinguished depending on the substance and/or the enzyme affected the strongest: an acute toxic effect which arises within a few hours, and independently, a retarded neuropathy which can only be proved after one or two weeks. Many organophosphorus compounds only become activated by metabolism. As far as the substances analysed here are concerned, an acetylcholinesterase-inhibiting effect has been discussed [57] in the case of TBP and TPP.

Compounds such as ortho-tricresyl phosphate (TOTP) and phosphates containing TOTP as an impurity, are no longer used as a flame retardant or softener. In contrast to acute neurotoxicity, retarded neuropathy can be associated with an additive effect, if small daily doses are taken over a longer period of time. The minimum toxic oral dose of TOTP for retarded neuropathy amounts to 250 mg kg^{-1} for chickens when administered once and to 5 mg kg^{-1} when given repeatedly [56].

Summing up, it can be stated that relatively few systematic investigations have been published so far which deal with the determination of organophosphorus compounds in indoor air in spite of their widespread use. This can be explained principally by their physical characteristics (see Appendix 3). Similarly to phthalates, OPCs are contained in a number of laboratory articles and reagents, which contribute markedly to blank value problems when determining these compounds (in particular TBP) and consequently to substantial problems in the assured quantification of OPCs in air.

Adsorption capacity of OPCs on glass surfaces or plastics used for sealing purposes in extraction devices, likewise considerably influence the measurement results (cf. also Chapter 4.2).

2.4 Chloroparaffins (CP)

Chlorinated paraffins (polychloro-n-alkanes) are produced by chlorinating paraffins and have the general summary formula of $C_x H_{(2x-y+2)} Cl_y$. They normally have a chain length of 10 to 30 carbon atoms and a chlorine content of 20 to 70 % [88]. At the beginning of the 1990's there were about 200 different commercially available chlorinated paraffin mixtures. The n-paraffin fractions used for the representation of chlorinated paraffins can be arranged into two groups:

1. Paraffin oils	C_{10}-C_{17}
2. Paraffin waxes	C_{18}-C_{30}

Statistically the chlorine atoms are preferentially distributed in the molecule on the secondary C-atoms. Therefore they consist of a mixture of carbon-homologues with different chain lengths, chlorine-homologues with different chlorine content and isomers with different positions of the chlorine atoms in the molecule, so that a multiplicity of congeners arises.

In a chloroalkane with 12 C-atoms for example all 6 possible isomers arise when monochlorination is applied, dichlorination produces 42 isomers and trichlorination 177. For this reason chlorinated paraffins exhibit very different characteristics: they are used as secondary softeners in plastics, as flame retardants, as high pressure additives in mineral oils and as additives in paints [88].

Table 4: Classification of chloroparaffins commercially available in the Federal Republic of Germany and Western Europe [88].

Carbon chain length		% Chlorine content (m/m)				
		10 - 30	31 - 40	41 - 50	51 –60	61 – 72
C 10-13 "short"					48 – 71 %	
C 14-17 "medium"				40 - 59 %		
C > 17 "long"	C > 17 "fluid"		26 – 59 %			
	C > 17 "solid"	< 20 %				69 - 72 %

Chloroparaffins are poorly reactive and easy to store at ambient temperature, at temperatures above 200 °C they split off hydrogen chloride and their colour becomes dark. In order to ensure thermal stability, stabilisers are added to the chloroparaffins: long-chained epoxides, glycidethers and triphenyl phosphates with a content below 1 %.

Chloroparaffins have been found in water, sediments and biological material in areas both near and far from industry. Within the EU Risk Assessments, the final report for chain lengths of C_{10} - C_{13} and the draft final report for chain lengths of C_{14} - C_{17} are available on the internet (http://ecb.jrc.it).

They get into the environment mainly via waste disposal and industrial waste water. Their input into the environment in the Federal Republic of Germany has been estimated at approx. 250 t per annum [88].

They are chemically and biologically relatively stable under environmental conditions. No details are known on degradation via hydrolysis, this reaction probably takes place only to a limited extent. No test results are available on the behaviour of chloroparaffins in the atmosphere, similarly, there are no reports known on sorption by soil and geo accumulation, however their enrichment can be expected. Their transport in the hydrosphere is probably via adsorption on suspended particles. They can enrich in sediments due to their low mobility, high persistence and low solubility in water. Traces of chlorinated paraffins were found even in the deep water of the East Atlantic (1200 m) and near the Bermudas [88]. No investigation results are known on photochemical degradation in water.

The chlorinated paraffins are biologically not degradable in standard tests, however they can be co-metabolised up to a chlorine content of 70 % by certain micro-organisms under aerobic conditions, if a further source of carbon is available. Since they are very lipophilic and possess a high adsorption capacity, they are predominantly stored in the fatty tissue and in organs such as liver and kidney with half-lives of 8 to 37 days [88].

The available investigations do not permit a suitable toxicological classification of the chloroparaffins, however they are suspected of having a carcinogenic effect and were therefore included in the list of MAK values in July 1990 as materials with justified suspicion of a carcinogenic potential [90].

The substances in the chloroparaffin class are very complex, thermally unstable mixtures which are difficult to determine analytically in the trace range. Up to now no method is available which would quantitatively determine chain length and chlorination degree of all chlorinated paraffins simply and specifically. It cannot be expected to achieve chromatographic separation into the individual congeners in the foreseeable future.

The reduction of the chloroparaffins to their alkanes may be an option to simplify the analytic determination. Thus the high number of congeners and their thermal instability can be reduced but the information on the chlorination degree will be lost however. Catalytic hydrodehalogenation is an appropriate and simple method to remove halogen atoms under mild conditions and replace them by hydrogen atoms.

3 Emission test chambers and cells

Emission test chambers enable the measurement of substances emitted from a material into the air under standardisable and to a large extent constant test conditions. Essential basics for performing emission measurements and the set-up of emission test chambers have been reported by several European reports [31, 32, 33, 34]. These are to a large extent included in the standards being currently drafted. To be mentioned in particular are the activities of CEN TC 264, WG 7 (Air properties, emissions from building materials) and CEN TC 112, WG 5 (Wood based materials, formaldehyde).

The standard DIN V ENV 13419, Part 1 - 3, [21, 22, 23] drafted by CEN TC 264, WG 7 includes the determination of emissions of volatile organic compounds (VOC) using emission test chambers and cells and the extraction, treatment and preparation of emission samples.

Comparative emission measurements on both formaldehyde [24], volatile organic compounds [25] and semi-volatile organic compounds [26] have been carried out within various investigations in BAM with respect to the volume of the 0.02m³ emission test chamber, which is based on DIN 55666 and conforms with ENV 13419-1. Suitability of the modified 0.02m³ emission test chamber, in comparison with other emission test chambers, has been verified.

In Germany, 1m³ emission test chambers are frequently used for emission tests. A 1m³ commercial VOC emission test chamber has also been available for several years [27].

Emission test cells used, for example FLEC (**F**ield and **L**aboratory **E**mission **C**ell) [28], have volumes of emission test cells and chambers ranging from 35 ml (FLEC) to above 12 m³ (large formaldehyde emission test chambers [29]), i.e. over a volume range of approximately six orders of magnitude.

A temperature of 23°C applied in the emission measurements is a common feature to all above-mentioned standards, while relative humidity has been set to either 45 % [29] or 50 % [21, 22].

Further important criteria, such as air exchange rate (n) and product loading factor (a), and the proportion of air exchange rate to product loading factor, called area-specific air flow rate [21, 22] have been differently defined.

As far as air flow velocity is concerned, in the majority of the cases a range of 0.1 - 0.3 m/s [13] and 0.3 ± 0.1 m/s [29] has been defined. The distance from the specimen surface for the measurement of air flow velocity has been defined as 10 mm [21].

In order to determine the emission behaviour of volatile organic compounds in small concentrations down to the lower µg/m³ range, not only must the usual parameters such as temperature, relative humidity, air exchange rate and air flow velocity be kept constant at specific values, but the test chambers must also satisfy a number of further special requirements. In particular:

- Inert emission test chamber walls [glass or high-grade steel (polished)] to minimize wall effects
- Thermally regulated blanket to minimize time based and spatial temperature gradients
- Minimise sealing materials capable of causing intrinsic emissions and adsorption and desorption effects
- Ability to clean the emission test chamber, for example through firing
- Clean air supply (free of VOC and dust)
- Clean water supply (free of VOC and particles)

The reason for choosing extremely inert emission test chamber wall materials is to keep adsorption effects near the emission test chamber walls to a minimum so that pollutant concentration in the air is not influenced by so-called wall effects. In addition to influencing pollutant concentration in the air during emission measurements, wall effects can impair subsequent investigations in the form of memory effects from the preceding measurements. A blank run is also necessary between two emission test chamber tests to provide a suitable desorption period for organic compounds that may have been adsorbed on the emission test chamber walls. In the case of semi-volatile compounds in the range of SVOC/POM wall effects may have serious impairing effects [26].

To avoid memory effects in large chambers, cleaning through firing at high temperatures (400 – 450 °C, thermal desorption) is recommended. In addition, small emission test chambers may also be subjected to cleaning with solvents.

Investigations within the framework of this project used 0.02m³ and 1m³ emission test chambers and BAM’s 0.001m³ emission test cells with the same standard environmental conditions (T = 23 °C and 50 % relative humidity) being applied throughout. The principle of a thermally regulated blanket was used for all emission test chambers and cells consistently.

Products were loaded into the chamber depending on product type (e.g. insulation material boards, pipe insulation etc.) and, because of missing reference data, it was based on an estimate of the area it occupied in the interior. A model room with a volume of 17.4 m^3 and a floor area of 7 m^2 was assumed as a basis for the following calculation of the product loading factor (DIN V ENV 13419-1) [21]. Unit-specific air flow rates were introduced for those products, whose surface could not be calculated (e.g. PC systems). Emission test chamber and cell parameters (volumetric air flow rate, temperature, relative humidity, area-specific air flow rate etc.) are separately displayed for each test series with the results in Chapter 5.

Furthermore all emission test chambers and cells were equipped with the same clean air supply system. Clean air was provided by an oil-free compressor in which a downstream cleaning unit removed moisture, VOC and dust from the compressed air. The cleaning unit (Ultrafilter Oilfreepac) consists of a pre-filter (dust and aerosol separation), air drying (heatless dryer - silica gel with automatic regeneration), charcoal cartridge for VOC adsorption and a fine filter and an afterfilter (submicrofilter < 0.01 µm, degree of separation 99.99999 %) to restrain both fine dust from the ambient air and rubbed-off charcoal particles.

Various humidification principles and equipment was used to achieve the necessary relative humidity: either a mixed humidification combining dry and moist partial currents, a condensation point humidifier or a steam humidifier.

Ultrapure water was used for humidification which was obtained from desalinated water. In the case of $\leq$ 1m^3 emission test chambers the water was sent through an aftercleaning unit (EASYpure UV D7402) for further desalination and removal of possible organic compounds.

An overview of the parameters in the individual emission test chambers is given in Table 5.

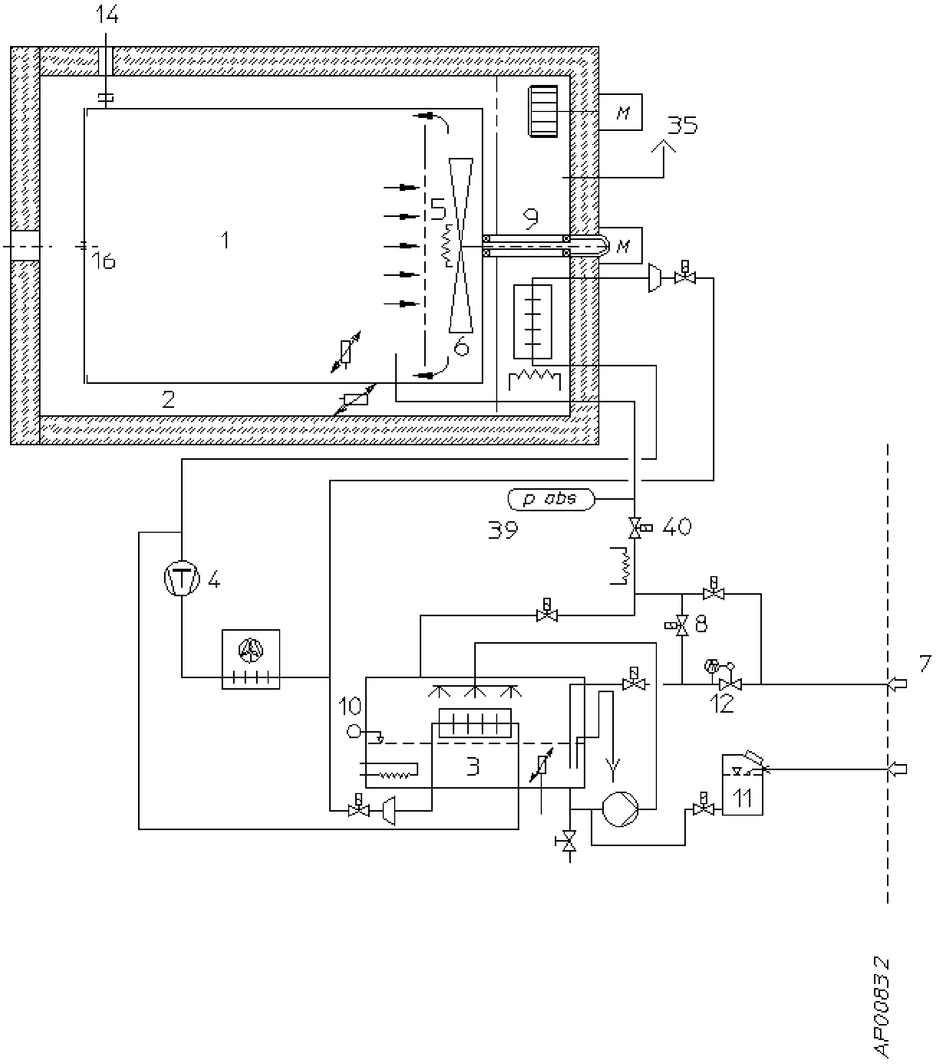
Table 5: Parameters of the emission test chambers used

	Unit	1m³ emission test chamber	0.02 m³ emission test chamber	BAM emission test cell
Volume	m³	1	0.02	0.001
Wall material		high-grade steel	glass	glass
Temperature (T)	°C	23		
Relative humidity (R.H.)	%	50		
Air flow rate (V°)	$m^3\ h^{-1}$	1	0.128	0.022
Air exchange rate (n)	h^{-1}	1	5.6	22
Area-specific air flow rate (q=n/L=V°/A)	$m^3\ m^{-2}\ h^{-1}$	1.25		
Air supply		Clean air		
Sampling		PU foam/(Tenax)		

Deviations from the parameters listed in Table 5 are indicated separately for each product group in with the results Chapter 5 .

3.1 1m³ emission test chamber

A standard VOC emission test chamber from the firm Vötsch Industrietechnik GmbH was used as the 1m³ emission test chamber for this project, which has been commercially available for some time, and conforms to DIN V ENV 13419-1 and reported on in the literature [27] (Figure 10).



1	Test space
2	Air jacket system
3	Climate module
4	Refrigeration unit
5	Additional heaters for desorption
6	Test space fan
7	Carrier gas connection
8	Rinsing
9	Special ventilation unit
10	Automatic water replenishment
11	Humidification water tank
12	Mass flow controller (1. MFC) for carrier gas
14	Connection for measuring gas and exhaust air
16	Entry port Septum
39	Absolute pressure measuring unit
40	Shut-off valve carrier gas

Figure 10: Schematic set-up of the standard 1m³ VOC emission test chamber (workshop drawing Voetsch Industrietechnik GmbH, basic equipment)

This emission test chamber has an interior test space of high-grade steel with low roughness, hermetically sealed from the surroundings. This separation is achieved, among other things, by the magnetic clutch applied to the test space fan, which is driven from the outside. Air conditioning of the emission test chamber is achieved through the use of a thermally regulated blanket and condensation point humidification. To clean the emission test chamber a heating system is available which eliminates memory effects through thermal desorption at up to 240 °C.

The area of the walls and fittings which are in principle capable of adsorption of semi-volatile compounds, is approximately 7 m^2.

For air sampling some connection points are provided to which the user can connect sampling tubes with 6 - 14 mm outer diameters. Further 1/4 in sampling connection points are available for special high-flow-rate sampling (not shown in Figure 10).

The emission test chamber was driven during the investigations with $n = 1\ h^{-1}$ air exchange rate.

3.2 0.02m³ emission test chamber

The 0.02m^3 emission test chambers (Figure 11) are based on 20-litre desiccators in accordance with DIN 55666 with further optimisation to make them conform with DIN V ENV 13419-1. They are equipped with inlet and exhaust connection points and one to three sampling connection points.

Air flow velocity is adjusted by a propeller which is connected through a magnetic clutch to the exterior speed-controlled motor.

In extensive pre-tests specially sealed ball bearings have been selected on the emission test chamber side of the propeller shaft in the magnetic clutch which, after careful cleaning of the surfaces, do not exhibit any provable emission.

Teflon slide bearings without the magnetic clutch did not prove failsafe in previous tests due to wear and attrition problems. Dry-run standard ball bearings in the magnetic clutch could not be used permanently either because of friction and attrition problems.

The air exchange rate was adjusted with the aid of a needle valve and flowmeter. The flange between desiccator and lid is sealed using a 0.1 mm thick polyethylene gasket and variable chucks.

Some connection points are provided for air sampling to which sampling tubes with 6 - 14 mm outer diameters can be connected.

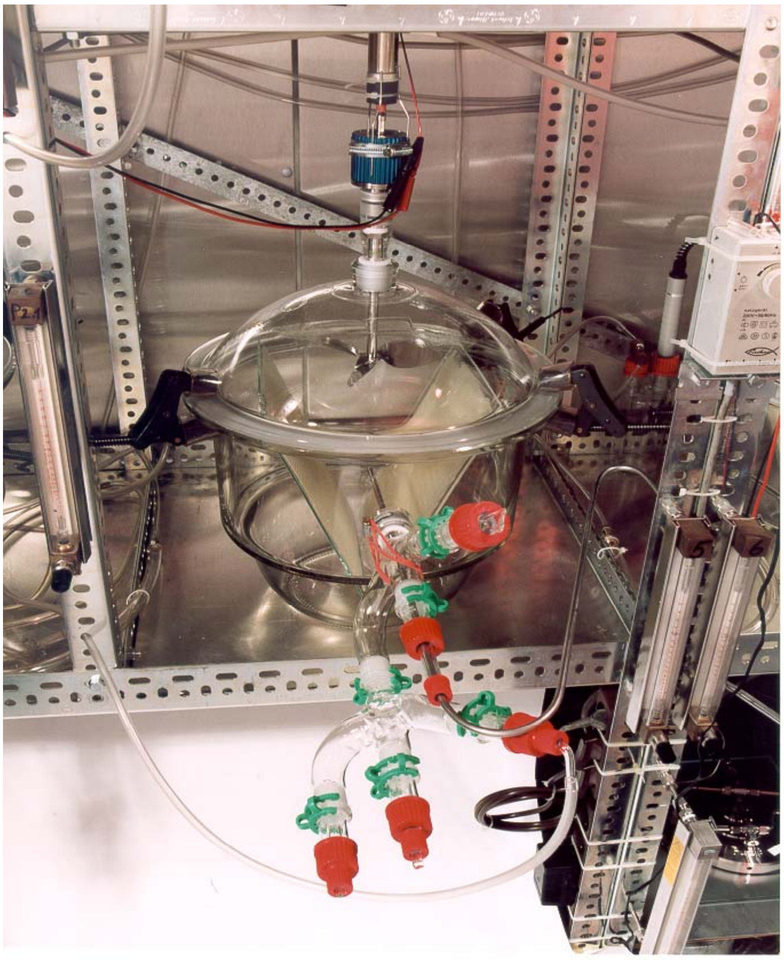


Figure 11: Emission test chamber equipment (0.02 m³) in climate chamber

3.3 BAM’s emission test cell (V = 0.001 m³)

Figure 12 illustrates BAM’s emission test cell, which is basically the top of a reaction vessel. The fan is identical in design to the system used in the 0.02 m³ emission test chamber and regulates flow velocity at the sample surface independently from the air exchange rate and air flow rate and homogenises the test cell air. The diameter is 15 cm, its volume is V = 0.001 m³. A good seal is guaranteed by a 1cm approx. wide polished strip on non-structured surfaces. The flow rate is 0.0221 m³/h and the emitting area 0.0177 m².

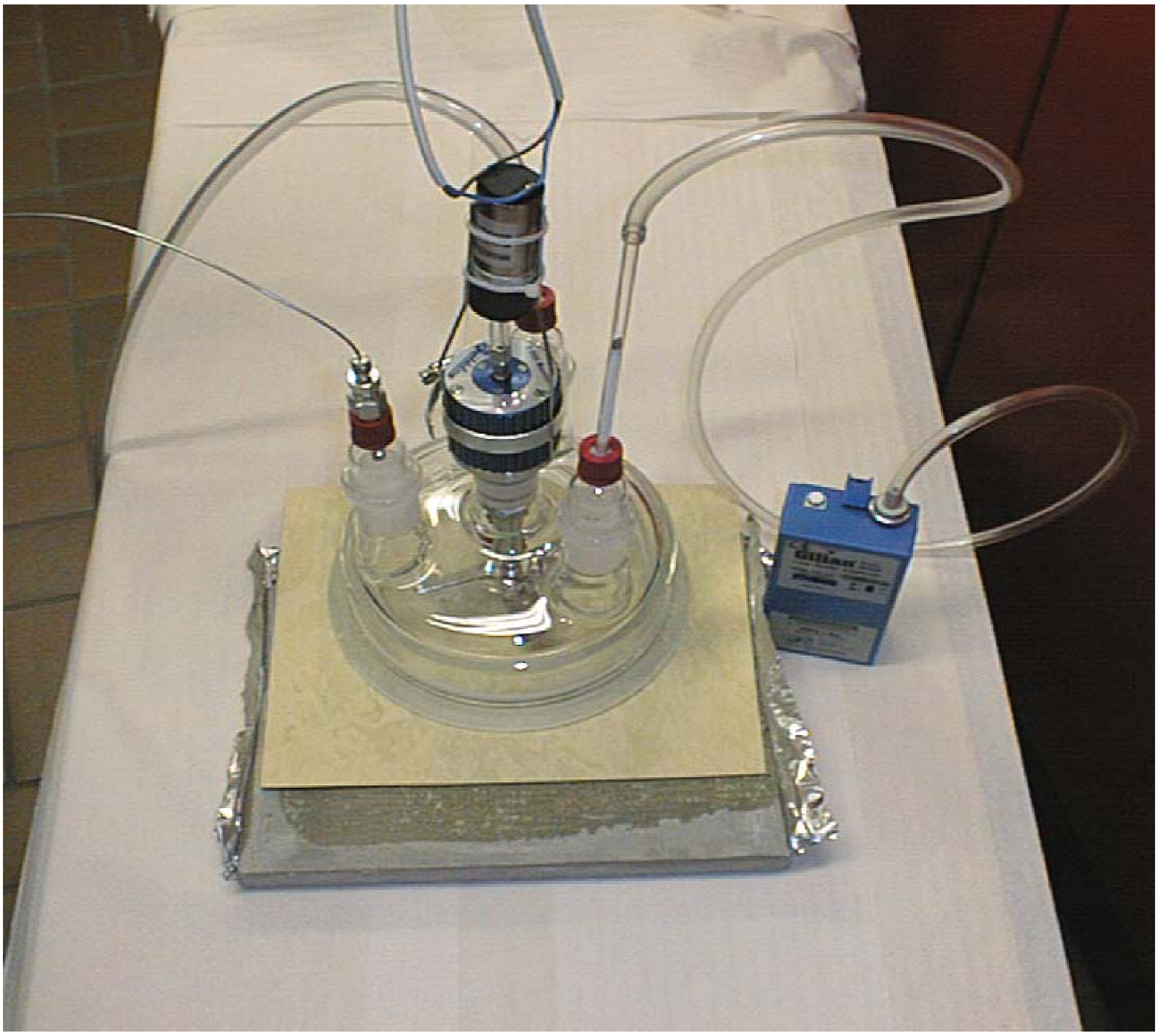


Figure 12: BAM’s emission test cell

3.4 Estimation of wall (sink) influence

Adsorption effects in emission chambers, i.e. near emission test chamber walls or fittings, generally require special attention, especially when measuring semivolatile compounds (SVOC). This is particularly valid when different chambers are compared or the area-specific emission rate $SER_a(t)$ is calculated from the concentration without having achieved steady-state conditions.

The best technique to reduce adsorption effects is to minimize the adsorption surface. The relevant quantity in this context is the ratio of the emitting surface area (source) to the wall surface (sink). For BAM's 0.001m³ emission test cell (wall area: 0.044 m², source area: 0.0177 m²) approximately 0.40 is obtained, for the 0.02m³ emission test chamber (wall area: 0.373 m², source area (insulation material): 0.103 m²) 0.27 and for the 1m³ emission test chamber (wall area: 7 m², source area (mattress): 1.41 m²) 0.20. These values have been calculated for selected samples and vary, in particular for the 0.02 and 0.001m³ emission test chambers depending on the tested product. Therefore when determining adsorption/desorption of substances, the greater the ratio, the faster the emission test chamber walls achieve equilibrium with the emission test chamber air. The wall effects then do not play any further role in the determination of emission rates.

4 Analysis of flame retardants in emission samples

Satisfactory analysis and sampling methods are necessary for the determination of the test material concentrations and/or emissions under given conditions in the emission test chamber. To develop the analytical method, the individual steps (sampling, preparation, storage, processing, measuring method) must be tested and the design and measurement parameters adjusted accordingly. For quality assurance and validation of the analysis method variance homogeneity of the calibration range must be examined and a regression model (linear, 2. degree, etc.) established. The lower limit of the analysis is determined by the detection and determination limits. The accuracy is tested with the help of the analyte recovery rate. This enables detection of the influence the processing steps have on the production of measurement data.

The emitted substances to be analysed are enriched for the purpose of sampling using a constant air flow and adsorption on polyurethane foam and/or Tenax TA (polyphenylene oxide).

Sample extraction from the PUR foam was carried out by soxhlet or ultrasonic bath extraction using suitable organic solvents. Solvent selection regarding solubility of the components, prevention of transverse contamination etc. was a part of the method development. Identification and quantitative determination took place using gas chromatography and mass spectrometry (GC/MS). In this combined procedure the substances were separated according to their chemical and physical characteristics in the gas chromatographic system as a function of time using a suitable separation capillary. The actual detection and quantification was performed by the mass spectrometer. Components that cannot be analysed by GC/MS due to their physicochemical characteristics were chromatographically separated by means of high performance liquid chromatography (HPLC) and consecutive UV detection.

Very volatile substances (for example TEP) were analysed by means of TENAX/thermodesorption. The substances enriched on TENAX (polyphenylene oxide) were heated to desorb them from the adsorbent and analysed by coupling with GC/MS.

Since no reference data are available on the emission behaviour of the flame retardants to be tested and little is known on the emission to be expected from semivolatile substances (SVOC) in general and from the target substances in particular, care was taken to ensure as favourable a source/sink relationship as possible when selecting the emission test chamber sizes (0.001 m^3, 0.02 m^3 or 1 m^3), i.e. the products were placed in emission test chambers with as small a volume as possible depending on their size.

The actual sampling time was considerably over the minimum sampling time of 28 days and was individually specified depending on the emission concentration and process to be expected during the test which was checked. Since very small concentrations were to be expected within the trace range depending on the vapour pressure and the usually unknown FR content in the product, sampling volumes between 2 - 40 m^3 were used in order to ensure sufficient sensitivity.

Preparation

Contamination and blank values were tested for all solvents and PUR foams used in the sampling before application. Glassware and materials were fired after use at 450 °C, cleaned in a laboratory dishwasher (demineralised water), dried at 150 °C and rinsed with toluene (PBFR) and/or acetone (OPC) before renewed use. In order to protect the photo-sensitive PBFR from light-induced degradation, brown glass was used and/or protected from light with aluminium foil (see Chemicals and Materials Used in Chapter 9).

Production and cleaning of PUR foam plugs/Tenax TA

PUR foam plugs were produced by punching them with a cork borer from special PUR foam mats cooled with liquid nitrogen (GA 3035, company Derenda). They were then placed into glass tubes (length: approx. 25 cm, internal ∅ : 12 cm) and cleaned by soxhlet extraction using toluene (3 hours) and acetone (2 x 2 hours) as extraction agents. The cleaning of the glass tubes was carried out by firing at 450 °C, washing in a laboratory dishwasher followed by rinsing with acetone and toluene (PBFR) and/or acetone and cyclohexane (OPC).

Very volatile compounds (for example TEP) were sampled with a glass tube filled with Tenax TA (length: 178 mm, external diameter: 6 mm, internal diameter: 4 mm), 200 mg Tenax TA (60 - 80 mesh) fitted with a rock wool plug. The sampling volume was 1 l (100 ml min^{-1}). The Tenax tubes had to be spiked with methylparathion dissolved in acetone before sampling.

4.1 Selected guide substances for the development of the analysis method

Polybrominated flame retardants

Available single substances were used for the determination of PBFRs and technical formulations for missing individual components, in particular high-brominated PBDE and PBB (see composition in Appendix 1).

Technical formulation:

- PentaBDE (DE-71-Great Lakes)
- OctaBDE (DE-79-Great Lakes)
- DecaBDE (DE-83-R-Great Lakes)
- HexaBB (Firemaster BP-6)
- OctaBB (FR 250 13 A Dow Chemical)
- DecaBB
- HBCD (CD-75-P-Great Lakes)
- TBBPA (BA-59P-Great Lakes)

Single standards:

- 4-MonoBDE (BDE3)
- 2,4’-DiBDE (BDE8)
- 2,4,6-TriBDE (BDE32)
- 2,2’,4,4’-TetraBDE (BDE47)
- 2,3’,4,4’-TetraBDE (BDE 66)
- 2,2’,4,4’,6-PentaBDE (BDE100)
- 2,2’,4,4’,5-PentaBDE (BDE99)
- 2,2’,3,4,4’-PentaBDE (BDE85)
- 2,2’,4,4’,5,5’-HexaBDE (BDE153)
- 2,2’,4,4’,5,6’-HexaBDE (BDE154)
- 2,2’,3,4,4’,5’-HexaBDE (BDE138)
- 2,3,3’,4,4’,5,6-HeptaBDE (BDE190)
- 2,2’-DiBB (BB4)
- 2,4’,5-TriBB (BB31)
- 2,2’,5,5’-TetraBB (BB52)
- 2,2’,4,5,5’-PentaBB (BB101)
- 2,2’,4,4’,5,5’-HexaBB (BB153)
- TBBPA-ring-$^{13}C_{12}$
- 3,3’,4,4’-TetraBDE-ring-$^{13}C_{12}$
- HB

For the determination of TBBPA a derivatisation was performed with acetic anhydride as per Chapter 9.2, using TBBPA-ring-$^{13}C_{12}$ as an internal standard.

Organophosphorus flame retardants (OPC)

Similarly, available single substances were used for the determination of OPCs and technical formulations for missing individual components:

Technical formulation:

- RDP*
- BDP*
- DPC*

Single standards:

- TEP*
- TBP*
- TEHP*
- TBEP*
- TCEP*
- TCPP*
- TPP
- TPTP
- TMTP

Chloroparaffins (CP)

The following single standards and technical formulations were used to determine chloroparaffins.

Technical formulation:

- CP-56*
- CP-70*

Single standards:

- Decane
- Undecane
- Dodecane
- Tridecane
- Tetradecane
- Pentadecane
- Hexadecane
- Heptadecane
- Oktadecane
- Nonadecane
- Eicosane
- Heneicosane
- Docosane
- Tricosane
- Tetracosane
- Pentacosane; octacosane
- Cyclodecane; cyclododecane

* These standards were courtesy of the manufacturers.

4.2 Operational parameters and substances for the analysis

4.2.1 Determination of polybrominated flame retardants (PBFR)

4.2.1.1 GC/MS

GC/MS system used:
Agilent GC Series 6890/ Bear Instruments Kodiak 1200 (mass range 10-1500 amu)

Carrier gas	Helium
Column pre-pressure	5.8 psi
Injection system	Cool-on-Column-Injector
Pre-column	Deactivated, Fused Silica, 2 m, 0.53 mm ID
Restriction capillary	Deactivated, Fused Silica, 3 m, 0.18 mm ID
Transfer line	310 °C
GC column	DB-5-ms; 15 m; 0.25 mm ID; 0.1 µm d_F
Temperature programme	70 °C (2 min) - 20 °C/min - 300 °C (15 min)
Ionisation method	EI; 70 eV; NCI (reactant gas: methane)
Source pressure NCI:	7 torr (methane)
Ion source T	200 °C (EI); 150 °C (NCI)
Detector voltage	1500 V
Emission current	200 µA

For the analysis of brominated compounds both electron impact ionisation (EI) and electron capture negative chemical ionisation (NCI) using methane as reactand gas is suitable.

An advantage of the NCI method as opposed to EI is a markedly better detection limit for brominated compounds. However NCI's disadvantage is that the structure of unknown compounds is difficult to clarify, since mass spectra with much less explicit peaks will be obtained, which basically present the bromine isotopes (79/81) as the most intensive fragments of brominated substances. Further fragments including mol peaks can likewise be observed, however they only occurred to a small degree under the given conditions for most guide substances. Occurrence and intensity of additional fragments and/or mol peaks depend on the state of tune of the MS system.

EI offers higher selectivity, since structure assurance is performed via several characteristic fragmentations, which are intensive enough to be used for detection both in Single (SIM) and Multiple Ion Monitoring Modus. The disadvantage of EI is an approximately identical response for compounds with higher bromine content.

The measurements on the samples showed that although NCI exhibited very high sensitivity in quantification (< 1 pg μl^{-1} absolute) for compounds with a bromine number of up to 6 when the bromine isotope mass of 79 was used, this was however not sufficiently specific in real samples due to disturbance by contamination and failed to ensure an unambiguous signal. Since this disturbing matrix load was limited to the front interval of the retention time, NCI was able to measure further highly brominated compounds eluting later. In this instance decisions had to be taken on a case-by-case basis.

For this reason brominated substances with a bromine number ≤ 6 were analysed using EI, while compounds with a bromine number > 6 were detected with the help of NCI. For selected samples the additional assurance of the results was achieved by both ionization techniques.

The analysis of the polybrominated flame retardants took place in the SIM modus (EI/NCI) using the following mass traces (quantification: underlined mass trace; see mass spectra in Appendix 2).

Hexabromobenzene	$M^{+}+4,M^{+}+6$	549.5,551.5
Hexabromocyclododecane	Br^{-}, $(M^{-}-5Br)$	79.3,81.3,157.8,159.8

Polybrominated biphenyls

EI modus:

Dibromodiphenyl	$(M^{+}-Br),(M^{+}-Br)+2,M^{+}+2$	230.7,232.7,311.6
Tribromobiphenyl	$(M^{+}-2Br),(M^{+}-2Br)+2,M^{+}+2,M^{+}$	229.8,231.7,310.6,389.6
Tetrabromobiphenyl	$(M^{+}-2Br)+2,(M^{+}-Br)+2,(M^{+}-Br)+4,M^{+}+4$	309.6,388.6,390.5,469.6
Pentabromobiphenyl	$(M^{+}-Br)+2\ (M^{+}-Br)+4,(M^{+}-Br)+4,M^{+}+4$	387.6,389.6,468.6,547.6
Hexabromobiphenyl	$(M^{+}-4Br)+2,(M^{+}-4Br)+4,(M^{+}-2Br)+4,M^{+}+6$	307.6,309.5,467.6,627.6

NCI modus:

Heptabromobiphenyl	Br^{-}	79.3,81.3
Octabromobiphenyl	Br^{-}	79.3,81.3
Nonabromobiphenyl	Br^{-}	79.3,81.3
Decabromobiphenyl	Br^{-}	79.3,81.3

Polybrominated diphenylethers

EI modus:

Monobromodiphenylether	M^{+}, $M^{+}+2$	248.1, 250.1
Dibromodiphenylether	$(M^{+}-2\ Br),M^{+}+2,M^{+}+4$	167.9,327.8,329.8
Tribromodiphenylether	$(M^{+}-2\ Br),(M^{+}-2Br)+2,M^{+}+4$	245.9,247.9,407.8
Tetrabromodiphenylether	$(M^{+}-2\ Br)+2,(M^{+}-2Br)+4,M^{+}+4$	325.8,327.8,485.6
Pentabromodiphenylether	$(M^{+}-2\ Br)+2,(M^{+}-2Br)+4,M^{+}+4$	403.7,405.7,563.6

Hexabromodiphenylether	$(M^{+}-2\,Br)+4,(M^{+}-2Br)+6,M^{+}+6$	483.7,485.6,643.6
Heptabromodiphenylether	$(M^{+}-2\,Br)+4,(M^{+}-2Br)+6,M^{+}+6$	561.6,563.6,721.6
NCI modus:		
Monobromo- to hexabromodiphenylether	Br^{-}	79.3,81.3
Heptabromodiphenylether	Br^{-}	79.3,81.3
Octabromodiphenylether	$Br^{-},(M^{-}-5Br)$	79.3,81.3,406.5,408.5
Nonabromodiphenylether	$Br^{-},(M^{-}-5Br)$	79.3,81.3,486.4,488.4
Decabromodiphenylether	$Br^{-}, (M^{-}-6Br)$	79.3,81.3,486.6,488.6
Internal standard		
NCI: $^{13}C_{12}$-3,3',4,4'-TetraBDE	Br^{-}	79.3,81.3
EI:$^{13}C_{12}$-3,3',4,4'-TetraBDE	$M^{+}+2, M^{+}+4$	495.6, 497.6
(Diacetyl)-TBBPA	$(M^{+}-(CH_3/2COCH_3))+4/+6$, $(M^{+}-2COCH_3+6, (M^{+}-COCH_3)+4/+6$	528.6,530.6, 545.7,585.8, 587.8
$^{13}C_{12}$-(Diacetyl)-TBBPA	$(M^{+}-(CH_3/2COCH_3))+4/+6$, $(M^{+}-2COCH_3+6, (M^{+}-COCH_3)+4/+6$	536.7,538.7, 555.8,557.8, 597.8

4.2.1.2 Reproducibility of the GC/MS system for PBFRs

For the determination of the reproducibility, multiple tests (n=10) were accomplished for selected guide substances (concentration: 250 pg μl^{-1}). The areas (A) of the guide substances were corrected by the area of the internal standard (A_{IS}) *3,3',4,4'-tetraBDE-ring-*$^{13}C_{12}$ and/or *diacetyl-TBBPA-ring-*$^{13}C_{12}$ for diacetyl-TBBPA. Table 6 displays the relative standard deviations *RSD (%)* and the A/A_{IS} values.

Table 6: Reproducibility of the Kodiak 1200/Bear Instrument (n = 10).

	EI Modus	*NCI Modus*
	RSD %	*RSD %*
2,2'-DiBB (BB4)	2.99	
2,4',5-TriBB (BB31)	2.74	
2,2',5,5'-TetraBB (BB52)	1.73	
2,2',4,5,5'-PentaBB (BB101)	2.01	
2,2',4,4',5,5'-HexaBB (BB153)	2.23	
2,2',3,3',4,4',5,5,6,6'DecaBB (BB209)	3.78	12.71
4-MonoBDE (BDE3)	1.05	
2,4'-DiBDE (BDE8)	1.51	
2,4,6-TriBDE (BDE32)	2.19	
2,2',4,4'-TetraBDE (BDE47)	2.51	
2,2',4,4',5-PentaBDE (BDE99)	2.05	
2,2',4,4',5,5'-HexaBDE (BDE153)	2.21	
2,2',3,4,4',5,6-HeptaBDE (BDE190)	3.53	5.43
2,2'3,3'4,4'5,5',6,6'-DecaBDE (BDE209)	2.5	6.77
HB	2.64	
HBCD	2.6	7.71
Diacetyl-TBBPA	4.06	

It has been shown that reproducibility is more unstable when NCI is used than with EI. As this was not observed all the time this fluctuation may be due to an instability in the methane gas pressure.

4.2.1.3 Detection und determination limits of PBFRs

The signal to noise ratio (SNR) of a standard solution was determined for selected guide substances in order to find the device-specific detection (DcL) and determination limits (DrL) of the MS.

The detection and determination limits can be calculated as follows:

$$DcL = 3 \cdot peak\ area_{noise} \cdot c_{subst} / peak\ area_{subst} \qquad [1]$$

$$DrL = 10 \cdot peak\ area_{noise} \cdot c_{subst} / peak\ area_{subst} \qquad [2]$$

The determination took place depending on the respective guide substance in the EI or NCI modus. Substances measured in the NCI modus are marked by an asterisk (Table 7).

Table 7: Detection and determination limits of guide substances in [pg μl^{-1}].

Guide substance	*DcL [pg μl^{-1}]*	*DrL [pg μl^{-1}]*
2,2'-DiBB (BB4)	2.1	6.9
2,4',5-TriBB (BB31)	0.96	3.3
2,2',5,5'-TetraBB (BB52)	1.7	5.7
2,2',4,5,5'-PentaBB (BB101)	2.3	7.6
2,2',4,4',5,5'-HexaBB (BB153)	4.3	14.4
2,2',3,3',4,4',5,5,6,6'DecaBB* (BB209)	9.7	32.7
4-MoBDE (BDE3)	0.3	1
2,4'-DiBDE (BDE8)	1.3	4.4
2,4,6-TriBDE (BDE32)	0.6	2.1
2,2',4,4'-TetraBDE (BDE47)	1.1	3.5
2,3',4,4'-TetraBDE (BDE66)	1.1	3.8
2,2',4,4',6-PentaBDE (BDE100)	1.1	3.6
2,2',4,4',5-PentaBDE (BDE99)	0.8	2.8
2,2',3,4,4'-PentaBDE (BDE85)	1.5	4.8
2,2',4,4',5,6'-HexaBDE (BDE154)	1.1	3.7
2,2',4,4',5,5'-HexaBDE (BDE153)	1.2	3.9
2,2',3,4,4',5'-HexaBDE (BDE138)	1.5	5.1
2,2',3,4,4',5,6-HeptaBDE (BDE190)*	0.8	2.5
2,2'3,3'4,4'5,5',6,6'-DeBDE (BDE209)*	10.8	36
HB	4.3	14.2
HBCD*	4.7	15.7
Diacetyl-TBBPA	4.5	15

* Determination performed using NCI modus

4.2.1.4 Verification of variance homogeneity

10 standard samples each of the lowest (x_1) and the highest (x_N) concentration of selected guidance substances were separately analysed within the provisional range of 5-10000 pg/µl to check variance homogeneity.

Guide substances	
2,2'-DiBB (BB4)	*4-MoBDE (BDE3)*
2,4',5-TriBB (BB31)	*2,4'-DiBDE (BDE8)*
2,2',5,5'-TetraBB (BB52)	*2,4,6-TriBDE (BDE32)*
2,2',4,5,5'-PentaBB (BB101)	*2,2',4,4'-TetraBDE (BDE47)*
2,2',4,4',5,5'-HexaBB (BB153)	*2,2',4,4',5-PentaBDE (BDE99)*
2,2',3,3',4,4',5,5,6,6'DecaBB (BB209)	*2,2',4,4',5,6'-HexaBDE (BDE154)*
HB	*2,2',4,4',5,5'-HexaBDE (BDE153)*
HBCD	*2,2',3,4,4',5,6-HeptaBDE(BDE190)*
Diacetyl-TBBPA	*2,2'3,3'4,4'5,5',6,6'-DeBDE(BDE209)*

The variance of the two respective series of measurement values was examined for homogeneity by means of the F-test [35].

$TV = s^2_N/s^2_1$

F (f_1=8; f_2=8, P 99%); F=6.03

For the given working zone and depending on the respective detection limit (see also Table 6) the test values determined for the guide substances were between 0.41 and 4.99 and thus under the F-value. This proves that variance homogeneity exists.

4.2.1.5 Range of linearity for PBFRs

Three concentration ranges (5 - 205 pg μl^{-1} (I), 200 - 1000 pg μl^{-1} (II), 1000-10000 pg μl^{-1} (III); 5 calibration solutions each equidistant in concentration; internal standard: 3,3',4,4'-TetraBDE-ring-$^{13}C_{12}$) were tested by means of Mandel's adjustment test (Equations 3 and 4) to check the linearity of the calibration functions used. For TBBPA the examination of the linearity took place as a diacetyl derivate. For this purpose the concentration ranges I - II (internal standard: TBBPA-ring-$^{13}C_{12}$) were derivatised and analysed as per Chapter 9.2.

$$DS^2 = (N-2)\, s^2_1 - (N-3) s^2_2 \qquad [3]$$

$$TV = DS^2 / s^2_2 \qquad [4]$$

$N = 10$

s^2_1 = *standard deviation of a first-degree (linear) function*

s^2_2 = *standard deviation of a second-degree (quadratic) function*

From the standard deviations s_1 (of the first-degree linear calibration function) and the standard deviations s_2 (of the second-degree calibration function) the difference of the variances DS^2 can be calculated. For the F-test the test value TV is calculated and compared with the table value F ($f_1 = 1$, $f_2 = N-3$, $P = 99$ %).

Linearity was checked for the following guide substances in NCI or EI modus:

Guide substances	
2,2’-DiBB (BB4)	4-MoBDE (BDE3)
2,4’,5-TriBB (BB31)	2,4’-DiBDE (BDE8)
2,2’,5,5’-TetraBB (BB52)	2,4,6-TriBDE (BDE32)
2,2’,4,5,5’-PentaBB (BB101)	2,2’,4,4’-TetraBDE (BDE47)
2,2’,4,4’,5,5’-HexaBB (BB153)	2,3’,4,4’-TetraBDE (BDE66)
2,2’,3,3’,4,4’,5,5,6,6’DecaBB (BB209)	2,2’,4,4’,6-PentaBDE (BDE100)
	2,2’,4,4’,5-PentaBDE (BDE99)
HB	2,2’,3,4,4’-PentaBDE (BDE85)
HBCD	2,2’,4,4’,5,6’-HexaBDE (BDE154)
Diacetyl-TBBPA	2,2’,4,4’,5,5’-HexaBDE (BDE153)
	2,2’,3,4,4’,5’-HexaBDE (BDE138)
	2,2’,3,4,4’,5,6-HeptaBDE(BDE190)
	2,2’3,3’4,4’5,5’,6,6’-DeBDE(BDE209)

The test values determined for the concentration ranges I - III for all examined guide substances were below the F-value of 12.25. The relative procedure standard deviations V_{xo} of the linear calibration functions were between 2-12 % in the EI modus and between 1-8 % in the NCI modus.

4.2.1.6 Sample extraction/analyte recovery rate

Toluene was used in the extractions in order to ensure as quantitative an extraction of the guide substances as possible, based on literature data [19, 20].

To clean the soxhlet apparatus and the glass fibre case a 2-hr pre-extraction was carried out with acetone and 2 hr with toluene.
To simulate real samples since no certified reference materials were available, the PUR foam plugs were supplemented with guide substances of the PBFR under simultaneous addition of 10ng $^{13}C_{12}$ - 3,3',4,4'-tetrabromodiphenylether. Two concentration ranges (8 ng/guide substance and 110 ng/guide substance) were tested using double determinations with an extraction period of 4 hr each.

The relative analyte recovery rate (ARR) is defined as the ratio of the average found from multiple measurements with the help of the standard addition procedure under repetition conditions $(\bar{x})$ to the conventional correct value x_{target} (Equation 1), related to 100 %.

$$ARR = \frac{\bar{x}}{x_{t\arg et}} \bullet 100\% \qquad [5]$$

The extracts were reduced down to 1-2 ml on a rotary evaporator (50 °C), up-concentrated to 20 µl in a nitrogen flow and the analyte recovery rate was determined for the guide substances. Simultaneously, the $^{13}C_{12}$-3,3',4,4'-tetraBDE standard was checked. To determine the analyte recovery rate of TBBPA it was derivatisated as per Chapter 9.2. Table 8 displays the determined percentage analyte recovery rate.

Table 8: Analyte recovery rate (n=2) of selected guide substances of PBFRs (8 ng/component and 110 ng/component) for soxhlet extraction using toluene.

	8 ng/component *ARR %*	*110 ng/component* *ARR %*
2,2'-DiBB (BB4)	70	78
2,4',5-TriBB (BB31)	78	83
2,2',5,5'-TetraBB (BB52)	108	99
2,2',4,5,5'-PentaBB (BB101)	115	105
2,2',4,4',5,5'-HexaBB (BB153)	105	106
2,2',3,3',4,4',5,5,6,6'DecaBB (BB209)	42	60.1
4-MonoBDE (BDE3)	142	70.6
2,4'-DiBDE (BDE8)	93.5	65.8
2,4,6-TriBDE (BDE32)	70.4	76.3
2,2',4,4'-TetraBDE (BDE47)	66.5	63
2,3',4,4'-TetraBDE (BDE66)	83.2	
2,2',4,4',6-PentaBDE (BDE100)	104	
2,2',4,4',5-PentaBDE (BDE99)	71.3	62
2,2',3,4,4'-PentaBDE (BDE85)	69.3	
2,2',4,4',5,6'-HexaBDE (BDE154)	74.6	
2,2',4,4',5,5'-HexaBDE (BDE153)	69.1	64
2,2',3,4,4',5'-HexaBDE (BDE138)	69	
2,2',3,4,4',5,6-HeptaBDE (BDE190)	97.2	
2,2'3,3'4,4'5,5',6,6'-DeBDE (BDE209)	35.1	45.1
HB	86.8	63
HBCD	75	116
Diacetyl-TBBPA	117	84
$^{13}C_{12}$- 3,3',4,4 TetraBDE	85	74

The analyte recovery rates over 100 %, for example for 4-monoBDE, are strongly affected by matrix overlays, and they become apparent in particular in connection with low SIM masses. Losses in the analyte recovery rate occur due to co-distillation effects during concentration on the rotary evaporator and when transferring the sample during sample processing. As a comparative measure the extracts were concentrated from 110 ml to 20 µl after repeated soxhlet extraction while blowing nitrogen onto the liquid surface. The analyte recovery rate was around 100% for all guide substances in both concentration ranges. A change of the solvent using hexane/acetone (50:50) produced a better analyte recovery rate, however an increase in the matrix load was observed in particular in the lower mass range. An increase in the time of extraction to 8 hours did not result in any improvement of the analyte recovery rate. On grounds of efficiency and cost considerations the rotary evaporator was used for concentration and toluene as an extraction agent.

Each extracted emission sample was reduced down to a minimum of 200 µl because of the above matrix problems and then analysed. For the correction of the analyte recovery rate of the selected guide substances, 20 ng $^{13}C_{12}$-3,3',4,4'-tetrabromo-diphenylether (target: 100 pg μl^{-1}) and 40 ng $^{13}C_{12}$ TBBPA (target: 200 pg μl^{-1}) was added to each PUR foam plug before extraction.

4.2.1.7 Breakthrough check

To check on the break-through of the adsorbed substances during sampling with PUR foam plugs and to test the accompanied losses, a simulation of real samples was carried out by supplementing each PUR foam plug with 400 ng of the guide substances specified in Table 7. The PUR foam plug (1) was transferred into a glass tube after the solvent volatilised and then another PUR foam plug (2) was attached (Figure 13).

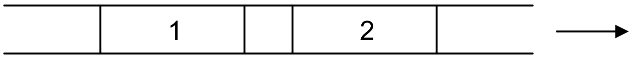


Figure 13: Supplemented PUR foam plug (1) and control foam plug (2) in a sampling glass tube.

Altogether an air volume of 20 m^3 was taken. The PUR foam plugs were extracted and analysed separately from each other as described in Paragraph 4.2.1.6. 0.5 to 2% of 4-monoBDE, 2,4'-diBDE and 2,2'-diBB with a was found in the control foam plug. The analyte recovery rate after extraction of the supplemented PUR foam plug (1) corresponded to the analyte recovery rate determined in Paragraph 4.2.1.6 for all further guide substances.

4.2.1.8 Results of the BSEF/Quasimeme Interlaboratory Study

The second international study on the analysis of polybrominated FRs in various environmental matrices and two standard solutions (QBC001SS, QBC002SS) was carried out between 1. November 2001 and 15. March 2002 within the framework of co-operation of *BSEF (Bromine Science Environmental Forum, Brussels, Belgium)*, the *Netherlands Institute for Fisheries Research (Ijuimden, The Netherlands)* and the *Quasimeme Programmes, FRS Marine Laboratory (Aberdeen, Great Britain)*. The study includes among others the analysis of BDE28, BDE47, BDE99, BDE100, BDE153, BDE154, BDE183, BDE209, HBCD, TBBPA. Altogether 36 laboratories took part in the investigation. The contents in the standard solutions mentioned were determined within the project for the purpose of analytical quality assurance. The graphics shown are copies from the final report „BSEF / Quasimeme Interlaboratory Study on brominated flame retardants“, Quasimeme Exercise 524 [58].

Figure 14, Figure 15 and Figure 16 display selected results of the tetrabrominated BDE47, the decabrominated decaBDE and HBCD.

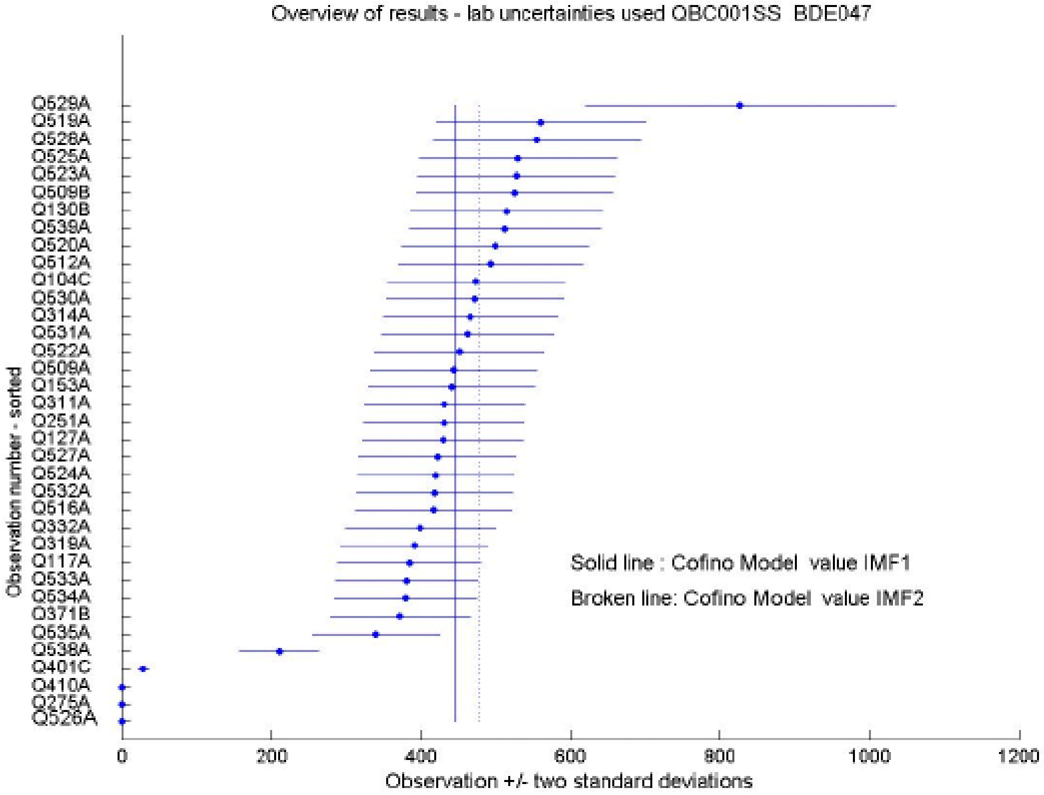


Figure 14: Results of quantification of BDE47 in a solution of unknown concentration.

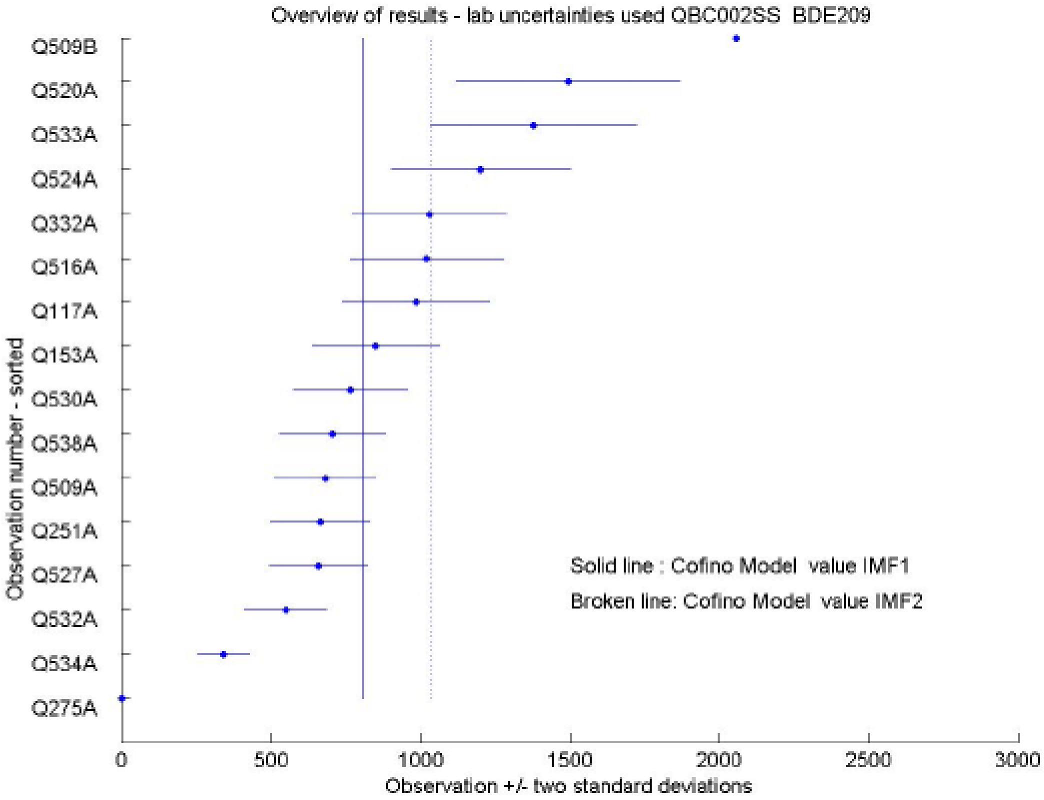


Figure 15: Results of quantification of BDE209 in a solution of unknown concentration.

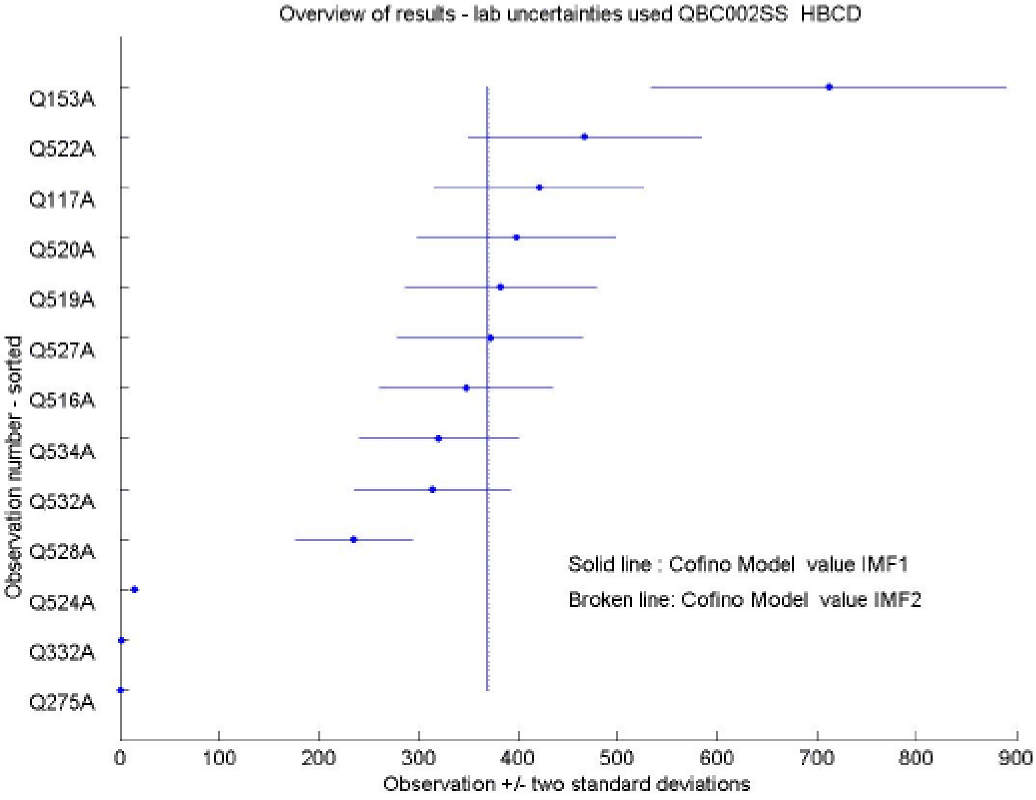


Figure 16: Results of quantification of HBCD in a solution of unknown concentration.

The laboratory code is not revealed here for commercial confidentiality reasons. The results for BDE47, HBCD and decaBDE lay within +/- two standard deviations, the execution of the analysis was thus successful in the context of the given conditions.

4.2.2 Determination of organophosphorus flame retardants (OPC)

4.2.2.1 GC/MS

GC/MS system:
GC 5890 Series 2 / HP MSD 5971A/ (mass range 50-600 amu)

Carrier gas	Helium
Column pre-pressure	5.8 psi
Injection system	Gerstel , PTV (KAS3)
Injector temperature programme	70 °C - 10 °C s^{-1} up to 280 °C - 5min
Transfer line	280 °C
GC column	HP-5-ms; 30 m; 0.25 mm ID; 0.25 µm d_F
Temperature programme	70 °C (1 min) - 10 °C min^{-1} - 300 °C (5 min)
Ionisation method	EI; 70 eV
Detector voltage	2000 V

Analysis of organophosphorus flame retardants by means of GC/MS is performed in the SIM modus using mass traces as listed below (Table 9). An ion (mass = QM) provides quantification, the two other ions (mass = IM1, IM2) provide a better assured peak identification.

Table 9: Mass traces QM, IM1 and IM2 used.

Substance	*Acronym*	*QM*	*IM1*	*IM2*
Tri(n-butyl)phosphate	*TBP*	*99*	*125*	*155*
Tris(2-chloroethyl)phosphate	*TCEP*	*249*	*143*	*251*
Tris(2-chloroisopropyl)phosphate	*TCPP*	*125*	*99*	*157*
Methylparathion	*ISTD*	*263*	*109*	*127*
Tris(1,3-dichloroisopropyl)phosphate	*TDCP*	*75*	*191*	*209*
Tris(2-ethylhexyl)phosphate	*TEHP*	*99*	*113*	*211*
Tris(2-butoxyethyl)phosphate	*TBEP*	*299*	*125*	*199*
Triphenylphosphate	*TPP*	*326*	*169*	*215*
Diphenylcresylphosphate	*DPC*	*340*	*168*	*243*
Tris(m-tolyl)phosphate	*TMTP*	*243*	*165*	*368*
Tris(p-tolyl)phosphate	*TPTP*	*243*	*165*	*368*
Recorcinol-bis-(diphenylphosphate)	*RDP*	*77*	*170*	*574*
9,10-Dihydro-9-oxa-10-phospha-phenanthren-10-oxid	*DOPO*	*216*	*168*	*199*

For the determination of TEP the following GC/MS system is used:

GC 5890 Series II PLUS / HP MSD 5972/ (mass range 50-550 amu)

Carrier gas	Helium
Column pre-pressure	1 bar
Injection system	Gerstel , PTV (KAS3); TDSA
Injector temperature programme	TDSA: 40 °C - 40 °C min^{-1} bis 290 °C – 5 min KAS3: -150 °C – 10 °C s^{-1} bis 290 °C – 5 min
Transfer line	320 °C
GC column	Rt_x 200 (30 m x 0.25 mm x 0.25 µm)
Temperature programme	40 °C (4 min), 5 °C min^{-1} to 140 °C 10 °C min^{-1} to 240 °C, 25 °C min^{-1} to 290 °C (3 min)
Detector:	280 °C
Detector voltage	2450 V

4.2.2.2 HPLC/UV

HPLC/UV system:
Agilent HP1100 with Diode Array Detector 1

Solvent	Solvent A: 30% Acetonitril Solvent B: 70% water
Pre-column	RP C-18; 2 cm × 2.0 mm ID; 5 µm d_F
HPLC column	Hypersil C-18; 12.5 cm × 2.0 mm ID; 5 µm d_F
Flow rate	0.20 ml min^{-1}
Column temperature	35 °C
Gradient programme	70 % Solvent B (up to 5min) - 0% Solvent B (up to 35 min) - 70 % Solvent B (up to 50 min)
UV detector	
Wave length	210 nm
Reference wave length	360 nm

4.2.2.3 Reproducibility of the GC/MS and HPLC/UV systems for OPCs

To the determination of the reproducibility multiple measurements (n=10) were accomplished for selected substances in independent experiments in each case for two different concentrations. Table 10 and Table 11 show the relative standard deviation *RSD (%)* of the values.

Table 10: Reproducibility of HP5971/MSD (n = 10).

	c, ng μl^{-1}	*RSD, %*	*c, ng μl^{-1}*	*RSD, %*
TBP	*5.3*	*2.3*	*10.6*	*2.7*
TCPP	*5.1*	*4.4*	*10.2*	*5.6*
Methylparathion	*2.5*	*6.0*	*2.5*	*5.6*
TPP	*5.8*	*7.8*	*11.7*	*3.2*
DPC	*5.3*	*2.8*	*10.7*	*3.4*
TMTP	*5.5*	*6.1*	*11.0*	*3.8*
TPTP	*5.0*	*5.4*	*9.9*	*3.4*
DOPO	*0.7*	*6.6*	*1.9*	*5.5*

Table 11: Reproducibility of HP1100/UV (n = 10).

	c, μg ml^{-1}	*RSD, %*	*c, μg ml^{-1}*	*RSD, %*
TPP	*11.65*	*0.9*	*5.83*	*0.8*
RDP	*4.57*	*2.3*	*1.83*	*1.2*
BDP	*3.78*	*2.9*	*1.51*	*2.0*

4.2.2.4 Detection und determination limits of OPCs

The signal to noise ratio (SNR) of a standard solution was determined for selected guide substances in order to find the device-specific detection (DcL) and determination limits (DrL) of MS and UV detectors (see calculation of detection and determination limits in Paragraph 4.2.1.3, Table 12).

Table 12: Detection und determination limits of selected guide substances in pg μl^{-1}.

	DcL, pg μl^{-1}	DrL, pg μl^{-1}
TBP	10	31
TCPP	17	55
TDCP	90	304
TPP	19	63
TmTP	52	174
TpTP	58	193
DOPO	15	51
TPP*	73	243
RDP*	57	190
BDP*	40	133
	DcL, $\mu g\ m^{-3}$	DrL, $\mu g\ m^{-3}$
TEP**	5	15

* Determination using HPLC/UV

** Determination using TENAX/Thermodesorption

4.2.2.5 Calibration

For the calibration of standard substances appropriate standard mixtures were produced for GC/MS and HPLC/UV analysis and analysed in triple measurements. Quantification by means of GC/MS takes place similarly to the real samples in SIM modus with 3 ions per substance in each case (see
Table 9).

It has been found that linearity of the calibration functions has been achieved for all organophosphorus compounds in the relevant concentration ranges (Figure 17, Figure 18, Figure 19) with BDP being the only exception.

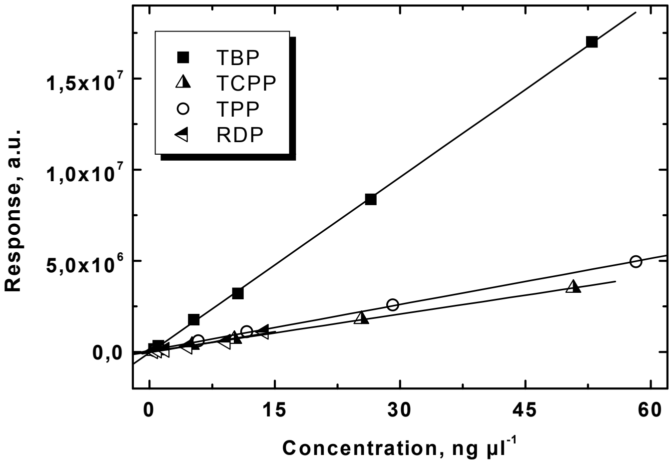


Figure 17: Calibration functions of TBP, TCPP, TPP and RDP(GC/MS).

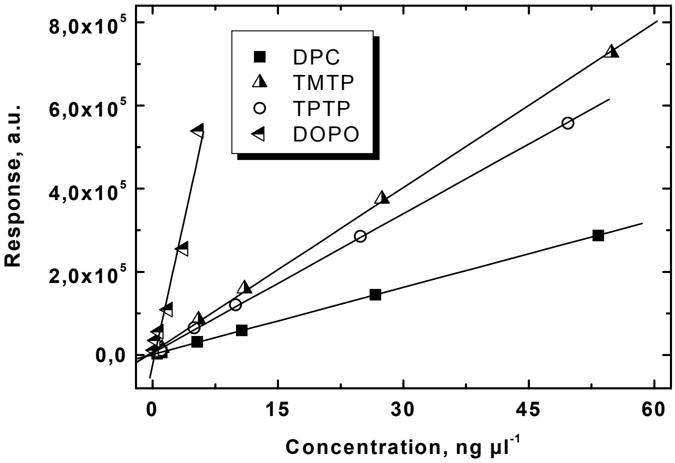


Figure 18: Calibration functions of DPC, TMTP, TPTP and DOPO (GC/MS).

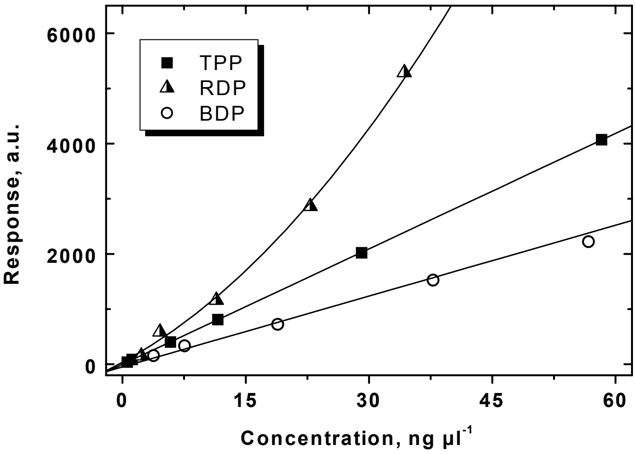


Figure 19: Calibration functions of TPP, RDP and BDP (HPLC/UV).

Table 13 displays the concentration ranges of the calibrations with the respective coefficient of correlation. Calibrations marked with an asterisk, refer to HPLC/UV.

Table 13: Range of concentration in [ng μl^{-1}] and correlation of the calibration function.

	Range of concentration [ng μl^{-1}]	*Coefficient of correlation*
TBP	*0.03 - 52.95*	*0.99998*
TCPP	*0.06 - 50.75*	*0.99994*
TPP	*0.06 - 58.25*	*0.99969*
DPC	*0.72 - 53.3*	*0.99996*
TmTP	*0.17 - 54.9*	*0.99973*
TpTP	*0.19 - 49.7*	*0.99977*
DOPO	*0.05 - 5.55*	*0.97778*
RDP	*0.19 - 15.7*	*0.98627*
*BDP**	*0.13 - 56.7*	*0.99770*

4.2.2.6 Sample extraction/analyte recovery rate

For the development of sample processing the two variants, soxhlet and ultrasonic bath extraction, were compared with one another on the basis of the analyte recovery rate in order to ensure optimum processing. The experiments were performed in each case in three independent experiments (plus a blank value) within a middle concentration range using double measurement. PUR foam plugs doped with the appropriate OPCs are extracted with acetone using toluene as a keeper. The processing of soxhlet extraction took place in each case for 4, 6 and 8 hours, the ultrasonic bath for 2×20 and/or 3×20 min. The results have shown that the most favourable extraction time is 6 hours for the soxhlet apparatus and 3×20 min for the extraction by ultrasonic bath. Therefore only the results of these test series are given in Table 14 to Table 17. Subsequently, the extracts from the rotary evaporator were reduced to approximately 2 ml, concentrated in a nitrogen flow to 1 ml and analysed by GC/MS. For the determination by HPLC/UV the sample is reduced in a nitrogen flow to a dry status then taken up in acetonitrile. The soxhlet apparatus was cleaned by an extraction with acetone for 2 hours and with toluene for 2 hours. The glassware used in the ultrasonic bath extraction was pre-cleaned with acetone.

The relative analyte recovery rate (ARR) is calculated as the ratio of the measured actual value, x_{actual} to the target value, x_{target} related to 100 % (see Paragraph 4.2.1.6).

Table 14: Medium analyte recovery rate and relative standard deviation (n=3) of selected OPCs plus blank value for ***soxhlet extraction*** *using acetone and toluene as keepers. Analysis: GC/MS.*

	c, ng μl^{-1}	ARR1	ARR 2	ARR 3	< ARR >	RSD %	BV
TBP	7.5	91.9	93.8	91.7	92.5	1.24	1.3
TCPP	7.7	92.2	98.0	96.3	95.5	3.12	0.1
TDCP	5.55	43.8	57.2	41.1	47.4	18.20	0
DOPO	0.7	0	28.4	13.5	13.8	101.7	0
TPP	9.2	98.3	105.9	105.6	103.3	4.17	0.1
DPC	7.6	96.5	104.8	101.3	100.9	4.13	0.1
TmTP	8.0	99.1	102.0	103.0	101.4	2.00	0
TpTP	7.5	92.1	99.7	99.6	97.13	4.49	0

Table 15: Medium analyte recovery rate and relative standard deviation (n=3) of selected OPCs plus blank value for ***soxhlet extraction*** *using acetone and toluene as keepers. Analysis: HPLC/UV.*

	c, ng μl^{-1}	ARR1	ARR2	ARR3	<ARR>	RSD %	BV
TPP	9.18	87.3	107.7	96.3	97.1	10.5	0
RDP	4.57	72.2	122.9	105.3	100.1	25.7	5.9
BDP	7.56	74.4	107.2	94.7	92.1	18.0	0.5

Table 16: Medium analyte recovery rate and relative standard deviation (n=3) of selected OPCs plus blank value for ***ultrasonic bath extraction*** *using acetone and toluene as keepers. Analysis: GC/MS.*

	c, ng μl^{-1}	ARR1	ARR2	ARR3	<ARR>	RSD %	BV
TBP	7.50	105.1	104.2	105.9	105.1	0.8	2.67
TCPP	7.67	104.3	102.9	103.9	103.7	0.7	0.1
TDCP	5.55	80.8	87.3	78.4	82.2	5.6	0
DOPO	0.74	14.2	21.0	23.7	19.6	24.9	0
TPP	9.18	110.3	109.7	115.5	111.8	2.9	0.1
DPC	7.59	107.8	108.0	108.5	108.1	0.3	0.7
TmTP	7.95	110.9	111.7	112.5	111.7	0.7	0
TpTP	7.55	105.85	103.3	108.4	105.9	2.4	0

Table 17: Medium analyte recovery rate and relative standard deviation (n=3) of selected OPCs plus blank value for ***ultrasonic bath extraction*** *using acetone and toluene as keepers. Analysis: HPLC/UV.*

	c, ng μl^{-1}	*ARR1*	*ARR2*	*ARR3*	*<ARR>*	*RSD %*	*BV*
TPP	*9.18*	*100.2*	*100.4*	*92.2*	*97.6*	*4.8*	*0*
RDP	*4.57*	*114.8*	*115.0*	*101.4*	*110.4*	*7.1*	*0*
BDP	*7.56*	*100.4*	*101.0*	*117.4*	*106.3*	*9.1*	*0*

The analyte recovery rates indicate that both extraction methods provide similar results (though processing of DOPO by means of soxhlet extraction has proved unsuitable). In addition since processing by ultrasonic bath is more gentle and requires less time and solvent, this method is preferred for the analysis of OPCs.

4.2.2.7 Comparison of GC/MS and HPLC/UV

Based on a selected test series the two methods GC/MS and HPLC/UV were compared with one another. 13 samples which contained TPP as an organophosphorus component, were quantified first by means of GC/MS, then analysed by HPLC/UV and quantified once again. The following Figure 20 shows the comparison of both methods, where quantification by GC/MS is set as 100%.

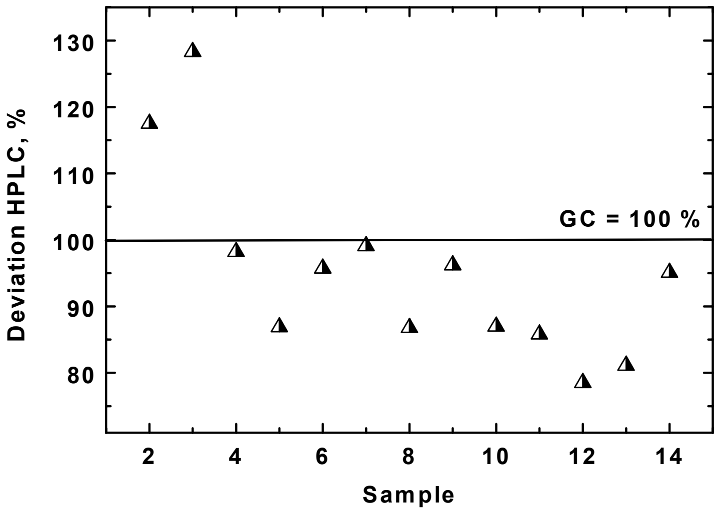


Figure 20: Comparison of GC/MS and HPLC/UV. The organophosphorus compound is triphenylphosphate (TPP).

Values determined by HPLC/UV are on the average 10% lower than those obtained by GC/MS. This difference is due to the additional sample processing.

4.2.2.8 Comparison of the systems Agilent GC Series 6890 / Bear Instruments Kodiak 1200 and GC 5890 Series 2 / HP MSD 5971A

The two GC/MS systems have been compared with one another based on a selected test series of 4 samples which contain TCPP as an organophosphorus component. The following Figure 21 shows a good agreement of both systems.

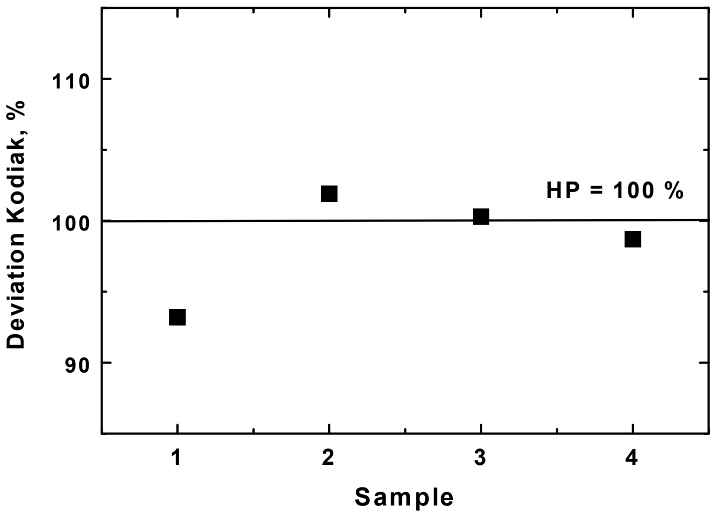


Figure 21: Comparison of the GC/MS systems Agilent GC Series 6890 / Bear Instruments Kodiak 1200 and GC 5890 Series 2 / HP MSD 5971A.

4.2.2.9 Sample simulation for selected OPCs

- Recorcinol-bis-(diphenylphosphate) [RDP]
- Bisphenol-A-bis-(diphenylphosphate) [BDP]
- 9,10-Dihydro-9-oxa-10-phospha-phenanthrene-10-oxide [DOPO]
- Diphenylcresylphosphate [DPC]
- Triphenylphosphate [TPP]

The determination of the emission profiles by emission test chamber measurements can be expected to lead to questionable results because of the low vapour pressures (and/or high boiling points) of DOPO, RDP, BDP and DPC at ambient temperature. To simulate a real sample, a 1cm × 6cm × 7cm piece of PUR foam (the same material as the sampling foam) was doped with 0.25g of the respective standard compound (in the case of DPC it is a technical mixture containing approx. 18% of TPP) and placed into a 0.02 m^3 emission test chamber.

Air sampling took place using suitably pre-purified PUR foam plugs (see Chapter 4) with an average of 18 m^3 of air sample volume over an entire test period of 200 days. The PUR foam plugs were extracted in the ultrasonic bath with acetone and processed by GC/MS and HPLC/UV for the purpose of quantification. Finally, the emission test chambers were rinsed with acetone and this fraction processed in a similar way as the other samples.

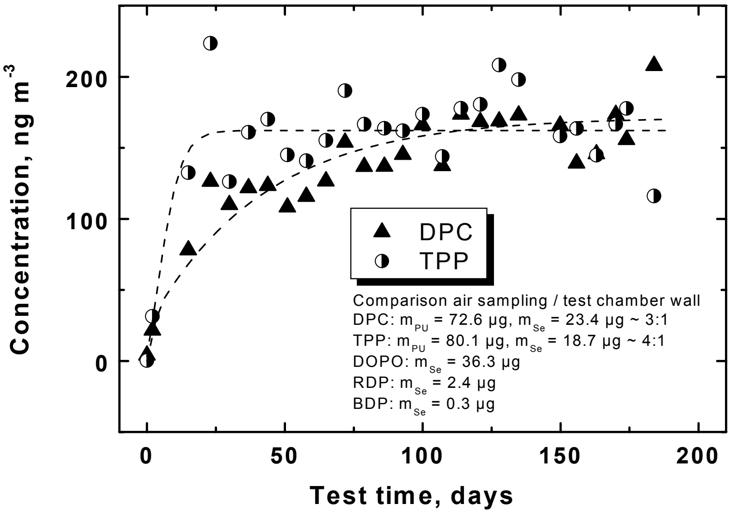


Figure 22: Concentration of DPC and TPP of a doped reference sample. Air sampling failed to prove the presence of other substances DOPO, RDP and BDP

Figure 22 shows the concentration of TPP and DPC in the doped reference sample. PUR foam sampling failed to determine concentration profiles for the remaining organophosphorus compounds DOPO, RDP and BDP under these conditions. Nevertheless a quantification of the rinsing fraction from the emission test chamber shows that OPCs are also emitted during the investigation period. Contrary to TPP (m_{PUR}: m_{Se} = 4:1) and DPC (m_{PUR}: m_{Se} = 3:1), adsorption on the chamber walls is predominant at these markedly low emission quantities. An increased emission was only observed after heating the sample (see Chapter 5.5) which was accompanied with a shift in the emission/sink equilibrium, and this enabled the emission measurement via air sampling using PUR foam.

4.2.2.10 Breakthrough check

To examine whether or not sampling leads to any material losses due to a breakthrough in the PUR foam plugs, two pre-purified foam plugs were placed in a glass tube (see Figure 13). The first PUR foam plug was doped with 200 µl of a solution of selected organophosphorus compounds ($c = 75\ ng\ µl^{-1}$). To simulate real sampling conditions a total of 26.8 m^3 of clean air was sucked through both foams over a period of 14 days. The foams were separately processed and analyzed (see Paragraph 4.2.2.6).

The analysis proved that 8% of the total TCPP content was in the control foam. As expected, PUR foam plug sampling is unsuitable for TBP: over 50 % of the total content was found in the foam plug (2). The analyte recovery rate for all further guide substances, obtained after extraction of the doped PUR foam plugs (1), corresponded to the analyte recovery rate determined in Paragraph 4.2.2.6.

4.2.3 Determination of chloroparaffins

4.2.3.1 GC/MS

GC/MS system:
HP GC 6890 plus/ Agilent MSD 5973

Carrier gas	Hydrogen and helium
Column pre-pressure	23.21 psi (160kPa)
Injection system	split/splitless injector
Transfer line	320 °C
GC column	DB-5-ms; 30 m; 0.25 mm ID, 0.25 µm d_F
Temperature programme	50 °C (3 min) - 15 °C/min - 280 °C (20 min) steady pre-pressure
Ionisation method	EI; 70 eV
Ion source T	230°C
Detector voltage	2300 V

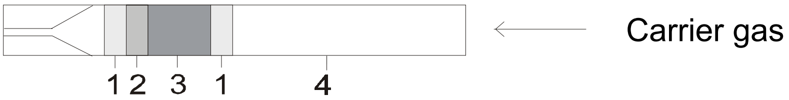
For the analysis of chloroparaffins the samples were first measured by GC/MS in SIM modus using the following mass traces:

Butyl residue	$C_4H_9^+$	57.10
Pentyl residue	$C_5H_{11}^+$	71.10
Hexyl residue	$C_6H_{13}^+$	85.10
Heptyl residue	$C_7H_{15}^+$	99.10

Another measurement was then performed under the same mass spectrometric conditions, however using a Pd catalytic converter placed into the liner of the injection system (see Figure 23).

Chloroparaffins are reduced to alkanes in this test and quantified afterwards.

The reduction of the chloroparaffins takes place directly in the injector of the gas chromatograph. The samples are injected into the insert filled with catalyst material produced by ourselves and hydrogenated catalytically by hydrogen at high temperature and high pressure. Subsequently, the reduced samples pass through the capillary separation column and into the detector.



1: Rock wool
2: Calcium carbonate
3: Pd catalytic converter
4: Vapourisation room of sample

Figure 23: Glass insert with filling

Since chloroparaffins are quantified as alkanes, an examination of alkanes which may still be in the sample before catalytic reduction was undertaken for the purpose of quality assurance.

4.2.3.2 Sample extraction/analyte recovery rate

Sample processing consisted of a soxhlet extraction and a consecutive cleaning by silica gel. Cleaning of the glassware took place via repeated rinsing with solvents of different polarity and a consecutive firing in the furnace at 400 °C. The complete soxhlet apparatus including sheath was pre-extracted with acetone for 2 hours and with cyclopentane for 2 hours. Afterwards the PUR foams were extracted for 8 hours with 60 ml of cyclopentane.

The extracts were reduced by the rotary evaporator (40°C) to 1-2 ml and concentrated to 200 µl under a light nitrogen flow. Subsequently, the samples were passed through a silica gel column. The solvent consisted of cyclopentane (1st fraction) and/or cyclopentane/dichloromethane (1:1; 2nd fraction). The 2nd fraction was re-used.

The samples obtained were reduced on the rotary evaporator (40°C) to 1-2 ml, concentrated to 20 µl in a light nitrogen flow and injected into the injector of the GC-MS for hydrogenation and quantification.

For the determination of the analyte recovery rate (Equation 5) the PUR foams were doped twice in each case with two chloroparaffin standard mixtures (CP-56 and CP-70) and extracted and processed as described above. Table 18 displays the determined analyte recovery rates.

Table 18: Analyte recovery rate (n=2) of chloroparaffin mixtures CP-56 and CP-70 with a concentration of 1 µg/µl.

Chloroparaffin mixture	ARR[%]
CP-56 (c=1 µg μl^{-1})	44
CP-70 (c=1 µg/μl^{-1})	59

Losses by extraction and consecutive reducing to 200 µl were determined likewise. The analyte recovery rates were 75 % for CP-56 and 88 % for CP-70.

Further losses occurred due to another cleaning of the silica gel column and by renewed reduction to 20 µl and transferring into other sample containers.

Increasing the extraction time from 4 h over 6 h to 8 h increased the analyte recovery rate, a further increase however provided no further improvement.

4.2.3.3 Reproducibility of the GC/MS system for chloroparaffins

Multiple determinations (n=6) were carried out for all alkanes used in standard to determine reproducibility.

Table 19: Reproducibility of HP GC 6890 plus/ Agilent MSD 5973 system.

Alkane (concentration 15 ng/µl)	***RSD %***
Undecane	5.42
Dodecane	5.29
Tridecane	5.25
Tetradecane	5.08
Pentadecane	5.78
Hexadecane	5.23
Heptadecane	4.56
Oktadecane	5.17
Nonadecane	4.44
Eicosane	4.06
Heneicosane	3.57
Docosane	3.43
Tricosane	3.40
Tetracosane	2.83
Pentacosan	2.24

4.2.3.4 Detection and determination limits of chloroparaffins

The signal to noise ratio (SNR) of a standard solution was determined for the selected guide substances in order to find the device-specific detection (DcL) and determination limits (DrL) (Equations 1 and 2) of the MS.

Table 20: Detection and determination limits of guide substances.

Alkane	*DcL [ng μl^{-1}]*	*DrL [ng μl^{-1}]*
Undecane	0.04	0.12
Dodecane	0.03	0.10
Tridecane	0.02	0.05
Tetradecane	0.02	0.05
Pentadecane	0.02	0.05
Hexadecane	0.02	0.05
Heptadecane	0.02	0.05
Oktadecane	0.02	0.06
Nonadecane	0.02	0.05
Eicosane	0.02	0.06
Heneicosane	0.04	0.11
Docosane	0.03	0.10
Tricosane	0.04	0.11
Tetracosane	0.03	0.10
Pentacosane	0.03	0.10

5 Results of emission chamber tests

5.1 Product selection

The results of emission measurements discussed below will be classified according to the following product groups:

- (1) Insulation foams
- (2) Assembly foams
- (3) IT devices
- (4) Circuit boards
- (5) Upholstered furniture, foams and mattresses

The following tables (Table 21, Table 22 and Table 23) display an overview of the tested products and the analysed flame retardants.

Table 21: Product group of insulation foams and guide substances.

Test series	***Product***	***Chamber***	***Measurement parameter***	***Target***
5.2	***Insulation foams***			
5.2.1	*PIR insulation foams, 2 different densities (ρ_1=30 g l^{-1}, ρ_2=80 g l^{-1})*	*0.02 m^3. 0.001 m^3*	*Standard**	*TCPP, POV****
5.2.2	*Insulating board polystyrene / XPS*	*0.02 m^3. 0.001 m^3*	*Standard**	*HBCD*
5.2.3	*Insulating board polystyrene / EPS*	*0.02 m^3. 0.001 m^3*	*Standard**	*HBCD*
5.2.4	*Insulating board, synthetic rubber, vulcanised*	*0.02 m^3*	*Standard**	*DecaBDE, DPC*
5.2.5	*Pipe insulation polyethylene*	*0.02 m^3*	*Standard**	*Chloroparaffins*

* *Standard conditions, clean air supply, 23 °C, 50 % relative air humidity*

** *Fire class B2*

*** *TBP, TCPP, TDCP, TPP, DPC, TMTP, TPTP, RDP, BDP, DOPO*

Table 22: Product group of assembly foams, IT devices and guide substances

Test series	***Product***	***Chamber***	***Measurement parameters***	***Target***
5.3	***Assembly foams***			
5.3.1	*1-K-PUR express pistol foam, new and stored, various surface qualities (smooth / sawn)* *(ρ = 21 g l^{-1})*	*0.02 m^3*	*Standard**	*TCPP*
5.3.1	*PUR assembly foam, B2 preparation**, smooth (ρ_1 = 20 g l^{-1})* *PUR door frame foam, sawn (ρ_2 = 25 g l^{-1})*	*0.02 m^3*	*Standard**	*TCPP*
5.3.1	*PUR pistol foam, B2 preparation**, smooth (20 g l^{-1})*	*0.02 m^3*	*Standard**	*TEP, TPP, DPC*
5.4	***IT devices***			
5.4.1	*PC work place A (PC, monitor, printer)*	*1 m^3*	*Standard* in operational modus*	*TBBPA, PBDEs, PBBs, HB, POV****
5.4.1	*PC work place B (PC and monitor)*	*1 m^3*	*Standard* in operational modus*	*TBBPA, PBDE, PBB, HB, POV****
5.4.1	*Printer case*	*0.02 m^3*	*Standard**	*TPP, RDP, BDP*
5.4.2	*Toner cartridge*	*0.02 m^3*	*40 °C*	*PBDE, PBB, HB*
5.4.3	*PC case, stored*	*0.02 m^3*	*Standard**	*TBBPA*
5.4.4	*TV case, stored*	*0.02 m^3*	*Standard**	*PBDE*

* *Standard conditions, clean air supply, 23°C, 50 % relative air humidity*

** *Fire class B2*

*** *TBP, TCPP, TDCP, TPP, DPC, TMTP, TPTP, RDP, BDP, DOPO*

Table 23: Product groups of circuit boards, upholstered furniture, foams, mattresses and guide substances

Test series	***Product***	***Chamber***	***Measurement parameters***	***Target***
5.5	***Circuit board***			
5.5.1	*Circuit board + case*	*0.02 m*^{3}	*23 °C* *and 60 °C*	*PBDE, HB, PBB, TBBPA, POV*
5.6	***Upholstered furniture and foam, mattresses***			
5.6.1	*Upholstered furniture stool, made of upholstery foam and covering*	*0.001 m*^{3}	*Standard**	*TCPP,PBDE, HB,PBB*
5.6.2	*Upholstery foam*	*1 m*^{3}	*Standard**	*TCPP*
5.6.3	*Mattress*	*1 m*^{3}	*Standard**	*TCPP*

* *Standard conditions, clean air supply, 23°C, 50 % relative air humidity*

** *Fire class B2*

*** *TBP, TCPP, TDCP, TPP, DPC, TMTP, TPTP, RDP, BDP, DOPO*

5.2 Product group 1 – insulation foams

Sample size and emission test chamber parameters

A model room with a total volume of V_t = 17.4 m^3 and an air exchange rate of n = 0.5 h^{-1} is assumed when sample dimensions of insulating boards are specified [21]. It is also assumed that the insulation surface of the model is A_t = 7 m^2. As an area-specific air flow rate of q = 1.243 m^3 m^{-2} h^{-1} is obtained from these data ($q = (n\ V_t)/A_t = V°/A_t$; *volumetric air flow rate:* $V°=8.7\ m^3\ h^{-1}$), samples with an emitting surface of A_{Em} = 0.103 m^2 are placed into the 0.02m^3 emission test chamber where the volumetric air flow rate is 0.128 m^3 h^{-1}. For the 0.001 m^3 emission test cell an emitting surface of A_{Em} = 0.0177 m^2 and a volumetric air flow rate of 0.022 m^3 h^{-1} is identified. The same model room is used for the calculation of q in the test series 5.2.4. The sample surface of the pipe insulation was calculated to 2.63 m^2 on the basis of a pipe length of 12 m (total ∅ : 0.07 m; wall thickness of the shell: 0.024 m), from which an area-specific air flow rate of $q = 3.3\ m^3\ m^{-2}\ h^{-1}$ is obtained. Thus a sample with a surface of 0.038 m^2 is used in the emission test chamber.

The measurements are undertaken under standard conditions (23 °C, 50 % R.H.). The sides of the cut sections are covered with aluminium adhesive tapes to make sure that emission is measured from the surface only and not from the narrow sides, which proportionally may contribute to an over-sized section for small samples in the emission test chambers.

Air sampling takes place with suitably prepared PUR foams (Chapter 4). Blank values were measured by means of PUR foam sampling for each emission test chamber before placing the sample in it.

Test series 5.2.1: Determination of TCPP emission from insulation foams

Objectives of the test series

- Determination of emission curves for TCPP from various PIR insulation foams
- Investigation of the influence of various sample densities ($\rho_1 = 30\ g\ l^{-1}$, $\rho_2 = 80\ g\ l^{-1}$) on the emission behaviour of TCPP
- Investigation of the influence of the emission test chamber size (comparison: 0.02m^3 emission test chamber / 0.001m^3 emission test cell) on the measurement

The PIR foams were welded in polyethylene foils and supplied directly by the manufacturer and declared to originate from current production. However the investigations performed indicated that the manufacturer's data on the flame retardant type were not entirely correct.

Sampling

Air sampling took place using suitably prepared PUR foams every 3rd to 4th day with an average sampling volume of 0.3 m^3 (0.001m^3 emission test cell) or 2.4 m^3 (0.02m^3 emission test chamber) per day over an entire test period of 60 days. The PUR foams were extracted in an ultrasonic bath with acetone (Paragraph 4.2.2.6), and quantitative determination was carried out by GC/MS (Paragraph 4.2.2.1). Finally, the emission test chambers were rinsed with acetone and, similar to other samples, this fraction was also processed.

Figure 24 shows the concentration of TCPP from two PIR (polyisocyanurate) insulation foams with different densities (Type I, ρ_1 = 30 kg m^{-3}; Type II, ρ_2 = 80 kg m^{-3}), the measurements took place in the 0.02m^3 emission test chamber.

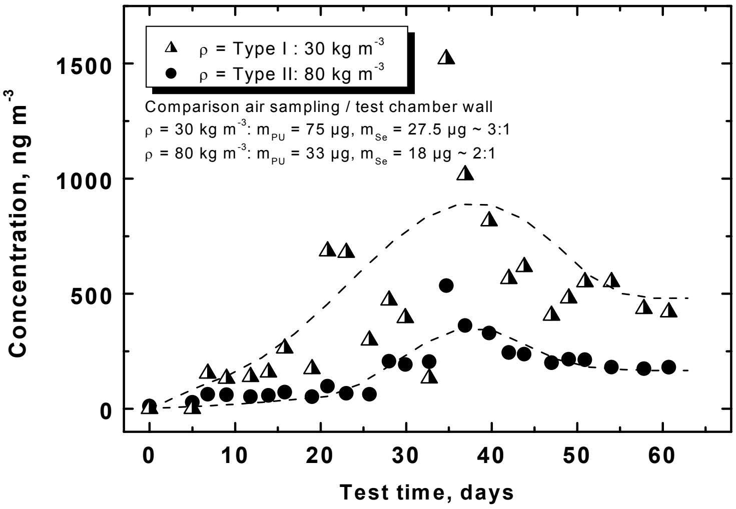


Figure 24: Concentration of TCPP from two PIR insulation foams with different densities (Type I, ρ_1 = 30 kg m^{-3}; type II, ρ_2 = 80 kg m^{-3}) as a function of test time.

Qualitatively similar concentration profiles were observed in both experiments. The concentrations increase slowly during the first 30 measurement days, and maxima of about 250 ng m^{-3} and 800 ng m^{-3} were obtained within the following 10 days. Afterwards the concentrations decreased to 170 ng m^{-3} and 480 ng m^{-3}.

The concentration curves indicate that steady-state conditions between the concentration of TCPP in the air and the adsorption on the chamber walls are established in about 50 days. However, migration of TCPP to the surface of the PIR insulation foam may be another potential cause of this concentration profile. The assumption that sink effects strongly influence the test results has been confirmed by the analysis of the rinsing fractions of the chamber walls. In the case of Type I insulation foam, a mass of m_{PUR} = 75 µg TCPP was determined via PUR sampling over the entire test period. Contrary to that a sink effect of m_{SE} = 27.5 µg TCPP was found on the chamber walls, i.e. altogether about 25 % of the emitted phosphoric acid ester is adsorbed on the chamber wall. In the case of Type II insulation foam this is about 33 %.

Considering the concentrations 170 ng m^{-3} and 480 ng m^{-3} as equilibrium concentrations, emission rates of 0.60 µg m^{-2} h^{-1} (Type I) and 0.21 µg m^{-2} h^{-1} (Type II) can be calculated with the help of the area-specific air flow rate of q = 1.243 m^{3} m^{-2} h^{-1}. These values can be confirmed by another type of calculation. Emission rates of 0.70

µg m^{-2} h^{-1} (Type I) and 0.35 µg m^{-2} h^{-1} (Type II) can be calculated from the total mass of the emitted TCPP (m_{PU} + m_{SE}) using the total test time of 1464 hours and an emitting area of 0.103 m^2.

The increased emission of TCPP from the insulation foam with the smaller density (Type I) is obviously due to an increased interface between the polymer phase and air. There is an approximate proportion of 2:1 TCPP in Type I (5 %) and Type II (approx. 2 %) according to the manufacturers' data. This relationship was confirmed by XRF screening.

Figure 25 shows the investigation of the influence of various emission test chambers and cells on the measurement of TCPP concentration using the example of a Type I PIR insulation foam in a 0.02m^3 emission test chamber and a 0.001m^3 emission test cell.

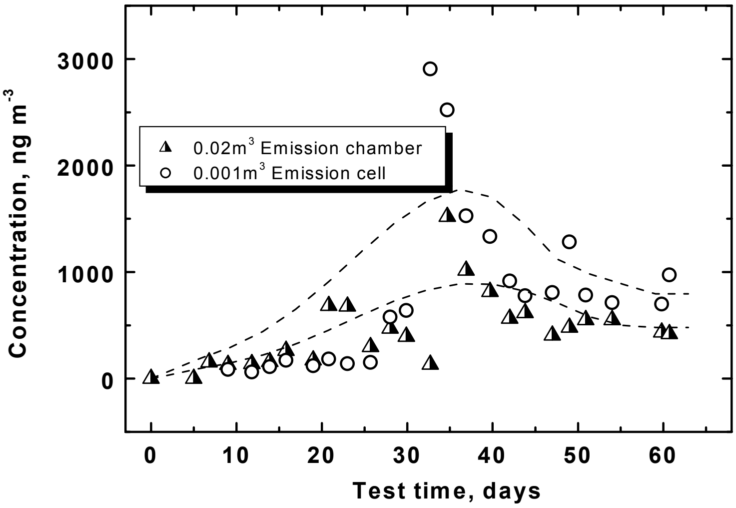


Figure 25: TCPP concentration profiles as a function of test time. The measurement was carried out in a 0.02m^3 emission test chamber and a 0.001m^3 emission test cell

Qualitatively comparable concentration profiles were found in both experiments. The concentrations rose to a maximum of about 800 ng m^{-3} (0.02 m^3 emission test chamber, see above) and 1800 ng m^{-3} (0.001 m^3 emission test cell) during the first 30 to 40 days. The values then decreased to 480 ng m^{-3} and 780 ng m^{-3} around the end of the 60-day period.

The higher concentration values of TCPP determined by the 0.001m^3 emission test cell result from a more favourable source to sink ratio of this experimental set-up. In the emission test cell a total mass of m_{PUR} = 17 µg was measured during the complete test period, while in the chamber a mass of m_{PUR} = 33 µg of the organophosphorus compound was determined via PUR sampling. In contrast, there is an emitting surface of 0.0177 m^2 in the emission test cell and 0.103 m^2 in the emission test chamber.

Test series 5.2.2: Determination of HBCD emission from polystyrene

Objectives of the test series

- Investigation of the emission behaviour of the cycloaliphatic, polybrominated flame retardant HBCD from extrudable polystyrene (XPS, Styrodur®, HBCD content: approx. <1 %) and expandable polystyrene, (EPS, Styropor®, HBCD content: approx. 1-2 % by weight).
- Determination of the influence of a 0.001m^3 emission test cell and a 0.02m^3 emission test chamber on the measured emission.

The sample material was obtained directly from the manufacturer and was specifically produced for the purposes of the tests.

Sampling

Air sampling was carried out using suitably prepared PUR foams (Chapter 4). The tests altogether took 105 days (0.001 m^3) and 120 days (0.02 m^3) for EPS and 110 (0.02 m^3) and 321 days (0.001 m^3) for XPS. The sample change took place weekly and/or every 14 days. The average sampling volume was 2.4 m^3 per day (0.02 m^3) and 0.36 m^3 per day (0.001 m^3). The PUR foams were processed as per Paragraph 4.2.1.6, the quantitative determination was made by GC/MS (Paragraph 4.2.1.1). At the end of the experiment the emission test chambers and cells were rinsed with acetone and then with toluene. The two fractions were combined, concentrated and likewise analysed by GC/MS.

Results and discussion

Under the given conditions no HBCD emission was proved for EPS. For the procedure a determination limit of 0.33 ng m^{-3} was determined for an average sampling volume of 10 m^3. Rinsing the chamber and cell provided 1 µg m^{-2} (0.001 m^3) and 3 µg m^{-2} (0.02 m^3). The values have to be regarded however as semi-quantitative, since HBCD cannot be removed completely by rinsing with a solvent from the glass surface.

Likewise no emission was proved for XPS in the 0.02 m^3 emission test chamber under the given conditions. 21 µg m^{-2} was found in the rinsing fraction. It must also be borne in mind in this instance that rinsing for the recovery of HBCD is not sufficiently quantitative.

The XPS sample in the 0.001 m^3 emission test cell showed trace concentrations of up to a maximum of 1.79 ng m^{-3} from a test period of 105 days, which then dropped below the detection limit after 150 days. The rinsing fraction of the emission test cell contained 0.327 µg m^{-2}.

The area-specific emission rates obtained from the rinsing fractions were as follows:

EPS (0.02 m^3): 4 ng $m^{-2}h^{-1}$
EPS (0.001 m^3): 1 ng $m^{-2}h^{-1}$
XPS (0.02 m^3): 29 ng $m^{-2}h^{-1}$
XPS (0.001 m^3): 0.1 ng $m^{-2}h^{-1}$

The determined emission rates show comparable values for EPS. Deviations arise however for XPS. This fluctuation may be connected with a low solubility and high adsorption capacity of HBCD, the values as such have to be regarded as semi-quantitative.

Test series 5.2.3: Determination of decaBDE (BDE 209) emission and further components from synthetic, vulcanised rubber

Objectives of the test series

- Investigation of the emission behaviour of decaBDE from vulcanised, synthetic rubber in a 0.02m^3 emission test chamber
- Determination of the emission of further potential polybrominated diphenylethers with a low bromine content, of the organophosphorus flame retardant/softener DPC and TPP.

The samples were delivered directly by the manufacturer, exact production dates unknown. The manufacturer indicated a decaBDE content of 6%. The material tested here was packed and delivered together with other insulation materials, which contained other flame retardant types (e.g. the sample of the test series 5.2.4).

The determination of decaBDE (and further PBDE) and DPC emission took place using PUR foam double sampling (Chapter 4). For qualitative checks of the contained PBFR a small amount of insulation material was extracted in the ultrasonic bath, concentrated up three times with toluene and measured by GC/MS.

Sampling - PBDE

The test for emission determination of polybrominated components altogether took 277 days. The sample change for air sampling took place every 14 days with an average sampling volume of 1.2 m^3 per day. The PUR foams were processed as per Paragraph 4.2.1.6, quantitative determination was carried out by GC/MS (Paragraph 4.2.1.1).

Results and discussion - PBDE

No decaBDE emission was measured during the 227-day test period. The determination limit of the procedure was 6 ng m^{-3} for an average sampling volume of 10 m^3.

Furthermore it was examined whether or not the material emits further PBDE congeners and isomers, which may result from the material production or from debromination during storage or may be contained in the technical decaBDE as impurities. Within this investigation, the presence of BDE17, BDE28, BDE47, BDE66, BDE100, BDE99, BDE85, BDE154, BDE153, BDE138, BDE190 and further congeners and isomers contained in the technical octaBDE was tested (see Ballschmitter number and technical product in Appendix 1). In addition, the presence of the isomers of monoBDE and diBDE was checked. BDE3 and BDE8 served as references (Chapter 4.1), since monoBDEs and diBDEs are not contained as such in the technical products. No positive proof was found for these selected PBDEs either.

The determination limits of the procedure including sample preparation for a medium sampling volume of 10 m^3 for the individual PBDEs were as follows:

MonoBDE/diBDE	2 ng m^{-3}
TriBDE	1.5 ng m^{-3}
TetraBDE/pentaBDE	0.8 ng m^{-3}
HexaBDE	1.2 ng m^{-3}.
HeptaBDE	2 ng m^{-3}
OctaBDE	3 ng m^{-3}
NonaBDE	3 ng m^{-3}

An analysis of the insulation foam proved positive for decaBDE. It was however not possible to prove any further debrominated congeners due to the high matrix load. Rinsing extracts of the emission test chamber did not prove positive for decaBDE. Traces of BDE47 and BDE99 were found in the rinsing extracts, the values were however below the determination limit.

Sampling - OPC

Sampling for the determination of organophosphorus compounds took altogether 188 days. Sample change took place every 14 days, and the intake volume was 50 l h^{-1}. This corresponds to an average sampling volume of 1.2 m^3 d^{-1}. PUR foams were processed as per Paragraph 4.2.2.6, the quantitative determination was performed by GC/MS and HPLC/UV (Paragraph 4.2.2.1).

Results and discussion - OPC

Figure 26 illustrates the concentrations of TPP and DPC from rubber insulation as a function of time. It was not possible to prove the presence of the remaining organophosphorus compounds with regard to the detection limits (see Paragraph 4.2.2.4). Qualitative and quantitative differences were equally observed. The two concentration profiles climb to a maximum of about 70 to 75 ng m^{-3} during the first 40 to 50 days. While the measurement results for DPC, oscillate constantly around 70 ng m^{-3} although with some scattering during the further part of the experiment, the concentration of TPP decreases slowly to a value around 40 ng m^{-3}.

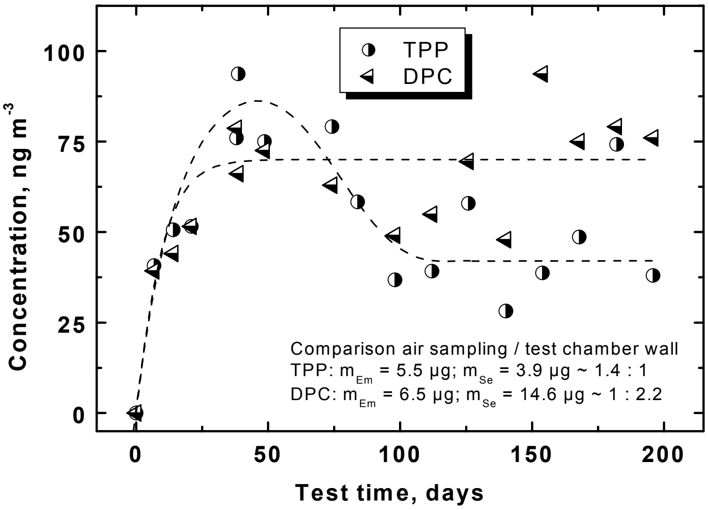


Figure 26: Concentration of TPP and DPC as a function of test time

Considering the concentrations 70 ng m^{-3} and 40 ng m^{-3} as equilibrium concentrations, emission rates of 87 ng m^{-2} h^{-1} (DPC) and 50 ng m^{-2} h^{-1} (TPP) can be calculated with the help of the area-specific air flow rate of q = 1.243 m^3 m^{-2} h^{-1}. The following table compares these values with the emission rates calculated from the total mass of the emitted OPC ($m_{total} = m_{PUR} + m_{SE}$) taking into account a test period of 4512 h (=188 d).

Table 24: Area *specific emission rates (SER_a) of TPP and DPC from a synthetic, vulcanised rubber.*

	$SER_{a,OPC} = m_{total} /(t_{total} \times A_{Em\cdot})$	$SER_{a,OPC} = c_{eq} \times q$
TPP	*20 ng m^{-2} h^{-1}*	*50 ng m^{-2} h^{-1}*
DPC	*46 ng m^{-2} h^{-1}*	*87 ng m^{-2} h^{-1}*

The values determined on the basis of different calculation principles are within the same order of magnitude.

For the verification of the emission tests the sample was extracted directly in the ultrasonic bath. For this purpose a small amount (1.0 g) of the sample was given in acetone and extracted in the ultrasonic bath for 2 × 15 min. Processing of the extract took place similarly to the emission samples (cf. Paragraph 4.2.2.6) with a consecutive analysis by GC/MS and HPLC/UV. TPP and DPC were identified unambiguously.

Test series 5.2.4: Determination of emission of chloroparaffins from polyethylene insulation foam

Objectives of the test series

- Investigation of the emission behaviour of chloroparaffins of unknown composition from a pipe insulation foam (0.02 m^3 emission test chamber)

The sample was delivered together with the sample of the test series 5.2.3 directly by the manufacturer (see above). It is a closed-cell polyethylene foam. The insulation material serves for the isolation of pipes in the sanitary and heating equipment field.

Sampling

The test period (PUR foam) was 203 days altogether. Sample changes took place weekly. The average sampling volume was 2.4 $m^3 d^{-1}$. PUR foams were processed as per Paragraph 4.2.3.2, the quantitative determination was performed by GC/MS (see Paragraph 4.2.3.1). [*]

Results and discussion

It was not possible to prove chloroparaffins in all samples tested.
According to manufacturer data, solid chloroparaffins with a chlorination degree of 70% and a chain length of C_{16-20} were used as CP-based flame retardants with an extremely low vapour pressure. Long-chain CPs with only 42 % chlorine content already exhibit steam pressures of $< 2.7 \times 10^{-4}$ Pa at 80 °C. Under these circumstances therefore no measurable outgassing was observed.

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[*] Sample processing and analytic determination was performed on the Berlin Technical University, Fasanenstr. 1A, 10967 Berlin, by Ms Dipl.-Chem. Stefanie Heimroth, Institute for Environmental Chemistry, Head: Prof. Dr. Wolfgang Rotard.

5.3 Product group 2 – assembly foams

Sample size and emission test chamber parameters

When defining sample dimensions, a model room (as per manufacturer model) with one door, two windows and a total volume of V_t = 30 m^3 with an air exchange rate of n = 0.5 h^{-1} is assumed. The assumed insulation area in the model is A_t = 0.324 m^2 (foamed area: door: 0.113 m^2; two windows: 0.211 m^2). From the area-specific air flow rate of q = 46.3 m^3 m^{-2} h^{-1}, a sample surface of 0.0028 m^2 is obtained which will be placed into the emission test chamber.
In order to achieve a more favourable source to sink ratio, test samples with the dimensions of 0.19 m x 0.03 m x 0.03 m (0.025 m^2) were placed into the 0.02m^3 emission test chamber. Due to the increased sample area a surface-specific air flow rate of q = 5.12 m^3 m^{-2} h^{-1} is obtained. The volumetric air flow rate was 0.128 m^3 h^{-1}. The measurements were accomplished under standard conditions (23 °C, 50% relative air humidity).
Air sampling took place with suitably prepared PUR foams (Chapter 4). Blank values of each emission test chamber were determined by means of PUR foam sampling technique before placing the samples into the chamber.
The samples were either foamed up directly in suitable forms or sawn off from a larger piece. The material was delivered welded in an aluminium/plastic foil sandwich or wrapped up in an aluminium foil by the manufacturer.

Test series 5.3.1: Determination of OPC emission from assembly foams

Objectives of the test series

- Determination of emission curves of various organophosphate compounds (TEP, DPC, TPP and TCPP) from assembly foams
- Investigation of the influence of various sample densities (ρ_1 = 20g l^{-1}, ρ_2 = 25g l^{-1}) on the emission behaviour of TCPP in an assembly foam (B2 formulation)
- Investigation of the influence of various sample surfaces (smooth / sawn) on the emission behaviour of TCPP in an assembly foam
- Investigation of the emission behaviour of TCPP as a function of sample age (testing new assembly foams at works, samples tested again after a storage of 6 months)

Sampling

Air sampling took place with suitably prepared PUR foams every 3 to 4 days and 7 days with an average sampling volume of 2.2 m^3 per day. The test took a total of 40 to 250 days depending on the sample and the organophosphate compound to be analysed. The PUR foams were extracted in an ultrasonic bath with acetone (Paragraph 4.2.2.6), the quantitative determination was performed by GC/MS (Paragraph 4.2.2.1). Identification of TEP took place via thermodesorption using Tenax sampling (Paragraph 4.2.2.6). At the end of the experiment the emission test chambers were rinsed with acetone and this fraction was processed similarly to the other samples.

Results and discussion

Figure 27 shows the concentration of DPC and TPP from a B2 PUR pistol foam with a smooth surface as a function of time. The experiment was carried out for a period of 250 days because of the low emission rates and the slow development of chamber equilibrium.

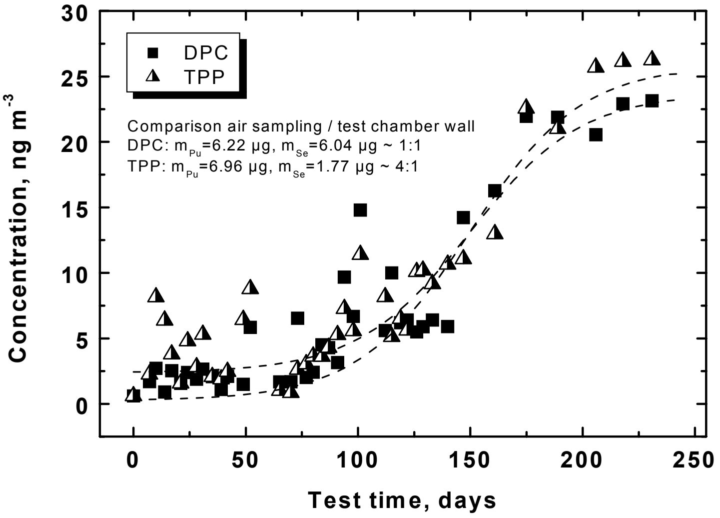

Figure 27: Concentration of DPC and TPP from a B2 PUR pistol foam as a function of test time.

Figure 27 clearly shows the sigmoid shape of the concentration profiles as chamber equilibrium is achieved. The strongest increase takes place within the period between 100 and 170 days: the concentration rises from about 5 ng m^{-3} to approx. 20 ng m^{-3}. A comparison of both emission curves indicates that the emission rates are very similar. This is all the more remarkable, as the tested sample contains very different amounts of two phosphoric acid esters. In the production of the pistol foam a technical flame retardant preparation was used, which contains only about 20 % of TPP beside DPC (see Chapter 6.2).

When comparing the emitted masses m_{PUR} determined by PUR sampling during the test with the masses m_{SE} proven at the chamber walls, a significant difference can be observed between DPC and TPP (see Table 25).

Table 25: Comparison air sampling /adsorption at test chamber wall.

OPC	m_{PU}	m_{Se}	m_{total}	$m_{PU} : m_{Se}$
DPC	*6.2 µg*	*6.0 µg*	*12.2 µg*	*1:1*
TPP	*7.0 µg*	*1.8 µg*	*8.8 µg*	*4:1*

In the case of TPP, altogether about 20 % of the emitted phosphoric acid ester is adsorbed by the chamber wall, in the case of DPC about 50 %. This means that during the test a higher portion of DPC is emitted from the sample than the concentration profile in Figure 27 suggests.

The following table displays emission rates ($SER_{a,OPC}$) calculated from the total mass of the emitted OPC ($m_{total} = m_{PUR} + m_{SE}$) taking into account the total period of test t_{total} = 5520 h (= 230 d) and an emission area of A_{Em} = 0.025 m^3. This overview is supplemented by emission rates which were obtained from the two equilibrium concentration values of 25 ng m^{-3} and 24 ng m^{-3} and the area-specific air flow rate of q = 5.12 m^3 m^{-2} h^{-1}. The deviations indicate that this system is not yet in equilibrium after a period of test of 240 days.

Table 26: Area-specific emission rates of TPP ($SER_{a,TPP}$) and DPC ($SER_{a, DPC}$) from a PUR assembly foam.

	$SER_a = m_{total} / t_{total} \times A_{Em}$	$SER_a = c_{eq} \times q$
TPP	*65 ng m^{-2} h^{-1}*	*130 ng m^{-2} h^{-1}*
DPC	*90 ng m^{-2} h^{-1}*	*125 ng m^{-2} h^{-1}*

The concentration profile of TEP, which is present beside DPC and TPP in the tested sample, shows a completely different shape. The concentration of this alkylated phosphoric acid ester is shown in Figure 28 as a function of time. Due to strongly differing concentration ranges of the emissions and a different method used for sampling (Tenax/thermodesorption), a separate figure has been selected. The concentration profile - high initial value of about 60 µg m^{-3} then a relatively steep drop to below 10 µg m^{-3} within the first 28 days - shows the typical concentration profile of a volatile component contrary to the semivolatile compounds DPC and TPP. The test signal falls below the detection limit of 5 µg m^{-3} within 50 days (Paragraph 4.2.2.4). Even after 135 days, TEP could not be detected.

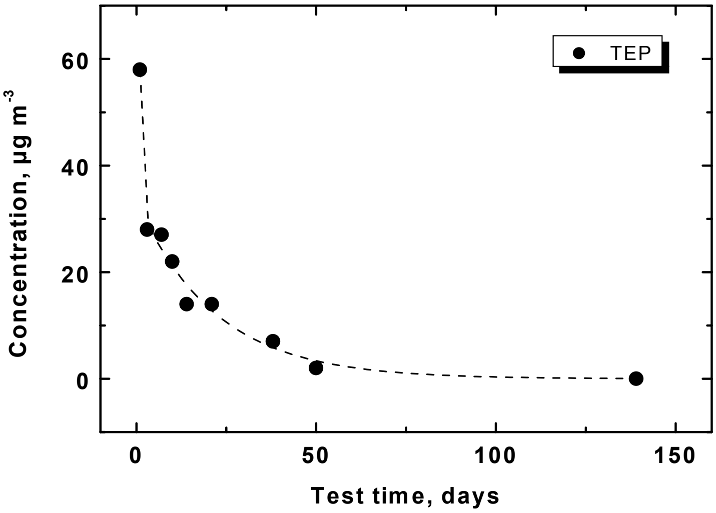

Figure 28: Concentration of TEP as a function of test time.

In another experiment a B2 PUR assembly foam (Type I) and a frame foam (Type II) with sawn surfaces were tested, which were present in different densities (Type I, ρ_1 = 20 g l^{-1}, Type II, ρ_2 = 25 g l^{-1}). Figure 29 shows the concentration profiles of TCPP as a function of time. The tests were performed for periods of 40 and 100 days. An XRF screening allowed the estimation of an FR content as 18 % (Type I) and 14 % (Type II).

At the beginning of the experiment the measured values rise fast to a maximum of approximately 15 µg m^{-3} and then fade away slowly - in this case - to an equilibrium value of about 3 µg m^{-3}. It can be seen that the two different test series exhibit no significant differences, therefore the test series of Type II was terminated after 40 days.

Considering the concentration of 3 µg m^{-3} as an equilibrium concentration in a steady state, the emission rate of about 16 µg m^{-2} h^{-1} can be calculated with the help of the area-specific air flow rate of q = 5.12 m^3 m^{-2} h^{-1}. An emission rate of 40 µg m^{-2} h^{-1} can be calculated from the total mass of the emitted TCPP (m_{PUR} + m_{SE} = 2.57 mg) using the total test time of 2400 hours and an emitting area of 0.025 m^2.

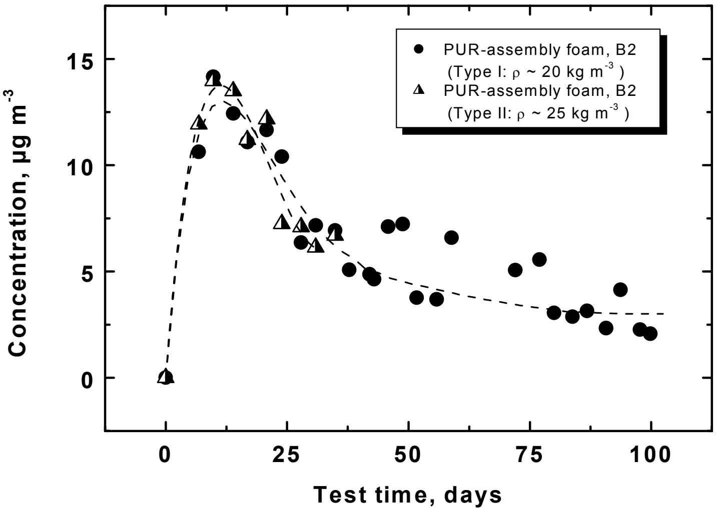

Figure 29: Concentration of TCPP from a PUR assembly foam and a PUR door frame foam with various densities as a function of test time.

In contrast to the test series 5.2.1 - insulation foams - the measured values of TCPP here reach a maximum much faster, lying substantially over the emissions from the insulation foams. The samples tested here clearly have a higher content of TCPP (factor 5), this alone however does not explain the increased emission rates.

The material of assembly foams exhibit a smaller density as opposed to the insulation foams. The markedly increased polymer/air interface within the sample strengthens the emission of TCPP. The tendency of this effect can already be seen in the test series 5.2.1 in the investigation of insulation foams with different sample densities. The influence of an increased emitting surface was examined determinedly using the example of a 1-C-PUR express pistol foam, which was placed into the test chambers with two different surface qualities.

Figure 30 and Figure 31 show TCPP concentration as a function of time. 1-C-PUR foam with the smooth surface was directly foamed up in a suitable aluminium form, the sample with the sawn surface was sawn off from a larger sample. Different surface treatments are supposed to simulate real conditions. Normally, assembly foams are cut to size after foaming out the gaps between brick-work and windows and doors.

Figure 30 shows the emission behaviour of new foams at works, Figure 31 illustrates the concentration profiles of identical samples after a storage of 6 months. The emission tests were carried out for 40 and 70 days in a 0.02m^3 emission test chamber.

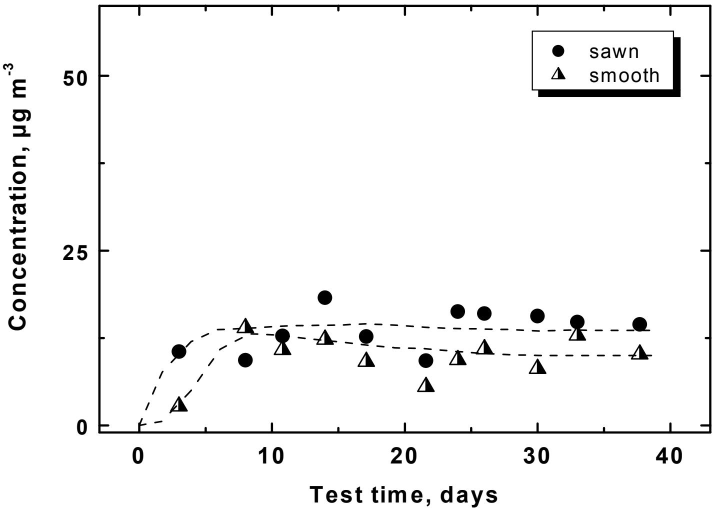

Figure 30: Concentration of TCPP as a function of test time. The two new 1-C-PUR express pistol foams exhibit different surface properties.

The new foams developed an equilibrium within the first 10 days. In the continued period of the test the emissions show a constant value within the measurement accuracy of between 10 and 15 µg m^{-3}. Even if the sawn surface shows a slight tendency to higher concentrations, the difference is not significant.

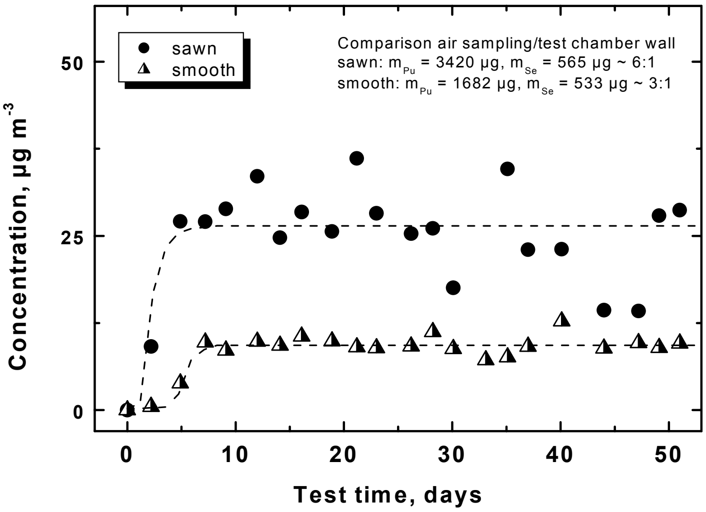

Figure 31: Concentration of TCPP as a function of test time. The two stored 1-C-PUR express pistol foams exhibit different surface properties.

The concentration profiles show a different shape after a storage of 6 months. As expected, an equilibrium develops during the first 10 days, but the curves show significant differences. The measurements on the smooth surface exhibit a constant concentration of 9.5 µg m^{-3}, but the values from the sawn sample oscillate around 26.5 µg m^{-3}, while latter ones show a strong scattering. The assumption that a sawn (and thereby increased) sample surface intensifies emission, seems to be confirmed in this case, however the effect seems to appear (for this system) only after longer storage. The wider scattering of the measured values may be attributed to the heavily roughened-up surface. The air flow in the emission test chamber may also detach individual particles from the sample surface after storage or aging, which leads to the impairment of the measurements.

Table 27 displays an overview of calculated emission rates for TCPP. The following parameters were used in the calculation: total masses of emitted OPC (m_{total} = m_{PUR} + m_{SE}), t_{total} = 912 h (= 38 d) and 1224 h (= 51 d), emission surface A_{Em} = 0.025 m^3; equilibrium concentration c_{eq} and area-specific air flow rate q = 5.12 $m^3m^{-2}h^{-1}$.

Table 27: Area-specific emission rates of TCPP ($SER_{a,TCPP}$) from a 1-C-PUR express pistol foam.

$SER_{a,\ TCPP}$	$SER_a = m_{total} / (t_{total} \times A_{Em})$	$SER_a = c_{eq} \times q$
PUR foam, sawn, new	-	$70\ \mu g\ m^{-2}\ h^{-1}$
PUR foam, smooth, new	-	$50\ \mu g\ m^{-2}\ h^{-1}$
PUR foam, sawn, aged	$130\ \mu g\ m^{-2}\ h^{-1}$	$140\ \mu g\ m^{-2}\ h^{-1}$
PUR foam, smooth, aged	$70\ \mu g\ m^{-2}\ h^{-1}$	$50\ \mu g\ m^{-2}\ h^{-1}$

The good agreements indicate that an equilibrium develops during the test. The different concentration profiles of TCPP from the new sawn foam in comparison to the aged sawn foam cannot be explained so far.

5.4 Product group 3 – IT devices

Test series 5.4.1: Determination of PBFR and OPC emission from IT devices (PC, monitor, printer)

Objectives of the test series

- Determination of concentration profiles of PBFR and OPC from two different, fully equipped PC work places (A and B) in 1m^3 emission test chambers under operational conditions.
- as a potential emission source a printer case will also be tested in an independent experiment (0.02m^3 emission test chamber).

Procedure

The full set-up of two PC work places (work place A: manufacturer 1 (keyboard, PC, mouse) manufacturer 2 (printer), manufacturer 3 (monitor); work place B: Manufacturer 4 (monitor, PC, keyboard, mouse); additionally multiple plugs for power supply, mains cable and cables) were tested in two independent experiments in 1m^3 emission test chambers.

The work place A consists of components of different manufacturers. The computer including mouse and keyboard (computer front case plastic: ABS) was bought in a supermarket. The date of manufacture is not known. The monitor (delivery: welded into a aluminium art foil, date of manufacture March 2001, TCO99-Label, plastic PC/ABS with TCO 99 conform halogen free FR on phosphorus basis) and the printer (delivery: in original packaging; determined types of plastic: ABS, PC-PS FR 40, HIPS, PC; Blue Angel labelled (FR with no halogens with the exception of plastic parts smaller than 25 g or installed directly near the heating and fuser unit (no PBDE, PBB and chloroparaffins)) were made available by the manufacturers directly for the investigations. The components of the work place B (delivery in original packaging, date of manufacture of the monitor about January 2002; PC/ABS plastic case with halogen free OPC (TPP); Blue Angel, TCO 99; date of system unit manufacture: January 2002, ABS plastic mixture without FR; Blue Angel, Nordic Swan; keyboard: SB plastic case without FR, key caps: PBT plastic without FR) were delivered likewise directly by the manufacturer. The investigations began after a brief temporary storage of 1-2 weeks.

The emission test chambers were operated under standard conditions (23^{o}C, 50% relative air humidity). For the simulation of operating conditions all energy saving modes were inactivated and a special software was installed, with which the computer accomplishes constantly calculations. The volumetric air flow in the emission test chambers was 1 m^3 h^{-1}. Since the area-specific air flow rate could not be determined, the unit-specific air flow rate was fixed at as 1 m^3 $unit^{-1}$ h^{-1}. Sampling took place using PUR foam (Chapter 4). Blank values were determined by means of PUR foam sampling technique for each emission test chamber before placing the sample inside.

The flame retardant types used were not known. With the help of XRF bromine, chlorine and phosphorus were tested in the components (Chapter 6.1).

Independent double determination sampling took place due to the different sample preparation and quantification for PBFR and OPC. Accordingly the results will be presented and interpreted separately.

Sampling – OPC

The tests were carried out for 120 days (work place A) or 140 days (work place B). The average sampling volumes equal on the average 2.2 m^3 d^{-1} with a sampling time of 7 days. The qualitative and quantitative analysis of the organophosphorus compounds took place by GC/MS and HPLC/UV (Paragraph 4.2.2.1, Paragraph. 4.2.2.6).

Results and discussion - OPC

The determined OPC emissions from the two PC work places show quantitatively and qualitatively different profiles in comparison to each other.

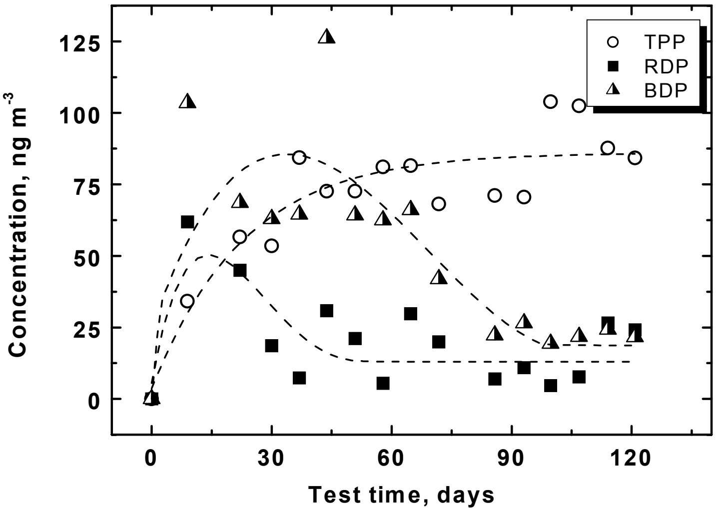

Figure 32: Emission profiles of various OPC as a function of time. PC work place A (PC, monitor, printer); 1m^3 emission test chamber

Both experiments exhibit the common feature of widely scattered measured values. This is probably due to different air flows within the test chambers and the examined devices.

On the one hand, air cannot be homogeneously mixed in the chamber due to sample shape and chamber structure, on the other hand the fans contribute to further turbulence within the devices (for example PC cooling fans). Furthermore, adsorption and desorption processes on the material surfaces should be considered in these very complex test objects. It has to be assumed that highly variable amounts of flame retardants are adsorbed on the foams with this kind of air sampling.

Figure 32 shows the emission behaviour of POCs from the PC work place A. TPP, RDP and BDP were clearly determined and quantified from the scope of the tested POCs. The remaining organophosphorus compounds could not to be detected in view of the detection limits indicated in Paragraph 4.2.2.4. The concentration profiles of the various POCs exhibit significant differences. Both high-boiling point RDP and BDP reach a maximum concentration of approximately 60 to 70 ng m^{-3} in 20 - 30 days, afterwards the concentrations drop within the investigation period to a value below 25 ng m^{-3}. The emission curve of triphenylphosphate grows constantly during the entire test period and reaches about 100 ng m^{-3} after 100 to 120 days. The system achieves a steady state in about 120 days, equilibrium concentrations c_{eq} derived from it are 85 ng m^{-3} for TPP, 13 ng m $^{-3}$ for RDP and 20 ng m^{-3} for BDP.

Since rinsing the chamber (7 m^2 overall internal surface) is not possible without complications, watch glasses (diameter: 22 cm) were used in order to obtain quantitative data on sink effects. They were rinsed in the ultrasonic bath with a 1:1 acetone/toluene mixture and processed and quantified similarly to the other samples. Exactly the same substances were found in the case of OPC that were determined and quantified by air sampling (Table 28).

Table 28: Comparison between emitted masses m_{PUR} determined during the test by PUR sampling and masses m_{SE} found on the chamber walls.

OPC	***m_{PUR}, µg***	***$m_{watch\ glass}$, µg***	***m_{Se}, µg***	***m_{total}, µg***	***m_{PUR} : m_{Se}***
TPP	*36.1*	*0.77*	*70.9*	*107.0*	*1 : 2*
RDP	*13.0*	*1.41*	*129.9*	*142.9*	*1 : 10*
BDP	*32.7*	*-*	*-*	*32.7*	*-*

Figure 33 and Figure 34 show the emission behaviour of OPCs from PC work place B for comparison. TCPP was clearly determined and quantified in addition to the organophosphorus compounds TPP, RDP and BDP. In contrast to PC work place A, all concentration profiles of the various OPCs show qualitative agreements. The emissions reach a maximum concentration of different heights after about 15 - 35 days, then the concentrations drop to a value around 50 ng m^{-3} within the investigation period. TPP and TCPP show a comparable emission behaviour with a maximum concentration of about 150 ng m^{-3}, RDP shows the smallest emission with a maximum concentration of about 50 ng m^{-3}, BDP exhibits the highest emission with a maximum concentration of approximately 275 ng m^{-3}.

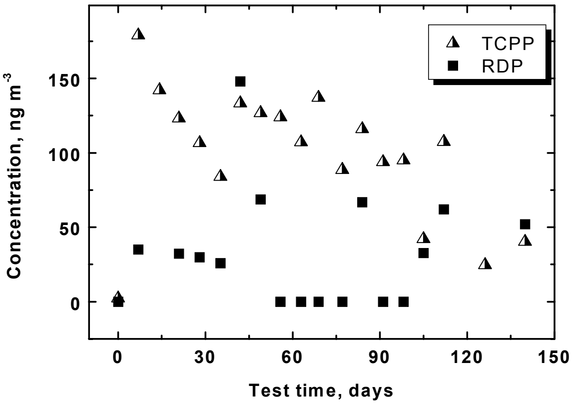

Figure 33: Emission profiles of various OPCs as a function of test time. The complete PC work place B (PC, monitor) was tested in a 1m^3 emission test chamber.

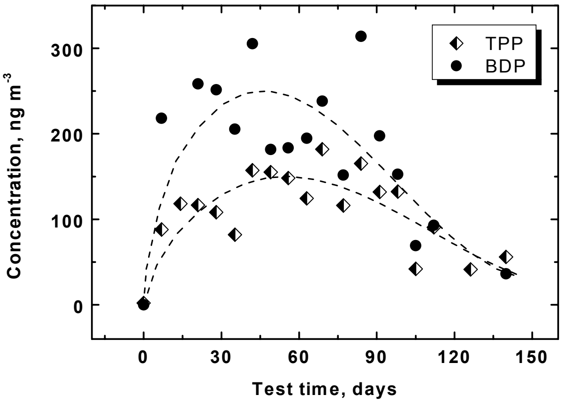

Figure 34: Emission profiles of various OPCs as a function of test time. The complete PC work place B (PC, monitor) was tested in a 1m^3 emission test chamber.

The figures clearly show that a steady state has not been reached within the investigation period. However on the basis of the measurements it has to be assumed that the value of the equilibrium concentration of all detected POCs is clearly below 50 ng m^{-3}. Thus a value of $SER_{u,POC}$ < 50 ng $unit^{-1}$ h^{-1} can be indicated as a unit-specific emission rate.

The positive determination of a halogenated phosphoric acid ester (TCPP), which contradicts the manufacturers' data, may possibly be attributed to contamination from packing materials.

Wall effects were determined by using a watch glass as in experiment A. After the sample was removed from the chamber, it was fired at 80 °C for 6 hours. During this firing phase air sampling was carried out under the usual conditions (0.54 m^3 total sample volume). As expected, increased concentrations were found at this temperature, although the sample (i.e. the primary source) was no longer in the emission test chamber. The emission arises from desorption of the chamber walls (secondary source).

Table 29: Comparison between emitted masses m_{PUR} determined during the test by PUR sampling and masses m_{SE} proved on the chamber walls.

OPC	**m_{PUR}, µg**	**$m_{watch\ glass}$, µg**	**m_{Se}, µg**	**m_{ges}, µg**	**$m_{PUR} : m_{Se}$**	**$c_{POC,80°C}$, µg m^{-3}**
TCPP	*18.5*	*0.36*	*66.3*	*84.8*	*1 : 3.6*	*0.16*
TPP	*20.1*	*0.32*	*58.9*	*79.0*	*1 : 2.9*	*1.89*
RDP	*6.1*	*-*	*-*	*6.1*	*-*	*3.45*
BDP	*29.1*	*0.65*	*119.7*	*148.8*	*1 : 4.1*	*0.70*

Emission rates may be estimated from the total mass of the emitted OPC ($m_{ges} = m_{PUR} + m_{SE}$) taking account of the total test time t_{total} = 2880 h (= 120 d, PC work place A) and t_{total} = 3360 h (= 140 d, PC work place B) and are listed in the following table. This compilation is supplemented by emission rates obtained from the steady-state equilibrium concentrations c_{eq} considering a unit-specific air flow rate of 1 m^3 $unit^{-1}$ h^{-1}.

Table 30: Unit-specific emission rates (SER_u) of TPP, TCPP, RDP and BDP from two PC work places.

	$SER_{POC} = m_{total} / (t_{total} \times 1\ St.)$	$SER_{POC} = c_{eq} \times q$
Work place A		
TPP	*37 ng $unit^{-1}$ h^{-1}*	*85 ng $unit^{-1}$ h^{-1}*
RDP	*49 ng $unit^{-1}$ h^{-1}*	*13 ng $unit^{-1}$ h^{-1}*
BDP	*11 ng $unit^{-1}$ h^{-1}*	*20 ng $unit^{-1}$ h^{-1}*
Work place B		
TPP	*25 ng $unit^{-1}$ h^{-1}*	*< 50 ng $unit^{-1}$ h^{-1}*
TCPP	*24 ng $unit^{-1}$ h^{-1}*	*< 50 ng $unit^{-1}$ h^{-1}*
RDP	*2 ng $unit^{-1}$ h^{-1}*	*< 50 ng $unit^{-1}$ h^{-1}*
BDP	*44 ng $unit^{-1}$ h^{-1}*	*< 50 ng $unit^{-1}$ h^{-1}*

The deviations indicate that the two systems failed to reach an equilibrium after 120 and 140 days. Furthermore it has to be considered that sink effects in the selected $1m^3$ chamber may strongly impair the test results. It is also questionable whether the watch glasses used for the simulation of wall effects reflect reality.

Sampling - PBFR

Sampling of work place A took place every 14 days by a PUR foam with a medium sample volume of 40 m^3 (Chapter 4). The total test time was 93 days. Sampling on work place B was performed likewise every 14 days over 152 days with a medium sample volume of 30 m^3.

Since the flame retardants contained in the samples were not known, the following substances were tested by GC/MS (Paragraph 4.2.1.1, Paragraph 4.2.1.6). TBBPA was determined as its diacetyl derivate (Chapter 9.2).

4-MonoBDE (BDE3)
2,4'-DiBDE (BDE8)
2,4,6-TriBDE (BDE32)
2,2',4,4'-TetraBDE (BDE47
2,3',4,4'-TetraBDE (BDE 66)
2,2',4,4',6-PentaBDE (BDE100)
2,2',4,4',5-PentaBDE (BDE99)
2,2',3,4,4'-PentaBDE (BDE85)
2,2',4,4',5,5'-HexaBDE (BDE153)
2,2',4,4',5,6'-HexaBDE (BDE154)
2,2',3,4,4',5'-HexaBDE (BDE138)
2,3,3',4,4',5,6-HeptaBDE (BDE190)
2,2',3,3',4,4',5,5',6,6'-DecaBDE
Components octaBDE DE-79-Great Lakes
(see Appendix 1)

2,2'-DiBB (BB4)
2,2',4,4',5,5'-HexaBB (BB153)

2,4’,5-TriBB (BB31)
2,2’,5,5’-TetraBB (BB52)
2,2’,4,5,5’-PentaBB (BB101)

TBBPA
HB

2,2’,3,3’,4,4’,5,5’,6,6’-DecaBB
Components octaBB FR 250 13-Dow Chemical
Components hexaBB Firemaster BP-6
(see Appendix 1)

Watch glasses (∅ 22 cm) were placed in the emission test chambers (work place A and B) to obtain quantitative data on sink effects (see also Results and discussion - OPC).

After the end of the experiment a certain part of the chamber wall was wiped off by two PUR foams soaked in toluene (surface: 0.09 m^2 (work place A); surface: 0.023 m^2 (work place B)). The PUR foams were extracted by soxhlet as per Paragraph 4.2.1.6 and likewise analysed with GC/MS (Paragraph 4.2.1.1). After finishing the experiment, the emission test chamber (work place B) was fired for 6 hours at 80 °C at an air exchange rate of 1 h^{-1} and sampled by PUR foam during firing (0.54 m^3 total sampling volume).

Results and discussion - PBFR

It was not possible to prove any emission of almost all tested guide substances under the given conditions for work place A. Traces of BDE47, BDE100, BDE99, BDE85 were detected (< 0.27 ng m^{-3}) but the concentrations dropped below the detection limit around the end of the test. HB was found in a medium concentration of 1 ng m^{-3} of. None of the PBFRs tested was found in the wiped sample taken after the experiment (surface: 0.09 m^2).

No emission of the guide substances tested was found in work place B. Only HB was found up to 6 weeks in a concentration of 1 ng m^{-3}. The values lay below detection limit for the rest of the test. The wipe sample taken after the test (surface: 0.023 m^2) showed none of the substances tested. It should be noted in this instance that both wiping samples for work places A and B were overlaid strongly with matrix and so were difficult to evaluate, and/or the detection limits were clearly higher compared with the emission samples.

Concentrations of 150 ng m^{-3} of BDE47, 27,8 ng m^{-3} of BDE100 and 61 ng m $^{-3}$ of BDE99 were found in PUR foam sample taken while firing the 1m^3 emission test chamber (work place B). Traces of an unknown HpBDE isomer and BDE153 were also found.

The test results altogether clearly showed a higher matrix load and thus smaller signal-to-noise ratio compared with the remaining emission chamber tests. This may be due to the complex sample matrix, which consists of a large number of plastic types, and the increased temperature (operating conditions) and, in addition, the sampling volumes which were much higher than for the other emission chamber tests.

No PBDE was found in the extracts (see Results and discussion - OPC) of the watch glasses placed in the two emission test chambers (work place A and B). Although HB was found in traces in the emission samples of both work places, the values of HB in the watch glass extracts were likewise below the detection limit. 116 ng m^{-2} of TBBPA was detected in work place A while the extract of work place B contained 64 ng m^{-2} of TBBPA.

Determination limits determined for a medium sampling volume of 35 m^3 are shown in the following list:

Depending on PBDE	0.3-5 ng m^{-3}
Depending on PBB	0.3-5 ng m^{-3}
HB	0.4 ng m^{-3}
TBBPA	0.4 ng m^{-3}

Sampling – OPC – printer case

As mentioned at the beginning of the chapter, not only complete PC work places were tested within this test series, but also selected individual components were analysed separately in 0.02m^3 emission test chambers to localise possible FR emission sources. The unit-specific air flow rate was 0.128 m^3 unit^{-1} h^{-1}. The measurement took place under standard conditions (23°C, 50% relative air humidity). A part of a printer case was examined as an individual component. The individual parts of the printer come from the same manufacturer as those of the printer tested in work place A, and were delivered together with it. Printer cases of PC/PS are usually flame-protected by POCs. Since halogenated organophosphorus compounds appear ever more problematic, organophosphorus compounds with high phosphorous content are being increasingly used. Air sampling took place with suitably prepared PUR foams (Chapter 4) every 3 to 4 days over the entire test period of 250 days. The PUR foams were extracted in the ultrasonic bath with acetone and processed accordingly. The qualitative and quantitative determination of the OPC took place by GC/MS and HPLC/UV (Paragraph 4.2.2.1 and Paragraph 4.2.2.2). The emission test chamber was rinsed with acetone at the end of the experiment and this fraction was processed similarly to the other samples.

TPP and BDP were clearly characterised and quantified as organophosphorus compounds in the experiment. Figure 35 shows the concentration profiles of TPP and BDP from a part of a printer case as a function of time. Different concentration profiles both qualitatively and quantitatively can be observed. The emissions of both POCs rise to comparable maximum concentrations of approximately 350 to 400 ng m^{-3} during the first 50 days. However significant differences appear later in the tests. While the BDP emission decreases very slowly in the observed period (to 90 ng m^{-3} in 250 days), despite some scattering, the concentration profile of TPP shows a plateau-like shape around 400 ng m^{-3}.

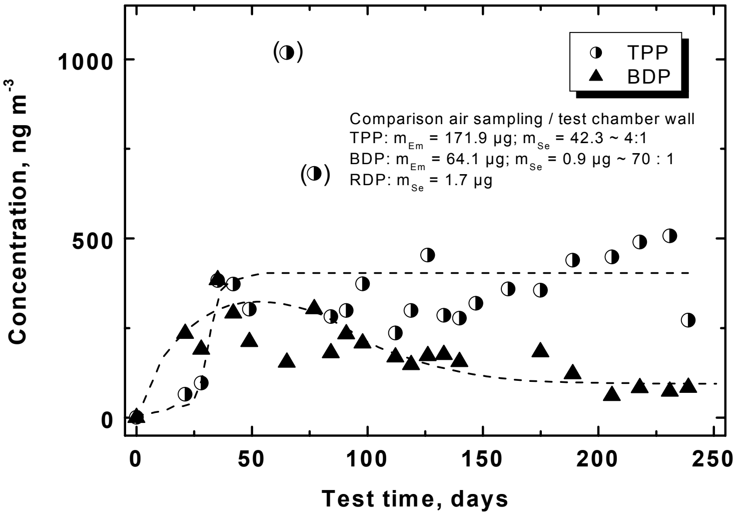

Figure 35: Concentration profiles of TPP and BDP from a printer case as a function of test time

About 20 % of the emitted mass of TPP was measured at the chamber walls in the rinse sample taken after the test; in the case of BDP the sink effect can be neglected. RDP could not be proven by air sampling, it was detected only in the rinse fractions. A direct analysis of the plastic proved positive both for TPP and for RDP and BDP.

Emission rates can be estimated from the total mass of the emitted OPC ($m_{total} = m_{PUR} + m_{SE}$) taking into account the total time of the test t_{total} = 5760 h (= 240 d), and are supplemented by emission rates obtained from the equilibrium concentration c_{eq} of the steady-state conditions with a unit-specific air flow rate of 0.128 m^3 $unit^{-1}$ h^{-1}.

Table 31: Unit-specific emission rates (SER_u) of TPP, RDP and BDP from a printer case.

	$SER_{u,OPC} = m_{total} /(t_{total} \times 1\ h)$	$SER_{u,OPC} = c_{eq} \times q$
TPP	*37 ng* $unit^{-1}\ h^{-1}$	*51 ng* $unit^{-1}\ h^{-1}$
BDP	*11 ng* $unit^{-1}\ h^{-1}$	*12 ng* $unit^{-1}\ h^{-1}$
RDP	*0,3 ng* $unit^{-1}\ h^{-1}$	*ND*

The values determined based on different calculation principles show a good agreement.

Test series 5.4.2: Determination of PBFR emission from the toner cartridge of a laser printer simulating operational conditions

- The emission test chamber with the printer toner cartridge is heated and tested at its operating temperature which is maintained precisely at 40 °C to characterise temperature dependence of the emission.

A used HP printer toner cartridge was tested as a sample, the plastic was proved as PS-FR.
The test was accomplished at 40°C and the unit-specific air flow rate was 0.128 m^3 h^{-1} $unit^{-1}$. Blank value of the emission test chamber was determined by PUR foam sampling before placing the sample inside.
The determination of PBFR emission (Chapters 4.2.1.1 and 4.2.1.6) took place using PUR foam.

Sampling - PBFR

The duration of the test was 158 days. Sample change took place every 14 days with a medium sampling volume of 25 m^3.
The flame retardant types were unknown, an analysis by XRF proved positive for bromine as reference to flame retardants, therefore the following guide substances were tested:

4-MonoBDE (BDE3)
2,4'-DiBDE (BDE8)
2,4,6-TriBDE (BDE32)
2,2',4,4'-TetraBDE (BDE47)
2,3',4,4'-TetraBDE (BDE66)
2,2',4,4',6-PentaBDE (BDE100)
2,2',4,4',5-PentaBDE (BDE99)
2,2',3,4,4'-PentaBDE (BDE85)
2,2',4,4',5,5'-HexaBDE (BDE153)
2,2',4,4',5,6'-HexaBDE (BDE154)
2,2',3,4,4',5'-HexaBDE (BDE138)
2,3,3',4,4',5,6-HeptaBDE (BDE190)
2,2',3,3',4,4',5,5',6,6'-DecaBDE
Components OctaBDE DE-79-Great Lakes
(see Appendix 1)

2,2'-DiBB (BB4)
2,4',5-TriBB (BB31)
2,2',5,5'-TetraBB (BB52)
2,2',4,5,5'-PentaBB (BB101)
2,2',4,4',5,5'-HexaBB (BB153)
2,2',3,3',4,4',5,5',6,6'-DecaBB
Components octaBB FR 250 13-Dow Chemical
Components hexaBB Firemaster BP-6
(see Appendix 1)

HB

To obtain a qualitative evaluation, the weighed amount of the plastic shell was extracted three times with 5 ml of toluene in the ultrasonic bath, the combined extracts were concentrated up to 1 ml and measured by GC/MS.

Results and discussion - PBFR

No emission of the guide substances investigated could be detected during the 158-day test. The determination limits are indicated for a medium sampling volume of 25 m^3 as follows:

depending on PBDE	0.3-5 ng m^{-3}
depending on PBB	0.3-5 ng m^{-3}
HB	0.4 ng m^{-3}

The rinse sample taken after the test failed to show any of the polybrominated flame retardants as speculated. The shell was defined as PS-FR and the XRF analysis proved positive for bromine. Solvent extraction of the plastic shell failed to provide any reference to polybrominated flame retardants. The plastic is possibly a polybrominated polystyrene or the PBFR used was different from those investigated.

Test series 5.4.3: Investigation of TBBPA emission from an old, stored case

Objectives of the test series

- Investigation of TBBPA emission from a stored case (0.02 m^3 emission test chamber).

The sample (size approx. 0.098 m^2) was made available for the investigations by the Institute for Inorganic Chemistry of the University Erlangen-Nuremberg, which obtained it from a recycling yard and tested within another project (Research Project f 116, BayFORREST).
The sample was a case (polymer: ABS) from the data processing field with the trade name EV 730 LR from the manufacturer Kaga Electronics. The manufacture date was 1995. The material had already been tested for flame retardants, the bromine content was determined at about 5.9 %.

Sampling

Sampling using PUR foam (Chapter 4) was performed every 14 days with a medium sample volume of 34 m^3. Since the surface-specific air flow rate could not be determined, the unit-specific air flow rate was indicated here as 0.128 m^3 $unit^{-1}$ h^{-1}. The measurement took place under standard conditions (23°C, 50% relative air humidity).
Sample preparation took place as per Paragraph 4.2.1.6. Before placing the sample into the chamber, the blank value was determined using PUR foam sampling. To determine TBBPA as per Chapter 9.2 derivatisation was performed and the derivative was determined by GC/MS (Paragraph 4.2.1.1).

Results and discussion

No TBBPA emission could be proved during a sampling period of 153 days. Determination limit of the procedure was 0.3 ng m^{-3} for diacetyl TBBPA.
After finishing the test the desiccator was rinsed with toluene and acetone. The analysis of the rinse solution resulted in 411 ng m^{-2} for diacetyl TBBPA. After conversion, a content of 356 ng m^{-2} TBBPA is obtained.
If one calculates the surface-specific emission rate from the mass adsorbed by the emission test chamber surface, where a surface of 0.098 m^2 and 3672 hours are taken into account, an amount of 369 pg m^{-2} h^{-1} is obtained.

Test series 5.4.4: Investigation of octaBDE emission from an old, stored television case

Objectives of the test series

- Investigation of emission of octaBDE and further PBDE from a stored television case (0.02m^3 emission test chamber).

The sample (size approx. 0.07 m^2) like the sample of the test series 5.4.3 was provided by the Institute for Inorganic Chemistry of the University of Erlangen-Nuremberg, which likewise obtained them likewise from a recycling yard. It is the rear wall of the television set Supercolor 30-TS 268666 made by Grundig with a manufacture date of 1979 or earlier. The type of polymer is ABS. The flame retardant type (technical octaBDE) and the bromine content (7.3 %) were determined.

Sampling

Sampling using PUR foam (Chapter 4) was performed every 14 days with a medium sampling volume of 23 m^3. The length of test was 105 days. The unit-specific air flow rate was 0.128 m^3 $unit^{-1}$ h^{-1}. The measurement took place under standard conditions (23°C, 50% relative humidity). Before placing the sample inside, the blank value was determined by PUR foam sampling. Sample preparation took place as per Paragraph 4.2.1.6. The extracts were determined by GC/MS (Paragraph 4.2.1.1).
The following guide substances were investigated:

4-MonoBDE (BDE3)
2,4'-DiBDE (BDE8)
2,4,6-TriBDE (BDE32)
2,2',4,4'-TetraBDE (BDE47)
2,3',4,4'-TetraBDE (BDE 66)
2,2',4,4',6-PentaBDE (BDE100)
2,2',4,4',5-PentaBDE (BDE99)
2,2',3,4,4'-PentaBDE (BDE85)
2,2',4,4',5,5'-HexaBDE (BDE153)
2,2',4,4',5,6'-HexaBDE (BDE154)
2,2',3,4,4',5'-HexaBDE (BDE138)
2,3,3',4,4',5,6-HeptaBDE (BDE190)
2,2',3,3',4,4',5,5',6,6'-DecaBDE (BDE209)
Components octaBDE DE-79-Great Lakes
(see Appendix 1)

Results and discussion

BDE28 (max. 0.5 ng m^{-3}), BDE47 (max. 8.01 ng m^{-3}), BDE66 (max. 0.24 ng m^{-3}), BDE100 (max. 0.27 ng m^{-3}) and BDE99 (max. 0.84 ng m^{-3}) were found by PUR foam sampling. BDE154 and BDE153 were found in traces, the values however lay below the determination limit.
The rinse from the emission test chamber wall furnished the contents displayed in Table 32.

Table 32: PBDE content in the rinse sample in relation to the rinsed surface.

BDE	47	100	99	154	153
ng m^{-2}	568	155	514	95	460

BDE 28, although contained in low concentration in the emission samples, it could not be found in the rinse sample. It is interesting that BDE154 and BDE153 could be detected only in traces in the emission samples, although it was proved at the chamber wall. BDE153 possesses the higher boiling point, however it is present here with a higher content in the rinse fraction compared with BDE 154. A higher content of BDE153 is there in the technical octaBDE product (ratio 8 : 1) in comparison to BDE154 (see also Appendix 1). The complete octaBDE product was found on highly brominated components in the rinse sample. Since individual standards were not available, the quantitative evaluation was made using the technical product as shown in Appendix 1. The most intensive isomer was determined from each congener group. Area-specific emission rates were calculated from the PBDE contents adsorbed by the chamber wall (Table 33).

Table 33: Area-specific emission rates (SER_a) of selected PBDE congeners

BDE	HeptaBDE	OctaBDE	NonaBDE	DecaBDE
ng m^{-2} h^{-1}	4.5	1.5	0.83	0.28

As the results indicate, the emission seems to be clearly measurable up to 6 bromine atoms, while adsorption at surfaces gains a clear influence for PBDEs starting from 7 bromine atoms.

5.5 Product group 4 – Circuit board

Test series 5.5.1: Investigation PBFR and OPC emission from a printed circuit board combined with a protective case

Objectives of the test series

- Investigation of PBFR and OPC emission from a fully equipped printed circuit board plus protective case under standard conditions and elevated temperature (0.02 m^3 emission test chamber; 1. test period: 23 °C, 50 % relative air humidity; 2. test period: 60 °C, 7 % relative air humidity).

After the end of test period 1, the sample was transferred into a second 0.02 m^3 emission test chamber. To simulate operating conditions, the 0.02 m^3 emission test chamber was placed in an insulation container for test period 2 and the temperature was held at a steady 60°C using a strip heater wound around the emission test chamber. The unit-specific air flow rate was 0.128 $m^3\ m^{-2}\ h^{-1}$. Blank values of both 0.02m^3 emission test chambers (unheated and heated) were determined by PUR foam sampling before placing the sample in the chamber.

The flame retardant types were only partially known. The circuit board was a prototype according to manufacturer data. The exact production date was not known, the sample was no longer fresh from production at the time of the beginning of the emission measurements. The case surrounding the printed circuit board was made of a recycled plastic. The safety data sheet indicates < 12% of a TPP flame retardant content. The printed circuit board was declared halogen free by the manufacturer, referring in particular to the circuit board base material. Chlorine, bromine and phosphorus contents of the individual elements were examined by XRF for the verification of the results as a reference for contained FRs. The results of the XRF are contained in Chapter 6 and discussed among the results in the following.

For the determination of PBFR (Paragraph 4.2.1.1; Paragraph 4.2.1.6) and OPC (Paragraph 4.2.2.1; Paragraph 4.2.2.6) double sampling was performed using a PUR foam plug (Chapter 4).

Sampling – PBFR

The sampling in test phase 1 took place on a weekly or 14-days basis with a sample volume of 1.2 m^3 per day. The test took 33 days.

The sampling in test phase 2 took place initially every 7 days and every 14 days starting from a test time of 21 days, with a sampling volume of 1.2 m^3 per day. Test phase 2 altogether took 110 days.

The following guide substances were tested:

4-MonoBDE (BDE3)
2,4’-DiBDE (BDE8)
2,4,6-TriBDE (BDE32)
2,2’,4,4’-TetraBDE (BDE47)
2,3’,4,4’-TetraBDE (BDE 66)
2,2’,4,4’,6-PentaBDE (BDE100)
2,2’,4,4’,5-PentaBDE (BDE99)
2,2’,3,4,4’-PentaBDE (BDE85)

2,2’,4,4’,5,5’-HexaBDE (BDE153)
2,2’,4,4’,5,6’-HexaBDE (BDE154)
2,2’,3,4,4’,5’-HexaBDE (BDE138)
2,3,3’,4,4’,5,6-HeptaBDE (BDE190)
2,2’,3,3’,4,4’,5,5’,6,6’-DecaBDE
Components octaBDE DE-79-Great Lakes
(see Appendix 1)

2,2’-DiBB (BB4)
2,4’,5-TriBB (BB31)
2,2’,5,5’-TetraBB (BB52)
2,2’,4,5,5’-PentaBB (BB101)

2,2’,4,4’,5,5’-HexaBB (BB153)
2,2’,3,3’,4,4’,5,5’,6,6’-DecaBB
Components octaBB FR 250 13-Dow Chemical
Components hexaBB Firemaster BP-6
(see Appendix 1)

TBBPA
HB

Selected components, in which bromine was previously detected by XRF, were removed from the circuit board after the end of the test. A weighed quantity of the respective plastic was broken into approx. 1-5 mm fragments and extracted with 5 ml 1:1 hexane / acetone mixture in the ultrasonic bath (15 min) and this was repeated three times. The fourth fraction was left to stand over several days. The four extracts were united, concentrated up to 1 ml and measured by GC-MS similarly to the emission samples.

Results and discussion - PBFR

The emission tests performed failed to detect TBBPA, HB, high brominated PBDE starting from 7 bromine atoms and the anticipated PBBs both in test phase 1 and 2, or these compounds were below the detection limit.

The following determination limits were determined for an average sampling volume of 16 m^3:

depending on PBDE	0.3-5 ng m^{-3}
depending on	0.3-5 ng m^{-3}
HB	0.4 ng m^{-3}
TBBPA	0.4 ng m^{-3}

The tribrominated BDE28 and the tetrabrominated BDE47 (see also Appendix 1) were detected in test phase 1 (Table 34).

Table 34: Detected PBDE of test phase 1 (unheated)

Test time in days	BDE28 [ng m^{-3}]	BDE47 [ng m^{-3}]
13	3.36	0.92
27	2.54	1.35
33	2.54	1.34

The values vary in the range 1-3 ng m^{-3}. A temperature in test phase 2 elevated to 60°C showed a clear rise in concentration of PBDE congeners already detected in test phase 1. In addition, further PBDEs could be identified. Figure 36, Figure 37 and Figure 38 show the determined concentration profiles.

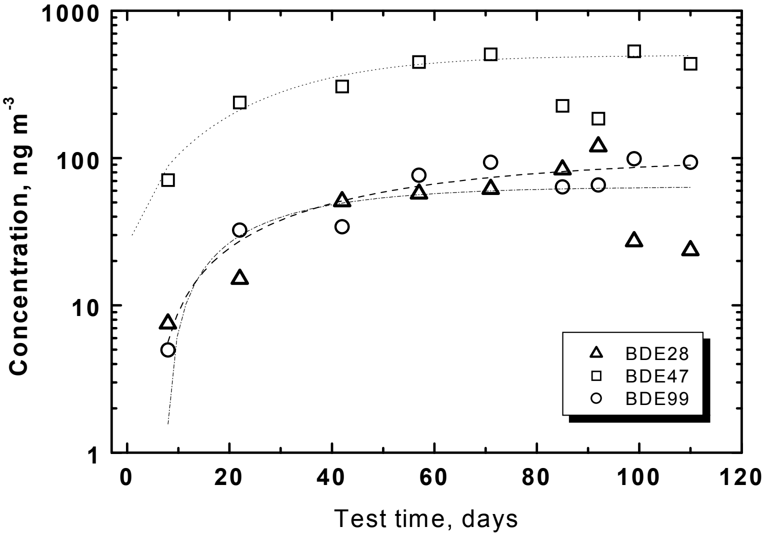

Figure 36: Concentration profiles of BDE28, BDE47 and BDE99 as a function of test time with heating (60°C) (s. also Appendix 1).

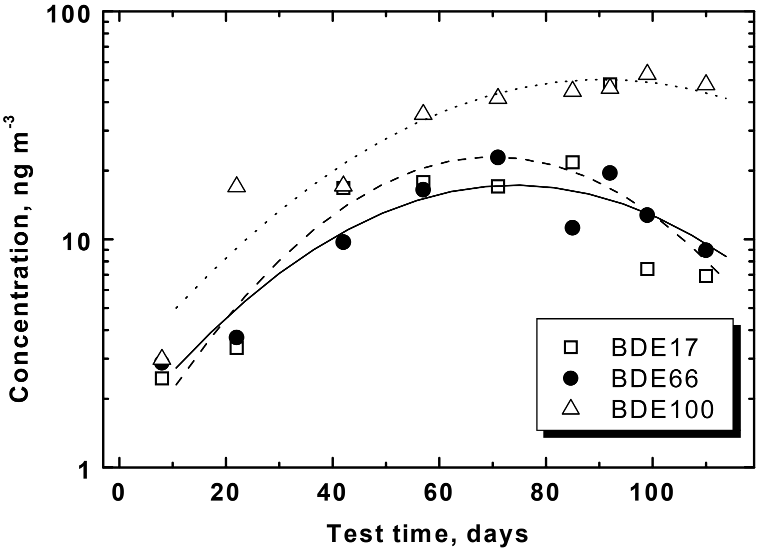

Figure 37: Concentration profiles of BDE17, BDE66 and BDE100 as a function of test time with heating (60°C) (s. also Appendix 1).

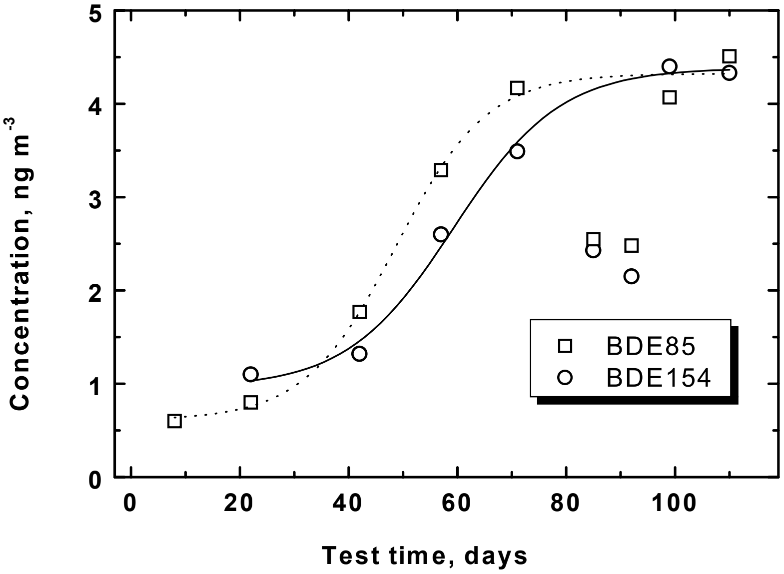

Figure 38: Concentration profiles of BDE85 and BDE154 as a function of test time with heating (60°C) (s. also Appendix 1).

For a better illustration of the emission profiles, an attempt was made in Figure 36, 37, and 38 to visualise the emission processes by curves. As Figure 36 indicates, BDE47 emission increases to a maximum of 500 ng m^{-3} compared with an average of 1 ng m^{-3} obtained from the measurements at 23°C (Table 34). This corresponds to an increase in the emission by about a factor of 500 while the temperature increases from 23°C to 60°C. An increase by about a factor of 16 from an average 3 ng m^{-3} to 50 ng m^{-3} was registered for the tribrominated BDE28.

It must be considered that BDE28 exhibits a lower vapour pressure in comparison to BDE47. However BDE28 is one of the main components in the commercially available technical PBDE and in particular, in the pentaBDE product BDE47. BDE28 is only contained in traces in this product (see Appendix 1). The pentabrominated BDE99, likewise a main component of the technical pentaBDE, cannot be detected at 23°C, however shows a clear increase to about 60 to 70 ng m^{-3} when the temperature is elevated to 60°C.

The tribrominated BDE17 and the tetrabrominated BDE66 are similarly contained in the technical product in small proportions and show concentrations of up to 20 ng m^{-3}. The pentabrominated BDE100, also a secondary component, shows maximum values of up to 50 ng m^{-3}.

In addition, traces of the hexabrominated BDE153 (max. conc.: 2.01 ng m^{-3}) and BDE138 (max. conc.: 0.6 ng m^{-3}) were detected beyond the test period.

Figure 39 illustrates the percentages of selected components in the technical pentaBDE product and PBDE contained in the emission samples. BDE47 was taken as 100% and the further congeners and isomers were compared in relation to it. The diagram shows that the emission decreases markedly with an increasing degree of bromination and decreasing volatility. This reduction is particularly obvious in the transition from the tetrabrominated BDE47 to the pentabrominated BDE99.

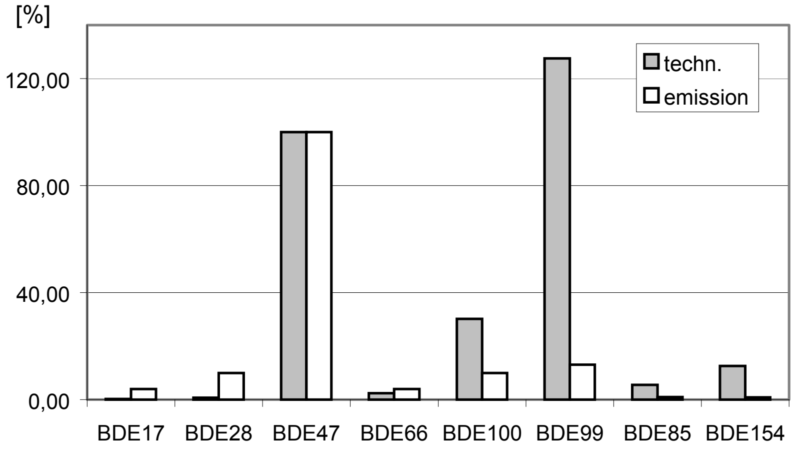

Figure 39: Comparison of the percentages of PBDEs in the emission samples with the components in the technical pentaBDE. BDE47 is set as 100%.

The desiccator was rinsed with toluene and acetone after the end of the test (test phase 2). The results on the rinse fraction are displayed in Table 35.

Table 35: Ratio of PBDE contents in the rinse sample to rinsed surface.

BDE	17	28	47	66	100	99	85	154	153	138
ng m^{-2}	19	53	617	91	188	589	38	56	37	6

Further investigated guide substances could not be detected.

The following emission rates were calculated from the data obtained [ng $unit^{-1}$ h^{-1}] (Table 36).

$m_{PUR} + m_{sink} = m_{total}$

m_{PUR} = sum of mass determined by emission
m_{sink} = mass determined by rinsing the emission test chamber

SER = m_{total}/(unit test time (h))

Table 36: Unit-specific emission rates (SER_u) in [ng $unit^{-1}$ h^{-1}].

BDE	17	28	47	66	100	99	85	154	153
ng $unit^{-1}$ h^{-1}	0.59	1.93	14.19	0.41	1.31	2.57	0.13	0.10	0.04

A qualitative analysis of the plastic extracts was performed in order to clarify the sources of PBDEs. Just PBDEs were determined due to time limitations in view of the emission results. The following table shows the plastic samples tested. PBDEs were detected in samples 1, 2, 3, 4 and 5. The results are displayed in Table 37.

Table 37: Investigation of selected components of the circuit board tested for FR emission.

No.	Component	Weighed sample [mg]	Substance
1		233.3	BDE47, 100, 99 in traces
2		633.3	BDE17, 28, 47, 100, 99, 154
3		601	BDE28, 47, 100, 99, 154
4		53.7	BDE28, 47, 100, 99, 154
5		610	BDE28, 47,100, 99, 154
6		59.6	-

The circuit board was declared halogen free by the manufacturer. Bromine was likewise detected by XRF in the base material. An intensive search among vendors provided the information that the solder stop lacquer used also contained a certain amount of bromine without any data on the chemical structure. Thus no clear decision could be made as to which form, and whether the detected bromine was present in the solder stop lacquer or in the base material. Similarly, no conclusions could be drawn from the existing data as to what extent the detected PBDE was used as a flame retardant in the plastic or it was an impurity in the materials.

Sampling – OPC

Sampling was performed in test phases 1 and 2 every 7 days with a sampling volume of 0.9 m^3 per day. Test phase 1 took 33 days and test phase 2 up to 110 days.
The qualitative and quantitative determination of OPCs took place by GC/MS and HPLC/UV. TPP, BDP and RDP were identified conclusively in the test as organophosphate compounds. The remaining OPCs could not be detected in view of the indicated detection limits (see Paragraph 4.2.2.4).

Results and discussion - OPC

Figure 40 shows the concentration profiles of TPP, RDP and BDP as functions of time under non-heated (23°C) and heated (60°C) conditions. No RDP or BDP emission could be detected by air sampling during the first 35 days. This behaviour has already been observed and discussed on simulated samples in Paragraph 4.2.2.9. The concentration profile of TPP in this period shows a different behaviour. After a short test time of about 5 days the concentration profile reaches a first maximum of approximately 100 ng m^{-3}, then drops to a value of approx. 40 ng m^{-3} in the later part of this first test phase.

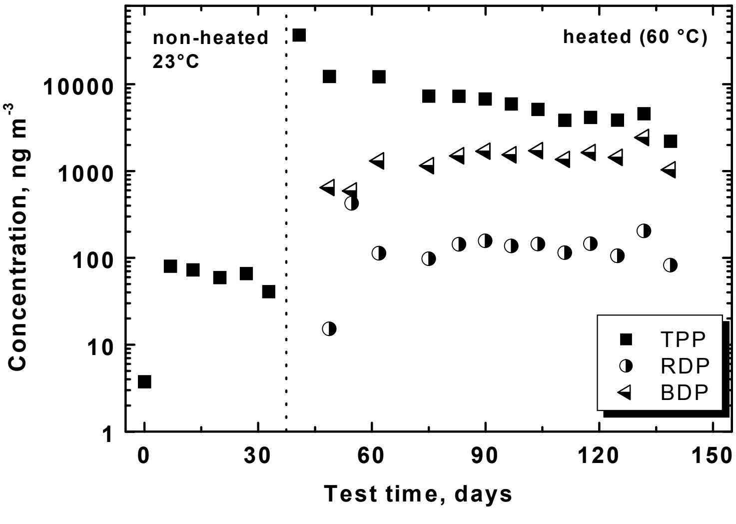

Figure 40: Concentration of TPP, RDP and BDP as a function of test time in non-heated (23°C) and heated conditions (60°C).

A clear change of the concentration profiles can be observed after heating the experimental setup and maintaining the temperature at 60°C precisely. The concentration of TPP, determined by air sampling, rises to a maximum value of approximately 30 µg m^{-3}, and then drops to 2 µg m^{-3} during the period investigated. At 60°C the two other OPCs also show characteristic concentration profiles which were determined by air sampling. In a transitional phase of approximately 40 days a maximum value is reached in both cases: 200 ng m^{-3} for RDP and 2 µg m^{-3} for BDP, a factor of 10 greater.

5.6 Product group 5 – Upholstered furniture and foam, mattresses

Test series 5.6.1: Investigation of PBFR and OPC emission from a piece of upholstered furniture

Objectives of the test series

- Investigation of PBFR and OPC emission from a piece of upholstered furniture (0.001 m^3 emission test cell).

The piece of upholstered furniture (stool) was purchased in England and delivered by ship to Germany packed in a plastic foil. Organisation and selection was performed with the support of Greenpeace UK. Flame retardant types and contents were not known. The stool was manufactured after receiving the order, the exact date of manufacture was not known. There were about 3 months between purchase and delivery. Investigations started immediately after arrival of the upholstered furniture.

A sample screening with the help of XRF disclosed phosphorus and chlorine in the upholstery furniture foam and bromine in the upholstery as an indication of flame retardants (Chapter 6.1).

A sample was cut from a piece of upholstered furniture to fit into the 0.001m^3 emission test cell and placed into a suitable steel container in order to seal the system from the outside. Testing concentrated on upholstery furniture foam covered with upholstery fabric. The area-specific air flow rate was 1.24 m^3 m^{-2} h^{-1}, and the volumetric air flow rate was 0.022 m^3 h^{-1}. The measurement took place under standard conditions (23°C, 50% relative air humidity). The blank value of the emission test cell was determined by PUR foam sampling before placing the sample inside. For qualitative evaluation a weighed amount of the upholstery material was extracted three times with 5 ml toluene in an ultrasonic bath, the combined extracts were concentrated to 1 ml and measured by GC/MS.

Sampling - PBFR

Dual sampling could not be performed due to design features of the 0.001m^3 emission test cell. Sampling using PU foam (Chapter 4) was accomplished every 14 days with 5 m^3 medium sampling volume.

Sample preparation took place as per Paragraph 4.2.1.6. Sample extracts were divided into two aliquots and the OPCs (Paragraph 4.2.2.1) and PBFRs (Paragraph 4.2.1.1) determined independently by GC/MS.

Since the flame retardant types were not known, the following PBFR guide substances were tested in the PUR foam extracts:

4-MonoBDE (BDE3)
2,4’-DiBDE (BDE8)
2,4,6-TriBDE (BDE32)
2,2’,4,4’-TetraBDE (BDE47
2,3’,4,4’-TetraBDE (BDE 66)
2,2’,4,4’,6-PentaBDE (BDE100)
2,2’,4,4’,5-PentaBDE (BDE99)
2,2’,3,4,4’-PentaBDE (BDE85)
2,2’,4,4’,5,5’-HexaBDE (BDE153)
2,2’,4,4’,5,6’-HexaBDE (BDE154)
2,2’,3,4,4’,5’-HexaBDE (BDE138)
2,3,3’,4,4’,5,6-HeptaBDE (BDE190)
2,2’,3,3’,4,4’,5,5’,6,6’-DecaBDE
Components octaBDE DE-79-Great Lakes
(see Appendix 1)

2,2’-DiBB (BB4)
2,4’,5-TriBB (BB31)
2,2’,5,5’-TetraBB (BB52)
2,2’,4,5,5’-PentaBB (BB101)
2,2’,4,4’,5,5’-HexaBB (BB153)
2,2’,3,3’,4,4’,5,5’,6,6’-DecaBB
Components octaBB FR 250 13-Dow Chemical
Components hexaBB Firemaster BP-6
(see Appendix 1)

Results and discussion – PBFR

No emission of the guide substances tested could be detected within a 168-day sampling period. Determination limit of the procedure was for the individual substances as follows:

depending on PBDE	1-8 ng m^{-3}
depending on PBB	1-7 ng m^{-3}

The emission test cell was rinsed after the end of the tests. None of the tested guide substances could be detected in this fraction.

On the other hand the analysis of the upholstery material extracts proved positive for decaBDE, several non-identified nonaBDE isomers, HBCDs and moderately brominated cyclododecanes and further non-identified polybrominated compounds. DecaBDEs and HBCDs are typical flame retardants used as textile coating.

Figure 41 shows the emission behaviour of TCPP as a function of test time. Concentration climbs slowly to approximately 45 µg m^{-3} during the first 100 days. This increase may be explained by organophosphorus compounds occurring in the upholstery foam, but not in the upholstery fabric. Based on our knowledge from previous emission tests such a marked 'chamber effect' is not to be expected. Steady state develops after another 50 days with an equilibrium concentration of 41 µg m^{-3}.

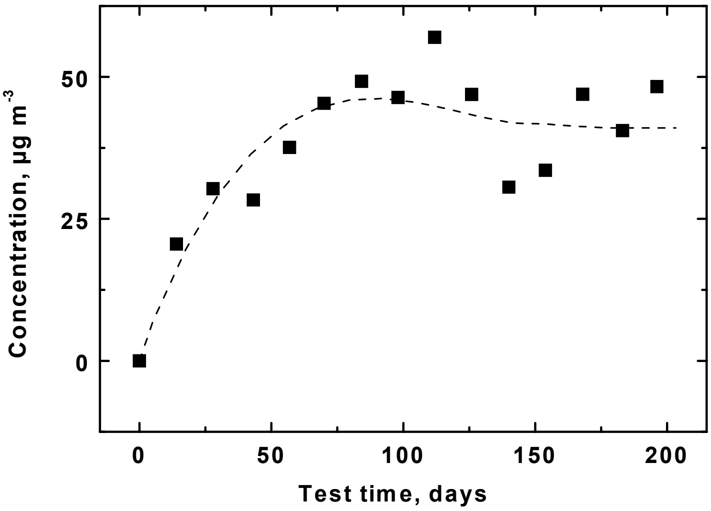

Figure 41: Concentration profile of TCPP from a piece of upholstered furniture as a function of test time

Test series 5.6.2: Determination of TCPP emission from a mattress

Objectives of the test series

- Determination of the concentration profile of TCPP and further OPCs from a flame retarded mattress (1m^3 emission test chamber)

The mattress was delivered directly by the manufacturer and its size was tailored to fit into the 1m^3 emission test chamber. It consisted of a PUR soft foam inside a fabric fleece and a textile cover. TCPP was indicated as the flame retardant used. This type of mattress was specifically used in the study. There were about 4 weeks between delivery and the beginning of the tests. The sample was wrapped in an aluminium and a plastic foil when delivered.

Sampling

Testing time was 32 days, sampling took place every 4 days and the average sampling volume was 4 m^3.

Area-specific air flow rate was 1 m^3 m^{-2} h^{-1} and the volumetric air flow rate equalled 1.44 m^3 h^{-1}. The measurement was performed under standard conditions (23–°C, 50% relative humidity). The blank value of the emission test chamber was measured by PUR foam sampling before placing the sample inside. Preparation of the sampling foams for both qualitative and quantitative OPC analysis took place as described in Paragraphs 4.2.2.6 and 4.2.2.1.

Figure 42 shows the emission behaviour of TCPP as a function of time. Within the first 10 days the concentration rises to a maximum of about 100 ng m^{-3} and within the next 10 days drops to about 10 ng m^{-3}. Since the concentration remained constant over another 10 days, the experiment was terminated.

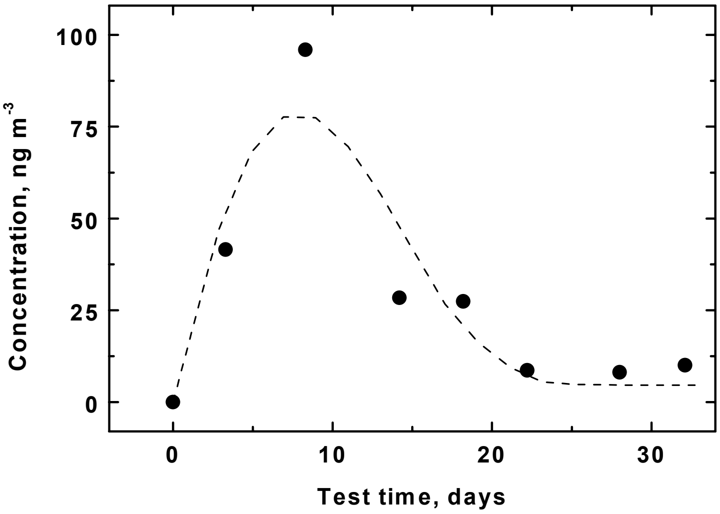

Figure 42: Determination of the TCPP concentration profile from a mattress (1m^3 emission test chamber).

Test series 5.6.3: Determination of TCPP emission from an upholstery furniture foam

Objectives of the test series

- Determination of OPC concentration from an upholstery furniture foam (1m^3 emission test chamber)

Upholstery foam was packed in an aluminium foil and delivered directly by the manufacturer. The material was polyether-based PU, the density was given as 27 kg m^{-3}. Tests on the sample were performed 3 months after sample delivery.

Sampling

Volumetric air flow in the chamber was 1 m^{-3} h^{-1} and the area-specific air flow rate q = 1.1 m^{-3} m^{-2} h^{-1}. The testing period was 30 days. Sampling lasted for 3-5 days with 2.4 m^{-3} average sampling volume. Preparation of the sampling foams for qualitative and quantitative OPC analysis took place as explained in Paragraphs 4.2.2.1 and 4.2.2.6. Blank value of the emission test chamber was determined by PUR foam sampling before placing the sample inside.

Results and discussion

Figure 43 shows the emission behaviour of TCPP as a function of time. There were marked quantitative differences in comparison to mattresses. At the beginning of the test, the concentration rises steeply to a maximum of nearly 70 µg m^{-3}. In the following part of the experiment the measured values constantly scatter around this value. Since the concentration did not change much during the test, the experiment was terminated after 30 days.

To sum up, the following area-specific emission rates (SER$_a$) can be derived for the product group from equilibrium concentrations c_{eq} and total emitted masses of TCPP. A good agreement of the values for the upholstered stool shows that the experimental setup was in equilibrium.

Table 38: Area-specific emission rates of the product group of upholstered furniture/mattresses

	$SER_a = c_{eq} \times q$	$SER_{a} = \dfrac{m_{total}}{t_{total} \times A_{EM}}$
Upholstered stool	*36 µg m^{-2}h^{-1}*	*28 µg m^{-2}h^{-1}*
Upholstery foam(1m^3)	*77 µg m^{-2}h^{-1}*	-
Mattress (1m^3)	*12 ng m^{-2}h^{-1}*	-

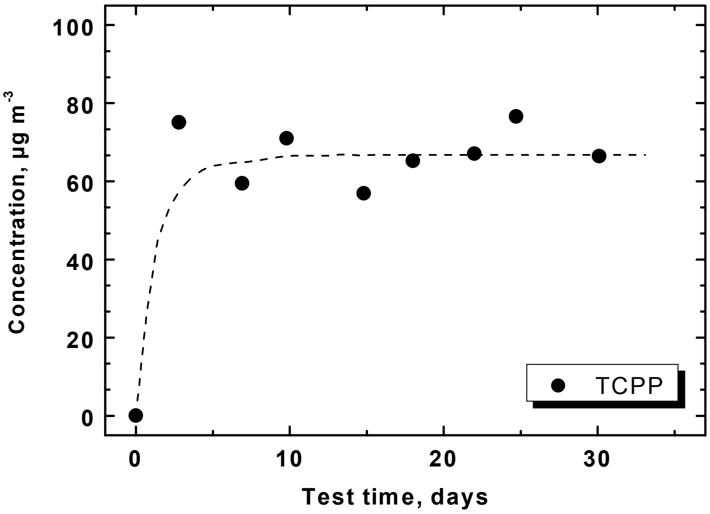

Figure 43: TCPP concentration profile from an upholstery furniture foam as a function of time.

6. Accompanying tests

6.1 Micro X-ray fluorescence (XRF)

The samples were investigated by x-ray fluorescence screening before starting the emission tests. The aim of this screening was to enable both qualitative and semi-quantitative scoping of the content and local distribution of PBFR and OPC in the samples.

The investigations were carried out by a micro X-ray fluorescence spectrometer of intax-GmbH, Berlin using a molybdenum target. The equipment is designed in such a way that tests can be carried out without a vacuum. The excitation tube (50 kV, 0.6 mA) and the detector (Xflash™ detector) are arranged in a measuring head, which is placed at a distance of 0.5 cm from the object's surface. The measuring head can be moved to any place with the help of a xyz stepping motor. A light emitting diode marks the position of the excitation ray to ensure an exact positioning of the measuring dot, while a CCD camera supervises the positioning.

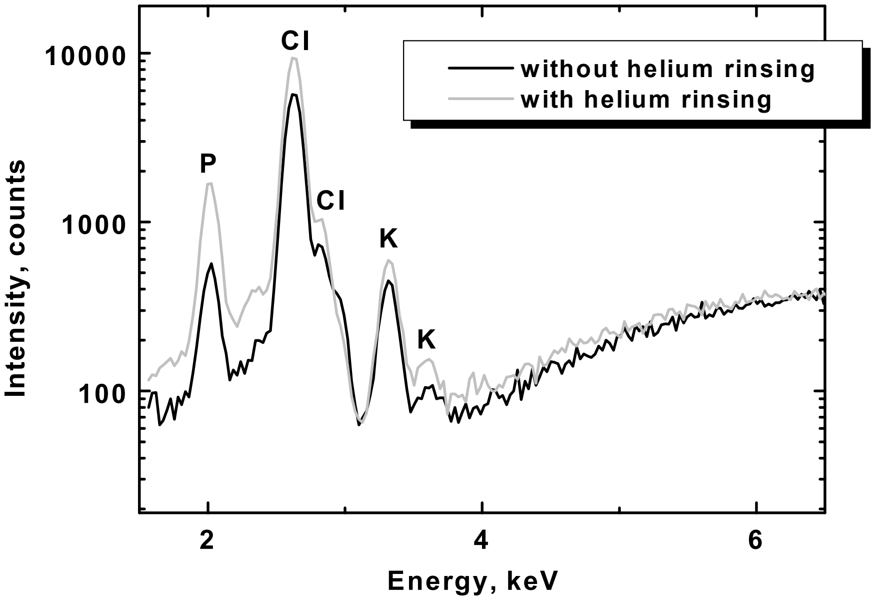

Figure 44: Measurement on a polyisocyanurate sample with and without helium rinsing. The effect of rinsing is clearly discernible: sensitivity of the fluorescence detector is markedly higher for light elements (for example phosphorous).

Sample measurement without the use of a vacuum is non-destructive, so that the objects to be measured do not suffer alterations before being placed into the emission chamber. An additional helium flushing between sample and detector increases sensitivity of the system, in particular towards light elements (see

Figure 45) [95]. Phosphorus, chlorine and bromine were selected as target elements. The following table (Table 39) contains a summary of qualitative results.

Table 39: Overview of qualitative results of XRF measurements.

Product group	***Product***	***P***	***Cl***	***Br***
Insulation foams	*PIR insulation foam*	*x*	*x*	-
	Insulating board, polystyrene / XPS	-	-	*x*
	Insulating board, polystyrene / EPS	-	-	*x*
	Insulating board, synthetic rubber, vulcanised	*x*	*x*	*x*
	Pipe insulation, polyethylene	-	*x*	-
Assembly foams	*1-K-PUR foam*			
	*PUR assembly foam, B2 formulation***	*x*	*x*	*x*
	*PUR pistol foam, B2 formulation ***	*x*	*(x)*	-
IT devices, *Manufacturer 4*	*Computer case – front panel*	-	-	-
	Circuit board, black component 1	-	-	*x*
	Circuit board, black component 2	-	-	*x*
	Circuit board, black component 3	-	-	*x*
	Circuit board, black component 4	-	-	*x*
	Circuit board, component 5	-	-	*x*
	Circuit board, blue component 6	-	-	*x*
	Circuit board, blue component 7	-	-	-
	Mainboard, white component 1	-	*x*	-
	Mainboard, white component 2	-	*x*	-
	Mainboard, white component 3	-	-	*x*
	Mainboard, black component 4	-	-	*x*
	Mainboard, black component 5	*x*	-	*x*
	Mainboard, green component 6	-	-	-
	Mainboard, dark green component 7	-	-	*x*
	Monitor case	*(x)*	-	-
	Mains cable	-	*x*	-
	Keyboard (keys)	*(x)*	-	-
	Toner cartridge, cylinder	-	-	-
	Toner cartridge, case	-	-	*x*

Table 39 cont'd: Overview of qualitative results of XRF measurements

Product group	***Product***	***P***	***Cl***	***Br***
Circuit board	*Case*	*x*	*x*	-
	Circuit board, white component	-	-	*x*
	Circuit board, black angular component	-	-	*(x)*
	Circuit board, black angular component	-	-	*x*
	Circuit board, solder resist	-	*x*	*x*
PC monitor	*Monitor case*	-	-	*x*
Television	*Television case*	-	-	*x*
Upholstered furniture	*Upholstered stool, upholstery foam*	*x*	*x*	-
	Upholstered stool, covering	-	-	*x*
	Mattress	*x*	*x*	-
	Upholstery foam (general)	*x*	*x*	-

A direct quantitative comparison of the different samples is not possible because of the different polymer matrices, since reference materials suitable for quantification are missing. Flame retardant content can be compared in chemically similar materials that contain only one organophosphorus or polybrominated component, as illustrated in Figure 45.

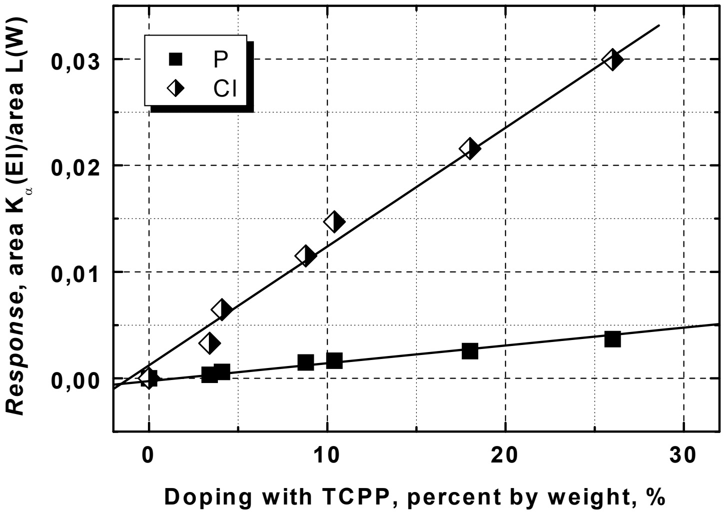

Figure 45: Response (net peak area of the K_α line of P, Cl / net peak area of the L line of tungsten) as a function of P and/or Cl mass fraction. The samples are PUR foams doped with different amounts of TCPP.

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P and Cl responses are plotted in Figure 45 as functions of P and Cl mass fraction of different reference samples. These samples were produced in such a way that PUR foams were treated with various solutions of TCPP in acetone in order to achieve an even distribution of phosphoric acid esters in the polymer matrix. Mass fraction was determined gravimetrically after the evaporation of the solvent. The measured values were standardised on a tungsten standard.

Based on this linearity, approximate mass fractions of the organophosphorus compounds can be estimated for some materials that have a comparable matrix (see Table 40).

Table 40: TCPP mass fraction estimated by XRF

Sample	*TCPP content per manufacturer*	*Response (P)*	*Response (Cl)*	*Content estimated by XRF*
PUR assembly foam (I)	*14 %*	*0.00273*	*0.02632*	*14 %*
PUR assembly foam (II)	*??*	*0.00260*	*0.02666*	*approx. 14 %*
PUR assembly foam (III)	*??*	*0.00347*	*0.03316*	*approx. 18 %*
PUR mattress foam	*??*	*0.00044*	*0.01027*	*approx. 2%*
PUR upholstery foam (stool)	*??*	*0.00165*	*0.01710*	*approx. 9 %*
PUR upholstery foam (general)	*??*	*0.00046*	*0.00998*	*approx. 2%*
PIR insulation foam (I)	*5 %*	*0.00234*	*0.01530*	*5 %*
*PIR insulation foam (II)**	*??*	*0.00119*	*0.00745*	*2.5 %*

**Manufacturer's data on PIR insulation foams (I) were used to determine TCPP content of PIR insulation foams (II).*

Determination without suitable reference substances is much more difficult for brominated flame retardants. Table 41 therefore lists the positive bromine findings divided into three classes in order to indicate an approximate order of magnitude. These values can be regarded as rough estimates only (percentages in per cent by mass).

Class I:	Total bromine content: < 3.5 %
Class II:	Total bromine content: 3.5 – 6.5 %
Class III:	Total bromine content: > 6.5 %

Table 41: Total Br mass content estimated by XRF (data in classes I-III)

Product group	***Product***	***Class***
Insulation foam	*Insulating board, polystyrene / XPS*	*I*
	Insulating board, polystyrene / EPS	*I*
	Insulating board, synthetic rubber, vulcanised	*I*
Assembly foams	*PUR assembly foam, B2 formulation*	*I*
PC	*Circuit board, black component 1*	*I*
	Circuit board, black component 2	*I*
	Circuit board, black component 3	*I*
	Circuit board, black component 4	*III*
	Circuit board, component 5	*I*
	Circuit board, blue component 6	*II*
	Mainboard, white component 3	*II*
	Mainboard, black component 4	*I*
	Mainboard, black component 5	*I*
	Mainboard, dark green component 7	*I*
Monitor	*Monitor case*	*II*
Printer	*Internal component (blue) 1*	*II*
	Internal component (blue) 2	*III*
	Circuit board, black component 1	*I*
	Circuit board, black component 2	*II*
	Circuit board, black component 3	*II*
	Circuit board, yellow component 4	*I*
	Circuit board, white component 5	*I*
	Circuit board, solder resist	*III*
Television	*Television case*	*III*
Circuit board + case	*Circuit board, white component 1*	*II*
	Circuit board, white component 2	*III*
	Circuit board, white component 3	*III*
	Circuit board, black angular component 4	*II*
	Circuit board, black angular component 5	*III*
	Circuit board, solder resist	*I*
Upholstered furniture	*Upholstered stool, covering*	*II*

6.2 NMR investigations on technical diphenylcresylphosphate

If pure substances are lacking, technical mixtures are used in the emission analyses. Since the examined samples may contain various technical formulations, knowledge of the composition of these formulations is crucial. The various isomers of the mixture are analysed and quantified by NMR spectroscopy based on the selected technical substance DPC.

The test is performed as ^{31}P-NMR at 161.98 MHz, uncoupling ^{1}H at 400.13 MHz; relax delay 10 s; scan number 8; scaling to 85 % H_3PO_4; reference $P(OCH_3)_3$ = 140 ppm. In this way there are 6 main components in the mixture to be identified (see Table 42). A comparison of this result with the chromatogram of the GC/MS analysis provides good agreement. Table 43 displays manufacturer data of component percentages as a comparison.

Table 42: NMR analysis of technical diphenylcresylphosphate

Substitution	*^{31}P-NMR*	*GC/MS retention time **
$(Ph)_3$ (=TPP)	*23.0 %*	*17.3*
$(Ph)_2$. (m-Cres)	*32.0 %*	*18*
$(Ph)_2$. (o-Cres)	*9.0 %*	*18.2*
(Ph). $(m\text{-}Cres)_2$	*15.8 %*	*18.6*
(Ph). (m-Cres). (o-Cres)	*7.9 %*	*18.9*
$(m\text{-}Cres)_3$	*4.7 %*	*19.4*

* Not to be generalised

Table 43: Components of technical DPC per manufacturers' data

Substitution	*^{31}P-NMR*	*GC/MS retention time **
$(Ph)_3$ (=TPP)	*25.0 %*	-
$(Ph)_2$. (m-Cres)	*44.0 %*	-
$(Ph)_2$. (o-Cres)		-
(Ph), $(m\text{-}Cres)_2$	*25.5 %*	-
(Ph), (m-Cres). (o-Cres)		-
$(m\text{-}Cres)_3$	*5.5 %*	-

* Not to be generalised

7 Summary and discussion

7.1 Insulating, assembly and upholstery foams

7.1.1 Halogenated organophosphorus compounds

Chlorinated organophosphates are used extensively in building products as flame retardants. TCPP is especially important in this respect, which, as this study shows, although mainly used in insulation foams, is also used in assembly and upholstery foams.

PIR foams tested within this study were delivered directly by the manufacturer from a current production. Manufacturers' data concerning flame retardant contents of these products could only be partly confirmed by XRF measurements; they did however supply a suitable starting point for the emission tests. Two different PIR foams were used in the tests, which differed not only in their densities (80 g l^{-1} and 30 g l^{-1}), but also in their flame retardant content (2.5 % and 5 %). Equilibrium concentrations and the total emitted mass during the tests permitted the estimation of emission rates within a range of 0.3 to 0.7 µg m^{-2} h^{-1}.

Experiments carried out in emission test chambers of different sizes (0.02m^3 emission test chamber and 0.001m^3 emission test cell) reflect the substantial problem of OPC analysis: a strong influence of the analysis results from a sink effect is to be expected due to polarity and low volatility (236 - 237 °C (5 mm Hg)) of TCPP. Experimental findings that about 25 % to 33 % of the emitted flame retardants are absorbed on the chamber walls, confirm this expectation.

Assembly foams used in this study were closed-cell PUR foams, which were delivered from in situ pressurised vessels. B2 assembly foams manufactured for the tests contained either preparations with a flame retardant content of 14 to 18 % TCPP or a preparation without added halogenated flame retardants using a mixture of technical DPC (approx. 10 % TPP) and TEP. TCPP contents and the remaining organophosphates determined by XRF tests fully confirmed manufacturer's data. TCEP was not detected in any of the insulation and assembly foams tested above the detection limits.

Much higher emission rates are to be expected from assembly foams due to their strongly increased flame retardant content compared to insulating materials. Experimental results by independent tests yielded TCPP emission rates between 40 and 70 µg m^{-2} h^{-1}.

Upholstered furniture and mattresses do not have to be generally treated with flame retardants. In the private sector there are no fire protection regulations for these applications in Germany. Indeed this is handled in the same way all over Europe with the exception of Great Britain and Ireland. Since there have been discussions at

European level to generalise the British standards by harmonising legal principles all over Europe, organophosphorus flame retardants may play a role in this field in the future. The products investigated in this study were a mattress (Germany), an upholstery foam (European Market, England) and an upholstered stool (English market; see also Polybrominated flame retardants, Section 7.1.3). A PUR soft foam flame retarded by TCPP was used in all cases. The TCPP contents expected according to manufacturer data (mattress: 3-7 %; upholstery foam: 5-10 %) were confirmed by XRF screening. The following emission rates were obtained: 75 µg m^{-2} h^{-1} for the upholstery foam, 36 µg m^{-2} h^{-1} for the upholstered stool covered with upholstery fabric and 12 ng m^{-2} h^{-1} for the mattress. An emission rate of TCPP from the upholstered stool, smaller by a factor of 2 in comparison to the foam, can be explained by the fact that the foam is covered with an upholstery fabric (see also Section 7.1.3). The reduced emission from the mattress cannot be the explained by available test results.

TCPP room air concentrations and emission rates determined belong to the highest values obtained within this study. Data in the literature show that FR substances principally only occur in indoor air in such a form that they are bound to particles [80]. This behaviour suggests that a correlation should be recognizable between dust concentration and FR emission. However, it is difficult to prove this correlation between TCPP content in indoor air and that in dust, or to derive the TCPP content in dust from experimentally determined indoor air concentrations. Relevant measurement results are not available either. An overview of the investigations on TCEP in indoor air and house dust [81] shows that the relationship is not yet sufficiently clarified. Data are contradictory in themselves and do not indicate a simple correlation [82]. A possible explanation is that there is a correlation with the smallest dust particles only. It might be necessary to assume that as there is an excess dust surface area, this is not saturated with adsorbed flame retardant molecules at the measured flame retardant concentrations.

7.1.2 Halogen free organophosphorus compounds

Emission rates of 125 ng m^{-2} h^{-1} DPC and 130 ng m^{-2} h^{-1} TPP, determined from equilibrium concentrations were obtained for halogen free OPCs from an assembly foam. Since the DPC preparation is a technical mixture containing TPP of up to 20 % (see Chapter 6.2), the nearly identical emission rates can be explained by comparable physicochemical data.

Similar DPC and TPP concentration profiles can also be observed in synthetic rubber which also contains brominated flame retardants in addition to organophosphates. Slightly reduced emission rates of approximately 85 ng m^{-2} h^{-1} for DPC and about 50 ng m^{-2} h^{-1} for TPP were estimated from steady-state equilibrium concentrations (see RDP and BDP in the Section on IT devices).

7.1.3 Polybrominated flame retardants

HBCD is used almost exclusively for flame retarding purposes in the polystyrene foams expanded polystyrene (EPS) and extruded polystyrene (XPS). To investigate the emission behaviour of HBCD, polystyrene samples were specifically manufactured for the tests' purposes and delivered directly by the manufacturer. Comparative measurements on EPS were performed in a $0.02m^3$ emission test chamber and in a $0.001m^3$ emission test cell. The aim was to test what influence the test chamber size and the resulting wall surface size (sink effect) exerts on the emission. The HBCD content was between 1-2 % according to manufacturer's data which corresponds to the average content in EPS formulations. No separation into the three isomers α–HBCD, β–HBCD and γ–HBCD contained in the technical product was performed in the tests.

No emission from EPS was detected with respect to the 0.33 ng m^{-3} determination limit of the procedure under the test conditions described in Section 5.2.2 during a 105-day test in the $0.001m^3$ emission test cell and during a 120-day test in the $0.02m^3$ emission test chamber. Rinsing the chamber and cell walls with organic solvents furnished a value between 1-3 µg m^{-2}.

HBCD emission from XPS and EPS was tested in a $0.02m^3$ emission test chamber and, as a comparison, in a $0.001m^3$ emission test cell. HBCD content was below 1 % according to manufacturer's data. The tests took 110 days in the $0.02m^3$ emission test chamber and 321 days in the $0.001m^3$ emission test cell. No HBCD emission was detected from XPS in the $0.02m^3$ emission test chamber under the conditions explained in Section 5.2.2. On the other hand, trace concentrations of up to 1.79 ng m^{-3} HBCD were found in the 0.001 m^3 emission test cell after 105 days. However the values fell again below the detection limit after 150 days and no HBCD was measured for the rest of the test. The chamber and cell walls were also rinsed with organic solvents in this instance after the end of the tests. The contents determined were within the range of 21 µg m^{-2} and 0.33 µg m^{-2}.

Area-specific emission rates calculated from the HBCD contents at the wall surfaces resulted in 1 - 4 ng m^{-2} h^{-1} for EPS and 0.1 - 29 ng m^{-2} h^{-1} for XPS. This means that the emitted mass flow rate can be considered moderate.

However, it cannot be discounted that HBCD residues may remain on the chamber walls due to their adsorption capability and low solubility and the measurements may fail to provide quantitative results. In addition it is difficult to estimate as to what extent HBCD remains stable on the glass surface of the emission test chamber and cell and to what extent it decomposes. It can be therefore assumed that the values are greater than determined in the tests. Another problem is that HBCD is subject to migration effects in the material and this can lead to an enrichment of HBCD on the material surface. This may cause an increase in emission after test periods longer than the maximum 321 days of the test performed here.

Due to its physicochemical characteristics HBCD is mainly present in a particle-bound form in the environment. This is confirmed by the contents determined on the wall surfaces of the emission test chamber and cell. Particle-bound environmental pollutants are subject to various spreading mechanisms and can lead to environmental contamination both in nearby regions and in distant areas, therefore the causes of this contamination are not always easy to identify. Studies proved the presence of HBCD in sediments and fish in Sweden and in Japan [61, 62], and a significant increase of HBCD was observed in bird's eggs [63]. In their investigation Zitko et al. point out a potential additional source of contamination by polystyrene foam distributed in the marine environment in addition to a release from discrete sources [64]. Mackey has developed a theoretical distribution pattern for HBCD in the environment, which suggests that 48 % is adsorbed by sediments and 51 % by soils. 0.3 % is estimated as an absorbed fraction in air and 1 % in water [65]. An enrichment in biota can be assumed to be due to an octanol/water coefficient of 6, which is confirmed by HBCD contents of up to 8000 ng/g fat in fish in Sweden [61]. Thus in principle an exposure risk for humans may result from food, based on the available data. Since HBCD is mainly present in a particle-bound form, an additional inhalation and oral intake route is possible through house dust and other sorts of dust. In Sweden 5.3 - 6.1 pg HBCD m^{-3} was found in air samples [66].

The emission behaviour of decaBDE from synthetic vulcanised rubber was investigated in a 0.02m^3 emission test chamber under the conditions specified in Chapter 2.3. No emission was found during a period of 277 days taking into account a determination limit of 6 ng m^{-3}. Even rinsing the emission test chamber walls with organic solvents failed to detect any decaBDE. However, it cannot be excluded that a measurable content may be present, since both decaBDE and HBCD are difficult to dissolve and exhibit a marked adsorption behaviour. High levels may remain on the chamber walls which cannot be analytically not accounted for. It has to be assumed similarly to HBCD that decaBDE is mainly present in a particle-bound form in the environment and thus particle-bound transport is undeniable. A further release into the environment can take place through the manufacturing industry's waste water. Concentrations between 10 µg kg^{-1} TS and 11.6 mg kg^{-1} TS of decaBDE were detected in sediments in Japan, up to 360 ng g^{-1} TS in sediments in Sweden and up to 200 ng g^{-1} TS in sediments in Germany [67, 68, 69, 61 and 19]. A concentration as high as 1 g of decaBDE per kg sediment was found in the USA in areas of the FR producing industry [70]. DecaBDE has not been detected in fish so far. This low bioaccumulation behaviour was confirmed by tests performed within the framework of current test systems, which found no detectable, or only low-level bioaccumulation [71]. Isolated studies such as an analysis of human fat samples, in which 400 and 700 ng kg^{-1} of decaBDE was found in two out of five samples, contra to this low-level bioaccumulation theory. Tests on air samples collected in the area of the FR producing industry provided concentrations of 0.016 to 25 µg m^{-3}. The estimation of exposure must take into account the inhalation and oral intake of particles contaminated with decaBDE, though available data fall short of providing the necessary basis for this. It is noteworthy that concentrations between 0.5 - 3 µg g^{-1} of decaBDE were measured in dust and 0.08 ng m^{-3} in indoor air of rooms equipped with televisions and computers [72].

Exposure via the food chain seems to be rather negligible due to a low-level bioaccumulation. In particular, decaBDE is difficult to analyse with regard to currently used analytic procedures and an evaluation of the concentrations in biota may currently not be possible due to the detection limits and data situation. There are however indications that decaBDE has a carcinogenic behaviour. Most of the published analytic studies are concerned with the analysis of moderately brominated PBDEs but fail to consider decaBDE.

The issue of decaBDE degradation by photolytic debromination in PBDE congeners and isomers of lower bromine content for example, which is possible in final products containing decaBDE, was also looked into within this project. In addition, PBDE impurities may occur in final products due to the production processes. Congeners and isomers were tested in emission samples within the tests performed as explained in Section 5.2.3, but they failed to provide positive proof for the selected PBDEs, among them tetraBDEs and pentaBDEs. A consecutive material analysis did not find any indication of the presence of debrominated PBDEs in the material itself, though the detection limit had to be set higher because of the matrix load. The trace range was not investigated here.

The determination of chloroparaffin emission (according to manufacturer's data: 70 % chlorine content, chain length C_{16-20}) from closed-cell polyethylene insulation foam took place in a 0.02m^3 emission test chamber under the conditions described in Section 5.2.4. No emission was detected during a test period of 203 days.

Potential PBFR emissions were tested in a piece of upholstered furniture with regard to upholstery foams (see also under halogenated organophosphorus compounds).
The tested piece of upholstered furniture was produced by an English manufacturer, and it was purchased in the country of origin specifically for the purposes of the tests. England and Ireland are at present, as described in Chapter 1.1, the only European countries demanding flame retardants within the private sector. The manufacturer declared that he used polybrominated flame retardants in his materials. In the emission samples, however, no emission was found during a 168-day test.
Since an XRF analysis clearly proved positive for bromine, particularly in upholstery, the material was more thoroughly analysed. The following flame retardants were found by the analysis: decabromodiphenylether, various nonabromodiphenylether isomers, hexabromocyclododecane and moderately brominated cyclododecanes and a number of non-identified brominated compounds. HBCD and decaBDE are used as standard compounds for back finishing in upholstery. These data confirm the results of the investigations on HBCD and decaBDE for insulation materials. No decaBDE emission and only low HBCD emission was found there too.

7.2 IT devices

7.2.1 Polybrominated flame retardants

Two PC workplaces were tested in $1m^3$ emission test chambers under the conditions described in 5.4.1 to investigate the emission behaviour of polybrominated and organophosphorus flame retardants from IT devices. It was very difficult to obtain information on flame retardants used in the individual products in the field of IT technology.

Potential sources for flame retardant emission are the plastics used in the cases. Which FR is actually used, depends on the respective polymer type as described in Chapter 1.1. Printed circuit boards may represent another source of emission. The base material, component parts and solder stop are sometimes treated with different flame retardants. In addition, there are flame retarded cables and small components. Therefore all guide substances of PBDE, PBB and OPC plus TBBPA and HB were tested in the emission samples.

Workplace A consisted of a monitor, a computer, a keyboard, a mouse and a printer from different manufacturers. The monitor was delivered directly ex factory. March 2001 was indicated as the manufacture date of the product and it carried a TCO99 label. The case plastic is PC/ABS according to manufacturer’s data, with a TCO99 conforming phosphorus based FR. Detailed information was not available. One of the selection criteria for the Swedish TCO label is that plastic parts of the device heavier than 25 g may not contain any FR with an organically bound chlorine or bromine content. However, this weight-related criterion does not apply to keyboards, where strictly no brominated and chlorinated FRs may be used.

The printer was likewise delivered directly in its original packaging ex factory. ABS, PC-PS FR 40, HIPS and PC were identified as case plastics. The printer is marked with the German environmental protection symbol "Blue Angel". Laser printers marked with "Blue Angel" may not contain halogenated FRs. Exceptions are plastic parts lighter than 25 g or components next to heating or fusing units. However PBDE, PBB and chlorinated paraffins may not be contained in them either.

The computer, mouse and keyboard was a system produced by Compaq and was purchased in a supermarket. As indicated in 1.1, Compaq declares ABS as the case plastic used in products for the German market which was confirmed for the computer front panel. Since Compaq models are TCO labelled and no halogen free flame retardant is available for ABS because of material properties, it is assumed that no flame retardant was used for this case.

The work place was tested for 93 days to test the emission of polybrominated FR. The middle sampling volume of every emission sample was 40 m^3. Traces of a tetrabromodiphenylether (BDE47) and three pentabromodiphenylethers (BDE100, BDE99 and BDE85) were detected among polybrominated FRs and the concentrations were below 0.27 ng m^{-3}. These values were below the detection limit at the end of the test. Interestingly enough hexabromobenzene (HB) was found in concentrations of around 1 ng m^{-3}.

The polybrominated flame retardants tested here belong to the semivolatile compounds and rank between SVOC (semivolatile organic compounds) and POM (particulate organic matter). They exhibit a more or less low steam pressure (around 10^{-6} Pa), but reliable data are difficult to come by (see also Appendix 4). Steam pressure data of tribromodiphenylether range for example according to literature data is between 4.70 - 4.95 Pa (25 °C) and 1.45×10^{-4} Pa (25 °C). This suggests that a considerable part of these substances is adsorbed on surfaces, which amounts to 7 m^2 of the wall surface in the $1m^3$ emission test chamber. Product surfaces themselves make a contribution of their own: they are the source of emission on the one hand, but also act as sinks whose effect is difficult to estimate in such complex devices as computers. In order to determine the fraction adsorbed on the wall surface of the emission test chamber, a part of the surface was wiped off by a solvent-soaked piece of PUR foam. However the analysis of the PUR foam failed to prove positive.

Since, based on available product information, it has to be assumed that polybrominated flame retardants are not contained in case plastics, all other technical components of the devices have to be considered as emission sources for these compounds. FR4 circuit boards are predominantly used in the computer industry, which, as described in 1.1, are usually reactively flame retarded by TBBPA. PBDE may sometimes be contained in moulding and casting compounds of flat units, in small components under 25 g, and also in FR2 circuit boards based on phenol resin. It is not clear to what extent this type of circuit board is used in the field of information technology. Emission of TBBPA as a reactive component can be regarded as low.

PBDE trace concentrations detected may possibly be traced back to PBDEs in small articles and flat units.

The cause of the occurrence of hexabromobenzene is difficult to identify. Hexabromobenzene has been used in PC/ABS case plastics. However, it should not be contained in the case plastics according to the specifications of the devices.

The parts of the device case of the printer were tested by XRF, as a dismantled printer of the same type was provided by the manufacturer. Bromine indicating the presence of brominated FR only proved positive in the PC PS FR 40 case plastic: an accessory plastic part attached to another component contained bromine. The type of plastic was not specified. Furthermore, bromine was detected in various circuit boards and components in the printer.

Work place B consisted of a monitor, a computer, a keyboard and a mouse from the same manufacturer and was delivered in its original packaging. January 2002 was declared as the date of manufacture for the monitor. The plastic case consists of

PC/ABS according to the manufacturers' data and is flame retarded by halogen free FR, probably TPP. The monitor is provided with the TCO99 and the "Blue Angel" labels. The system and computer unit likewise was manufactured in January 2002. The computer front panel consists of ABS according to manufacturer's data, contains no FR and is provided with the "Blue Angel" and "Nordic Swan" environmental labels. The keyboard is made of SB plastic without any flame retardant. The key caps are manufactured of PBT plastic without any additional flame protection. No information was available from the manufacturer on the other components in the products and their flame retardants.

Emission tests on polybrominated flame retardants were performed over a period of 152 days. The middle sampling volume from the emission sample was 30 m^3.

The work place showed no emission of polybrominated flame retardants. The only exception was hexabromobenzene, which, as in work place A, was found in trace concentrations around 1 ng m^{-3}, which dropped below detection limit for the rest of the test. A part of the surface was also wiped off with a piece of solvent-soaked PUR foam and analysed after the end of the emission tests. Polybrominated flame retardants were not detected. In order to achieve a more effective and sensitive sampling of the adsorbed components, the 1m^3 emission test chamber was fired after the end of the test under the conditions specified in Section 5.4.1 and a 0.54m^3-volume sample was taken using PUR foam. Interestingly enough 150 ng m^{-3} of a tetraBDE (BDE47) and 28 and 61 ng m^{-3} of two pentaBDE (BDE100, BDE99) were measured. In addition, traces of an unknown heptaBDE isomer and hexaBDE BDE153 were found. In order to be able to identify possible emission sources, chlorine, phosphorus and bromine were analysed by XRF as flame retardant indicators at the beginning of the test in selected components such as case, main board and selected circuit boards (Chapter 6). Bromine was found in some of the components of the circuit boards and the main board. They may form the source for the detected concentrations of the above PBDE. A number of small parts may be considered as possible sources, which were however not investigated in greater detail. The results on the PC work places suggest that very low emission can be expected, in particular of polybrominated flame retardants.

Emission chamber tests by the Bavaria State Institute of Trade on the emission behaviour of two PCs and two monitors under operating conditions resulted in PBDE trace concentrations in the lower ng m^{-3} range [74, 75]. Noteworthy in these investigations is that PBDEs with a higher bromine content such as heptaBDE to decaBDE proved positive. These compounds were not found in our emission tests. PBDEs seem now to be of low importance in the field of information technology, at least for the large case components, which are particularly relevant for emission. An evaluation of the results must however consider that semi-volatile components are predominantly bound to dust particles in interiors.

As a comparison, FR emission was additionally tested on two old cases provided by the University of Erlangen-Nuremberg. A case (Section 5.4.3) came from the field of data processing and was manufactured in 1995 and flame retarded using TBBPA. No TBBPA emission was found during a test period of 153 days taking into account a determination limit of 0.3 ng m^{-3} for diacetyl TBBPA. The rinsed samples taken at the wall surfaces after the tests furnished a TBBPA content of 356 ng m^{-2}. The area-specific emission rate, calculated from the analysed component was 369 pg m^{-2} h^{-1}.
The second old case (Section 5.4.4) was a part (0.07 m^{-2}) of a television rear panel manufactured in 1979 or earlier. According to the data of the University of Erlangen-Nuremberg the flame retardant used was octaBDE. A triBDE (BDE28: max. 0.5 ng m^{-3}), two tetraBDE (BDE47: max. 8 ng m^{-3}; BDE66: max. 0.24 ng m^{-3}) and two pentaBDE isomers (BDE100: max. 0.27 ng m^{-3}, BDE99: max. 0.84 ng m^{-3}) were found in measurable concentrations in the emission samples.
Again, the wall surfaces were rinsed with organic solvents after the end of the test to determine the influence of sink effects. 568 ng m^{-2} of tetraBDE (BDE47) and 514 ng m^{-2} of pentaBDE (BDE99) were found in this instance. Interestingly enough, clearly detectable contents of two hexaBDE isomers (BDE154: 95 ng m^{-2} and BDE153: 460 ng m^{-2}) were also determined, of which only traces were present in the emission samples. BDE153 has a higher boiling point in comparison to BDE154, nevertheless a higher content was measured. The reason for this may be that a higher percentage of BDE153 is present in the technical octaBDE product than BDE154 (ratio 8:1). These results suggest that a PBDE emission risk also exists for a lower bromine content when highly brominated PBDE products such as octaBDE are used. It should be noted however that the sample tested was over 20 years old and it is not clear whether the PBDEs resulted from decomposition during the long storage time, or they were already present as impurities in the product. In addition, octaBDE was found qualitatively in the rinsed fractions. The technical octaBDE consists of different brominated PBDEs. Since single standards were not available, only the main components were quantified with the help of the technical product. The following emission rates were obtained from the FR contents determined at the wall surfaces: heptaBDE showed an emission rate of 4.5 ng m^{-2} h^{-1}, the area-specific emission rate for the most intensive octaBDE was 1.5 ng m^{-2} h^{-1} and 0.83 ng m^{-2} h^{-1} was determined for nonaBDE and 0.28 ng m^{-2} h^{-1} for decaBDE.

7.2.2 Organophosphorus compounds

TPP, RDP and BDP emission was found in both PC work places tested. The printer case showed the same qualitative findings. The experiments reflect therefore the current trend to use triaryl and bisphosphates as flame retardants.
The unit-specific emission rate of TPP is common to all three product groups tested and is between 30 and 50 ng unit^{-1} h^{-1} considering the measurement inaccuracy. These calculations were based on equilibrium indoor air concentrations of c_{eq} = 85 ng m^{-3} (PC work place A) and c_{eq} < 50 ng m^{-3} (PC work place B). These values fall below those of Carlsson et al. [52], who had determined a room air concentration of 94 ng m^{-3} TPP near new PC work places in a comparable study. The trend of reduction in TPP concentration over a longer time of operation was confirmed for the PC work place B.

Emission concentrations under steady-state conditions and a comparison of the unit-specific emission rates for the two other organophosphates reveal significant differences. RDP dominates the emission (SER_{RDP} ~ 13 - 49 ng unit^{-1} h^{-1}) for the PC work place A, while BDP with emission rates of SER_{BDP} = 40-50 ng unit^{-1} h^{-1} and 12 ng unit^{-1} h^{-1} dominates the measurements for the PC work place B and the printer case additionally tested. However further data are missing to enable interpretation of the measurements in detail.
The clearly positive proof of a halogenated phosphoric acid ester (TCPP), which first contradicted manufacturer's data, is possibly due to contamination from the original packaging.

Emission of additives from materials is considerably affected by temperature. A flame retarded circuit board (Section 5.5.1) was examined in two test periods, once at 23 °C and then at 60 °C to investigate the influence of temperature on possible emissions. The circuit board was of type CEM3, whose base material was flame retarded by a reactive organophosphorus component. The circuit board is additionally encased by a plastic case and this case contains < 12 % of TPP according to manufacturer's data.
The investigations at 23 °C supplied values between 1-3 ng m^{-3} for a triBDE (BDE28) and a tetraBDE (BDE47). The emission chamber test at 60 °C clearly showed an increase in concentration of the proven PBDE and more PBDEs were identified. Thus BDE47 exhibited a concentration of 500 ng m^{-3}. Furthermore three pentaBDE (BDE85, BDE99 and BDE100), another triBDE (BDE17) and a hexaBDE (BDE154) were identified. The emission test chamber was rinsed after the end of the test and the unit-specific emission rate was calculated from the data obtained after the analysis of the rinse fraction and the overall emission of the single PBDEs. So an emission rate of 0.6 and 1.9 ng unit^{-1} h^{-1} was calculated for the two

tribromodiphenylether BDE17 and BDE28. Tetrabromodiphenylether BDE47 supplied the highest value with 14 ng unit^{-1} h^{-1}. Further emission rates calculated were: 0.4 ng unit^{-1} h^{-1} for tetraBDE 66 and 1.3 ng unit^{-1} h^{-1} for pentaBDE BDE100, 2.6 ng unit^{-1} h^{-1} for BDE99 and 0.1 ng unit^{-1} h^{-1} for BDE 85. Emission rates determined for hexabromodiphenylether were 0.1 ng unit^{-1} h^{-1} for BDE154 and 0.04 ng unit^{-1} h^{-1} for BDE153. Further polybrominated flame retardants investigated within the project were not found. The circuit board was declared halogen free by the manufacturer. Bromine, chlorine and phosphorus were examined in the individual components of flat units. Selected units that proved positive for bromine were further examined to identify possible PBDE sources. Qualitative analyses of plastics in six selected elements of flat units clearly proved positive in five cases for those PBDEs found in emission samples.

Temperature influence is also clearly visible in connection with organophosphorus compounds. Under standard conditions no RDP and BDP emission can be detected by air sampling. TPP concentration approaches an equilibrium value of about 40 ng m^{-3}, which corresponds to an emission rate of 5 ng unit^{-1} h^{-1}.

Heating and maintaining the temperature of the experimental setup at 60 °C precisely results in a clear change of the concentration profiles. Concentration of TPP, determined by air sampling, rises to a maximum value; the equilibrium concentration of 2 µg m^{-3} determined from the experiment, leads to an emission rate of 250 ng unit^{-1} h^{-1}. The two other OPCs also show characteristic concentration profiles at 60 °C, which can be determined by air sampling. Unit-specific emission rates 25 ng unit^{-1} h^{-1} for RDP (c_{eq} = 200 ng m^{-3}) and 250 ng unit^{-1} h^{-1} for BDP (c_{eq} = 2 µg m^{-3}) can be calculated from the steady-state equilibrium concentration.

7.3 Summarised display of emission rates

The determined area-specific and unit-specific emission rates for the tested products and flame retardants are displayed in Table 44.

Table 44: Area-specific emission rates (SER_a) and unit-specific emission rates (SER_u).

	SER_a /SER_u	$SER = c_{eq} \times q$	$SER = \frac{m_{tot}}{t_{tot} \text{ x } A_{EM}}$
TCPP			
PIR insulation foam type I (ρ = 30 kg m^{-3})	µg $m^{-2}h^{-1}$	0.60	0.70
PIR insulation foam type II (ρ = 80 kg m^{-3})	µg $m^{-2}h^{-1}$	0.21	0.35
Assembly foam (ρ = 20 kg m^{-3})	µg $m^{-2}h^{-1}$	16	40
Assembly foam (sawed), new	µg $m^{-2}h^{-1}$	70	-
Assembly foam (smooth), new	µg $m^{-2}h^{-1}$	50	-
Assembly foam (sawed), old	µg $m^{-2}h^{-1}$	140	130
Assembly foam (smooth), old	µg $m^{-2}h^{-1}$	50	70
Upholstered stool	µg $m^{-2}h^{-1}$	36	28
Upholstery foam(1m^3)	µg $m^{-2}h^{-1}$	77	-
Mattress (1m^3)	µg $m^{-2}h^{-1}$	0.012	-
PC/Monitor B	ng unir$^{-1}h^{-1}$	< 50	24
HBCD			
EPS (20l)	ng $m^{-2}h^{-1}$	-	4
EPS (1l)	ng $m^{-2}h^{-1}$	-	1
XPS (20l)	ng $m^{-2}h^{-1}$	-	29
XPS (1l)	ng $m^{-2}h^{-1}$	-	2
DPC			
Rubber (20l)	ng $m^{-2}h^{-1}$	87	46
Assembly foam	ng $m^{-2}h^{-1}$	125	90
TPP			
Insulation rubber (20l)	ng $m^{-2}h^{-1}$	50	20
Assembly foam	ng $m^{-2}h^{-1}$	130	65
PC/Monitor/Printer (A)	ng unit$^{-1}h^{-1}$	85	37
PC/Monitor (B)	ng unit$^{-1}h^{-1}$	< 50	24
Printer case	ng unit$^{-1}h^{-1}$	51	37

Table 44 cont'd.

	SER_a / SER_u	$SER = c_{eq} \times q$	$SER = \frac{m_{tot}}{t_{tot} \times A_{EM}}$
RDP			
PC/Monitor/Printer (A)	*ng unit*$^{-1}$*h*$^{-1}$	*13*	*49*
PC/Monitor (B)	*ng unit*$^{-1}$*h*$^{-1}$	*< 50*	*2*
Printer case	*ng unit*$^{-1}$*h*$^{-1}$	*-*	*0.3*
BDP			
PC/Monitor/Printer (A)	*ng unit*$^{-1}$*h*$^{-1}$	*20*	*11*
PC/Monitor (B)	*ng unit*$^{-1}$*h*$^{-1}$	*< 50*	*44*
Printer case	*ng unit*$^{-1}$*h*$^{-1}$	*12*	*11*
TBBPA			
Printer case, old	*ng m*$^{-2}$ *h*$^{-1}$	*-*	*0.37*
Television case, old			
TriBDE (BDE28)	*ng m*$^{-2}$ *h*$^{-1}$	*-*	*0.2*
TetraBDE (BDE47)	*ng m*$^{-2}$ *h*$^{-1}$	*-*	*6.6*
PentaBDE (BDE100)	*ng m*$^{-2}$ *h*$^{-1}$	*-*	*0.5*
PentaBDE (BDE99)	*ng m*$^{-2}$ *h*$^{-1}$	*-*	*1.7*
HexaBDE (BDE154)	*ng m*$^{-2}$ *h*$^{-1}$	*-*	*0.2*
HexaBDE (BDE153)	*ng m*$^{-2}$ *h*$^{-1}$	*-*	*1*
HeptaBDE	*ng m*$^{-2}$ *h*$^{-1}$	*-*	*4.5*
OctaBDE	*ng m*$^{-2}$ *h*$^{-1}$	*-*	*1.5*
NonaBDE	*ng m*$^{-2}$ *h*$^{-1}$	*-*	*0.8*
DecaBDE	*ng m*$^{-2}$ *h*$^{-1}$	*-*	*0.3*
Circuit board			
TriBDE (BDE17)	*ng unit*$^{-1}$ *h*$^{-1}$	*-*	*0.6*
TriBDE (BDE28)	*ng unit*$^{-1}$ *h*$^{-1}$	*-*	*1.9*
TetraBDE (BDE47)	*ng unit*$^{-1}$ *h*$^{-1}$	*-*	*14.2*
TetraBDE (BDE66)	*ng unit*$^{-1}$ *h*$^{-1}$	*-*	*0.4*
PentaBDE (BDE100)	*ng unit*$^{-1}$ *h*$^{-1}$	*-*	*1.3*
PentaBDE (BDE99)	*ng unit*$^{-1}$ *h*$^{-1}$	*-*	*2.6*
PentaBDE (BDE85)	*ng unit*$^{-1}$ *h*$^{-1}$	*-*	*0.1*
HexaBDE (BDE154)	*ng unit*$^{-1}$ *h*$^{-1}$	*-*	*0.1*
HexaBDE (BDE153)	*ng unit*$^{-1}$ *h*$^{-1}$	*-*	*0.04*

SER: emission rate
c_{eq}: *„equilibrium“ concentration*
q: *area- and unit-specific air flow rate*
m_{tot}: *total emitted mass*
t_{tot}: *total time of test in h*
A_{EM}: *area of the sample tested in* m^2

8 Summary

Flame retardant emission has been tested on a number of consumer goods and building products within this project. The products tested (insulation and assembly foams, IT devices, upholstered furniture, upholstery foams, mattresses and circuit boards) were selected so as to include those relevant for indoors emissions of flame retardants. The tests were performed in emission test chambers and cells of various sizes in combination with suitable sampling and analysis methods. The flame retardants analysed were polybrominated diphenylethers, polybrominated biphenyls, hexabromocyclododecanes, tetrabromobisphenol A, chloroparaffins and aryl and alkyl phosphoric acid esters.

The physicochemical characteristics of the flame retardants analysed, mainly semivolatile organic compounds (SVOC), require an air sampling by adsorption on PU foams. Sample extraction from these PUR foams took place by means of soxhlet or ultrasonic bath extraction using suitable organic solvents. Identification and quantitative determination was accomplished by gas chromatography/mass spectrometry (GC/MS) or High Performance Liquid Chromatography (HPLC) with UV detection.

The 28-day time period of the tests originally aimed for had to be extended to at least 100 days, in some cases even to 200 days, in order to achieve a steady state necessary for the measurements. Experimental design was handicapped by the partial lack and contradiction of available information causing substantial excess costs due to the need to apply additional methods for material analysis.

The procedures used are well suited to prove the emission of organophosphorus compounds, in particular tris(1-chloro-2-propyl) phosphate (TCPP) and triphenylphosphate (TPP). Exceptions are recorcinol-bis-(diphenylphosphate) (RDP) and bisphenol-A-bis(diphenylphosphate) (BDP), for which the emission tests by air sampling are dominated by sink effects. Results obtained so far show that the analysis methods are well suited to be applied to brominated flame retardants with up to six bromine atoms. With decreasing volatility the influence of sink effects becomes stronger and hampers the determination of emission. Thus hexabromocyclododecane (HBCD) was detected on the wall surfaces of emission test chambers, but apart from traces, not in emission test chamber air. The results are not sufficient for a comprehensive representation of the emission behaviour and interpretive assessment of flame retardants. There are further gaps in our knowledge, for example, concerning the explanation of high flame retardant concentrations in house dust. Nevertheless, the study provides a substantial basis for follow-up investigations. It appears desirable to extend the investigations to long-term measurements over 1 year test periods for example, and to determine the influence of material aging and various flame retardant concentrations on the emission, which was not possible to accomplish here due to the lack of sufficient information and suitable products.

9 Chemicals and materials

Substances	Manufacturer/Distribution
2,2’-Dibromo biphenyl, 97 %, RBF-081	Ultra Scientific
2,4’,5-Tribromo biphenyl, 97 %, RBF-087	Ultra Scientific
2,2’,5 Tribromo biphenyl, 97 %, RBF-085	Ultra Scientific
2,2’,5,5’-Tetrabromo biphenyl, 97%, RBF-089	Ultra Scientific
2,2’,4,5,5’-Pentabromo biphenyl, 97 %, RBF-099	Ultra Scientific
2,2’,4,4’,5,5’-Hexabromo biphenyl, 97 %, RBF-094	Ultra Scientific
Decabromo biphenyl, 95%, RBF-102	Ultra Scientific
Hexabromo biphenyl, tech, Firemaster BP-6, RBF-075	Ultra Scientific
Octabromo biphenyl, tech, FR 250 13 A Dow Chemical RBF-074	Ultra Scientific
4-Monobromo diphenylether, 50 µg/ml in n-Nonan, EO-4915	Promochem
2,4’-Dibromo diphenylether, 50 µg/ml in n-Nonan, EO-4101	Promochem
2,4’,6-Tribromo diphenylether, 50 µg/ml in n-Nonan, EO-4107	Promochem
2,2’,4,4’-Tetrabromo diphenylether 50 µg/ml in n-Nonan, EO-4111	Promochem
2,3’,4,4’-Tetrabromo diphenylether 50 µg/ml in n-Nonan, EO-4112	Promochem
2,2’,4,4’,5 –Pentabromo diphenylether 50 µg/ml in n-Nonan, EO-4091	Promochem
2,2’,3,4,4’ –Pentabromo diphenylether 50 µg/ml in n-Nonan, EO-4092	Promochem
2,2’,4,4’,6 –Pentabromo diphenylether 50 µg/ml in n-Nonan, EO-4194	Promochem
2,2’,4,4’,5,5’-Hexabromo diphenylether 50 µg/ml in n-Nonan, EO-4093	Promochem
2,2’,4,4’,5,6’-Hexabromo diphenylether 50 µg/ml in n-Nonan, EO-4925	Promochem
2,2’,3,4,4’,5’-Hexabromo diphenylether 50 µg/ml in n-Nonan, EO-4093	Promochem
2,3,3’,4,4’,5,6-Heptabromo diphenylether 50 µg/ml in n-Nonan, EO-4117	Promochem
Pentabromo diphenylether, DE-71-Great-Lakes tech, USC912	Promochem
Octabromo diphenylether , DE-79-Great-Lakes tech, USC910	Promochem
Decabromo biphenylether, DE-83-R-Great-Lakes USC902	Promochem
Hexabromocyclododecane, CD-75-P-Great-Lakes USC908	Promochem

Substances	Manufacturer/Distribution
Hexabromobenzene, 98 %	Aldrich
Tetrabromo bisphenol A, BA-59P-Great-Lakes	
USC916	Promochem
3,3',4,4'-Tetrabromo diphenylether ($^{13}C_{12}$, 99%)	
50 µg/ml in n-Nonan, EO1439	Promochem
Tetrabromo bisphenol A-ring-$^{13}C_{12}$ ($^{13}C_{12}$, 99%)	Promochem
50 µg/ml in Methanol CLM-4694-1.2	
Triphenylphosphate	Acros Organics
Tri-p-tolylphosphate	Acros Organics
Tri-m-tolylphosphate	Acros Organics
Chlorinated paraffins CP-56	Hoechst
Chlorinated paraffins CP-70	Hoechst
Dekane, >99,8%	Fluka
Undekane, für GC	Merck
Dodekane, für GC	Merck
Tridekane, >99,5%	Fluka
Tetradekane, für GC	Merck
Pentadekane, >99,5%	Fluka
Hexadekane	Alltech
Heptadekane	Alltech
Oktadekane	Alltech
Nonadekane	Alltech
Eikosane	Alltech
Heneikosane	Alltech
Dokosane	Alltech
Trikosane	Alltech
Tetrakosane	Alltech
Pentakosane	Alltech
Oktakosane	Alltech
Cyclodekane, 98%	Aldrich
Cyclododekane, >99%	Merck
n-hexane, Suprasolv, organic trace analysis	Merck
Dichloromethane, Suprasolv, organic trace analysis	Merck
Aceton, Suprasolv, organic trace analysis	Merck
Methanol, Suprasolv, organic trace analysis	Merck
Ethanol, Suprasolv, organic trace analysis	Merck
Ethylacetat, Suprasolv, organic trace analysis	Merck
Toluol, Suprasolv, organic trace analysis	Merck
Cyclohexan, Suprasolv organic trace analysis	Merck
Cyclopentane, purum >99%	Fluka
Ammonia, 25%	Merck
Calcium carbonate, p.a.	Merck

Substances	Manufacturer/Distribution
K_2CO_3, p.a.	Merck
Acetic anhydride, p.a	Merck
Clean Up Extraction Columns, CUSIL, Size 1000mg/6ml	United Chemical Technologies, INC
Glass fiber tubes, 33 x 130 mm	Schleicher & Schuell
Silica gel 60, Korngröße 0,063 – 0,2 mm	Merck
Mineral wool	Steinhacker
glass beads, AD 0,17-0,18 mm	Braun Biotech International
Palladium chloride, 59,59%	Chempur

9.1 Operating material (Sampling)

9.1.1 1 m^3-Standard-VOC-Emission test chamber

Heraeus Vötsch GmbH

Air purification system, millipore filter, OFP 0012
Sub-microfilter, SMF 03/10
Firm Ultrafilter GmbH

9.1.2 0.02 m^3-Emission test chamber:

Desiccator-bottom part, planar flange DN300 and NS-tube 24/29
Desiccator-top DN300 equipped with NS-Tube 24/29
Flowmeter 210 l/h

Propeller mixer for ventilation:

DC-Micromotor Series 26 P, Typ 26117 AR, 6V
precision gear Series 26 PG, Typ 2510,
Firm Megatron Bauelemente GmbH,

Sealed magnetic mixer MRK 1/20 (NS29/32)
Propeller mixer, 3 vanes, type R 1385
Firm Werkstätte
VA-ball bearing, diameter 16mm*8mm*height 5mm, 688.ZZ.VA
Firm Hohndel-Desch

Air purification system, millipore filter, OFP 0035
Sub-Microfilter, SMF 0012 Superplus
Firm Ultrafilter GmbH

Heating system (20 L-emission test chamber)

Thermal insulation housing, metal, special design
Firm Slipi GmbH

Insulating material FT 006 softinsulation, silica fiber
Firm Carbolite GmbH

Electric band heater

Electric contact thermometer, plug MS 121s, length well 50 mm, 0-100°C, cable connection, length 0,8 m, laboratory relay, 220V/10A

Firm Werkstätte

9.1.3 BAM-emission test cell (0,001 m^3)

Flanged sealing lid DN 150

Ventilation system

Propeller mixer, 4 vanes, type R 1345
Firm Werkstätte

Sampling system and volumescope

WISA-membrane pump, type 303.004.012.2

Firm ASF Thomas Industries GmbH & Co. KG

REMUS 4 G 1,6 gas meter, 16 l/h - 2,5 m^3/h

Firm Kirchner GmbH

9.2 Derivatisation of tetrabromo bisphenol A with acetic anhydride

Derivatization of TBBPA was done as described elsewhere with some modifications[1]. 500 µl toluene, 400 µl acetone, 100 µl acetic anhydride and a modicum of kalium carbonate were added to a 1.5 ml glass vial. After adding a defined aliquot (1/4) of the sample extract the vial was sealed and heated up to 80°C for one hour.

A mini silica gel column (1 g) was used for the clean-up. The column was pre-cleaned with 10 ml dichloromethane and 20 ml toluene/acetone (80:20). After adding the sample extract elution was performed using 10 ml toluene/acetone (80:20). (In order to guarantee complete elution an additional volume of 10 ml of the same solvent was used and checked for diacetylated TBBPA)

The eluate was evaporated to 200 µl by rotary evaporator and flow of nitrogen.

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[1] Instruction of Fa. Sofia GmbH, Chemische Labor f. Softwareentwicklung und Intelligente Analytik im IGZ-Adlershof, Rudower Chaussee 5, 12489 Berlin

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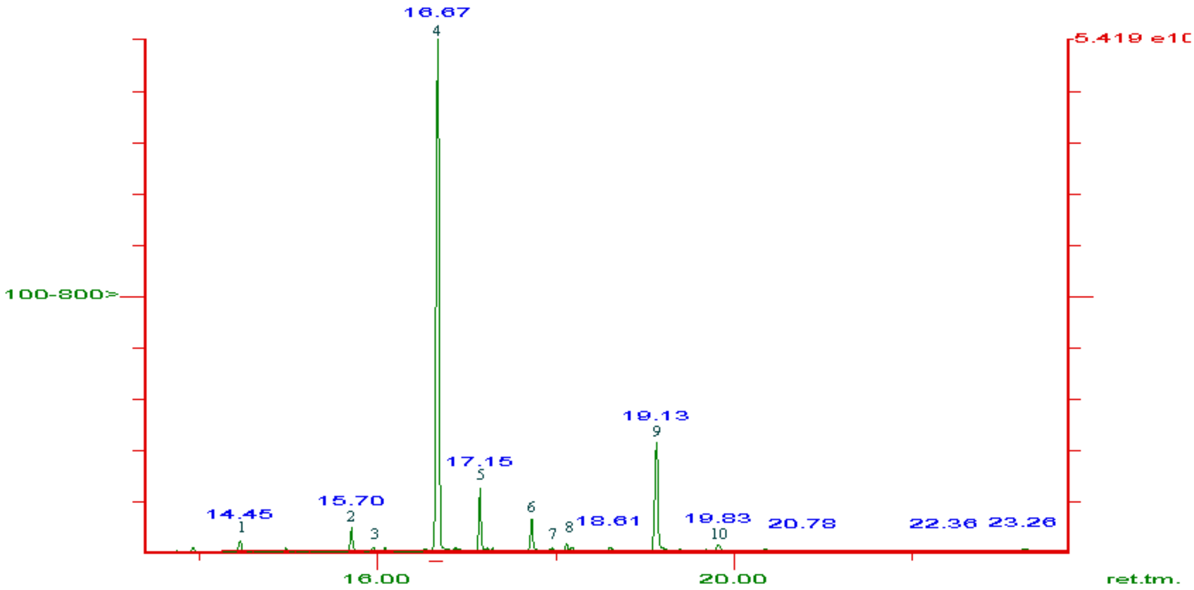
Appendix 1

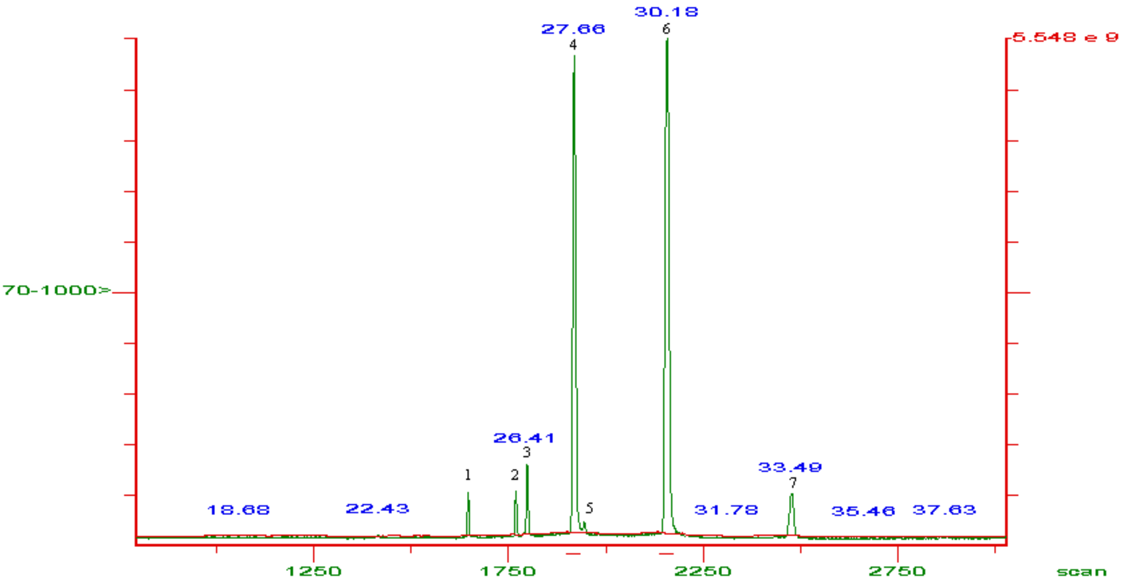
Chromatogram and composition of the technical PBDE and PBB

Hexabromobiphenyl (Firemaster BP-6)



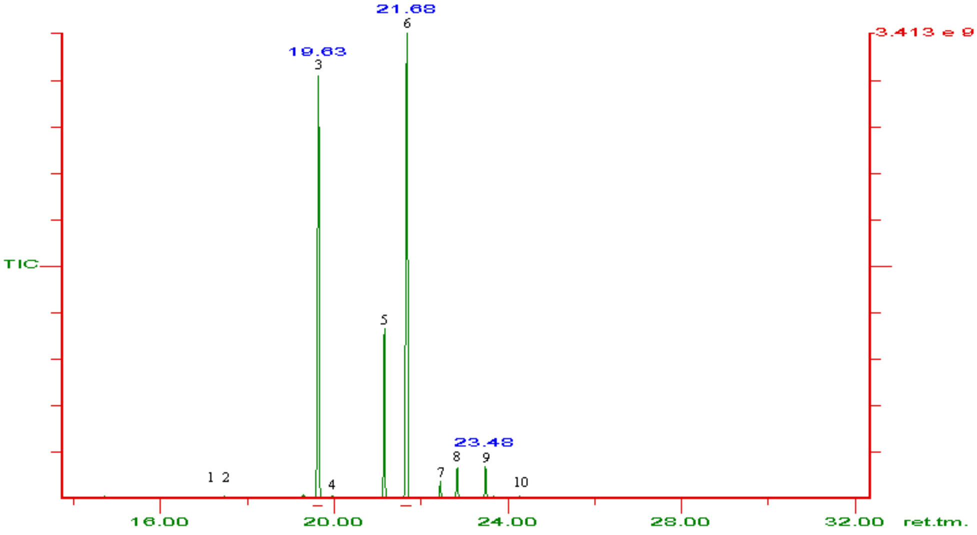
	Ballschmitter Nr.		Weight-% /19/
1	101	2,2',4,5,5'-PentaBB	1,76
2	118	2,3',4,4',5-PentaBB	3,51
3	149	2,2',3,4',5,6-HexaBB	0,72
	132	2,2',3,3',4,6'-HexaBB	0,41
4	153	2,2',4,4',5,5'-HexaBB	54,33
		HexaBB	0,82
		HexaBB	0,34
5	138	2,2',3,4,4',5'-HexaBB	8,2
		HexaBB	0,68
6	167	2,3',4,4',5,5'-HexaBB	4,82
7	178	2,2',3,3',5',5,6-HeptaBB	0,90
8	187	2,2',3,4',5,5',6-HeptaBB	1,3
8	156	2,3,3,4,4'5'HexaBB	2,44
8	157	2,3,3',4,4',5'HexaBB	1,14
9	180	2,2',3,4,4',5,5'HeptaBB	19,23
	169	3,3',4,4',5,5'HexaBBoder	
	172	2,2',3,3',4,5,5'HeptaBB	0,39
10	170	2,2',3,3',4,4',5HeptaBB	1,8

Octabromobiphenyl (FR 250 13 A Dow Chemical)



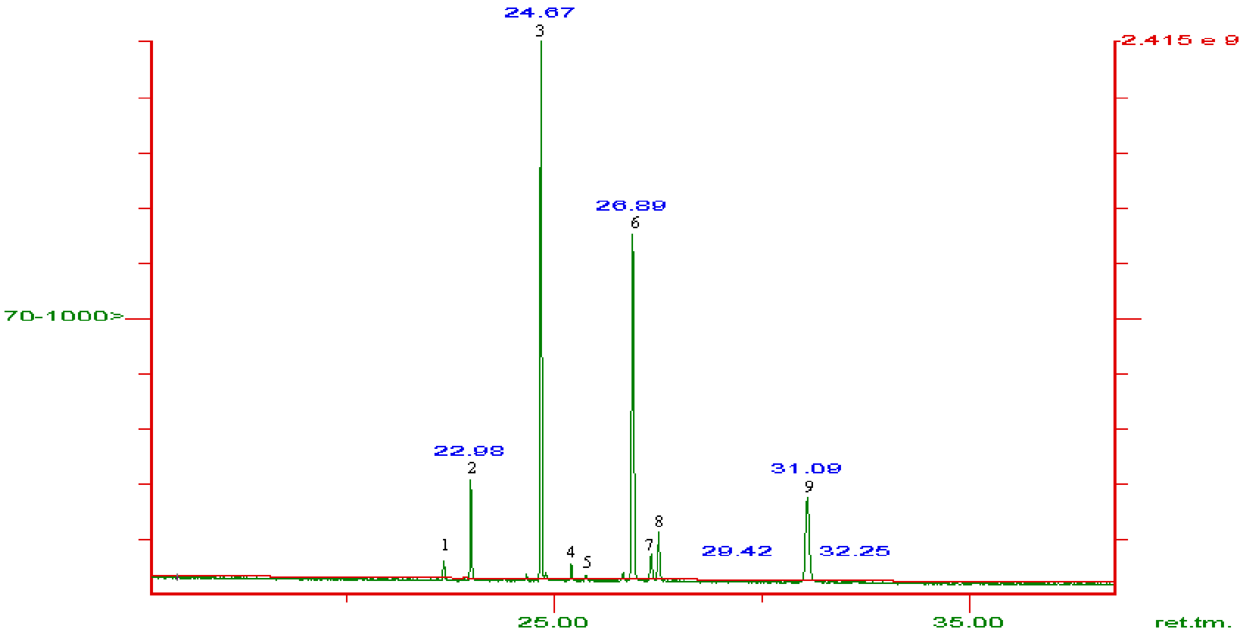
	Ballschmitter Nr.		*Weight-% /19/*
1	180	2,2',3,4,4',5,5'-HeptaBB	1,03
2	198	2,2',3,3',4,5,5',6-OctaBB	1,31
3	203 od. 196	2,2'3,4,4',5,5',6-OctaBB 2,2',3,3',4,4',5,6'.OctaBB	2,5
4	194	2,2',3,3',4,4',5,5'-OctaBB	32,84
5	208	2,2',3,3',4,5,5',6,6'-NonaBB	0,77
6	206	2,2',3,3',4,4',5,5',6-NonaBB	53,64
7	209	2,2',3,3',4,4',5,5',6,6'-DecaBB	7,91

Pentabromodiphenylether (DE-71-Great Lakes)



	Ballschmitter Nr.		*Weight-% /19/*
1	17	2,2,4'-TriBDE	0,067
2	28	2,4,4'-TriBDE	0,22
3	47	2,2',4,4'-TeBDE	32,96
4	66	2,3',4,4'-TeBDE	0,77
5	100	2,2',4,4',6-PeBDE	9,96
6	99	2,2'4,4',5-PeBDE	42,03
7	85	2,2',3,4,4'-PeBDE	1,82
8	154	2,2',4,4',5,6'-PeBDE	4,15
9	153	2,2',4,4',5,5'-PeBDE	4,77
		HxBDE	0,70
10	138	2,2',3,4,4',5'-HxBDE	0,46

Octabromodiphenylether (DE-79-Great Lakes)



	Ballschmitter Nr.		*Weight-% /19/*
1	154	2,2',4,4',5,6'-HexaBDE	1,19
2	153	2,2',4,4',5,5'-HexaBDE	8,10
3		HeptaBDE	40,17
4		HeptaBDE	2,01
5	190	2,3,3',4,4',5,6-HeptaBDE	0,84
6		OctaBDE	21,42
7		OctaBDE	5,51
8		OctaBDE	8,27
9		NonaBDE	12,49

Appendix 2

Mass spectrum of BFRs and OPCs

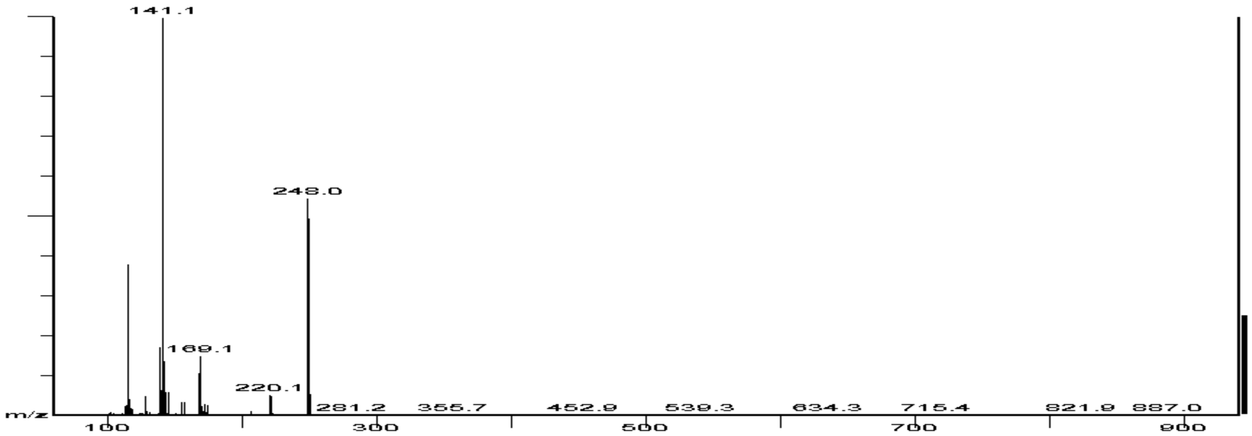


Fig.46: Mass spectrum of MonoBDE (EI-mode)

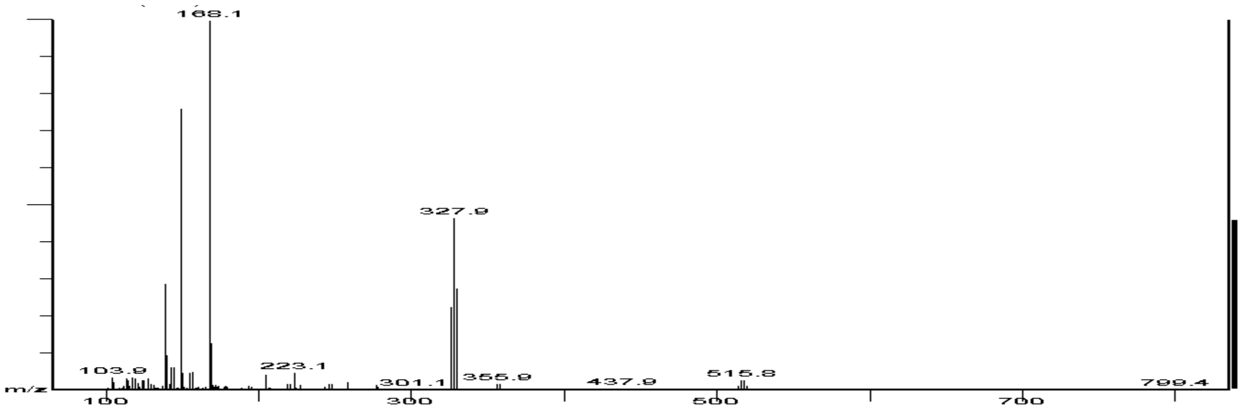


Fig. 47: Mass spectrum of DiBDE (EI-mode)

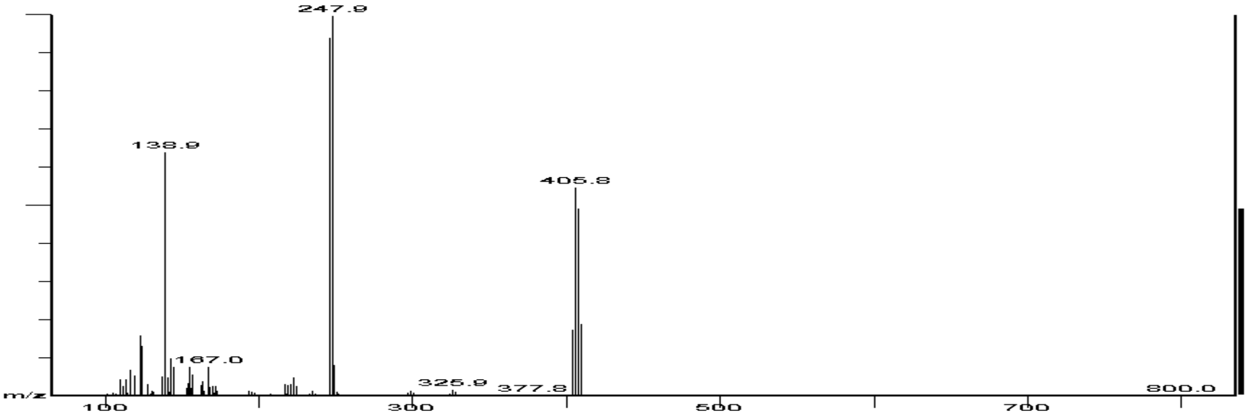


Fig.48: Mass spectrum of TriBDE (EI-mode)

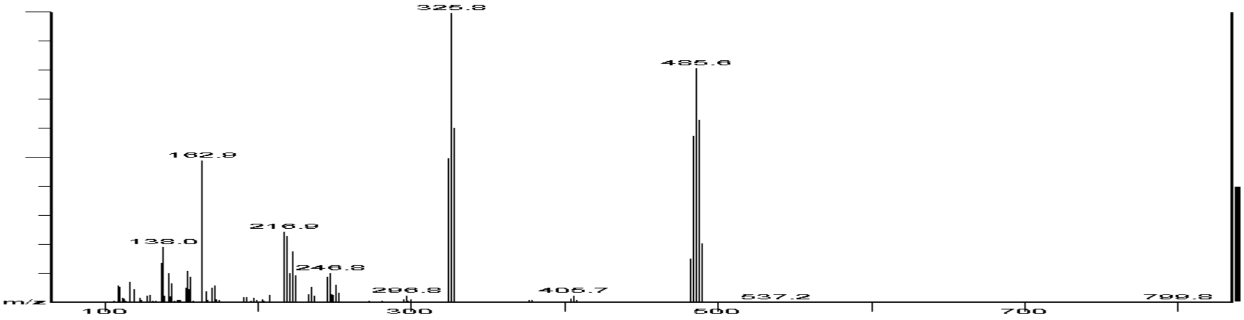


Fig.49: Mass spectrum of TetraBDE (EI-mode

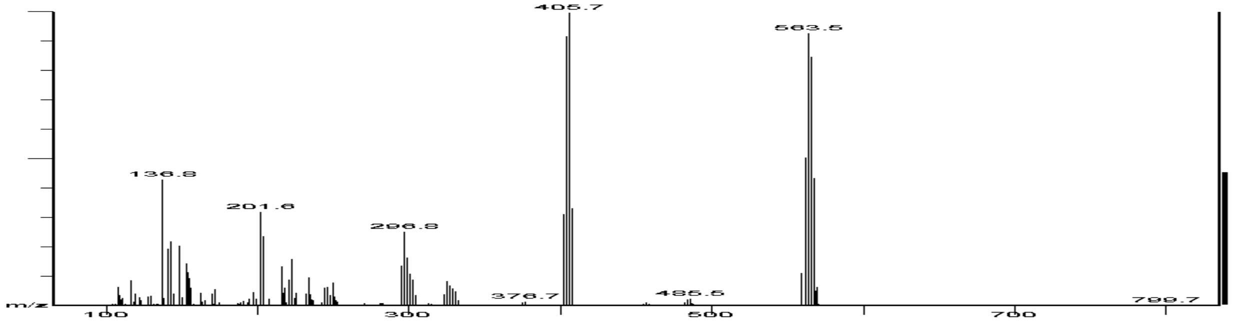


Fig. 50: Mass spectrum of PentaBDE (EI-mode)

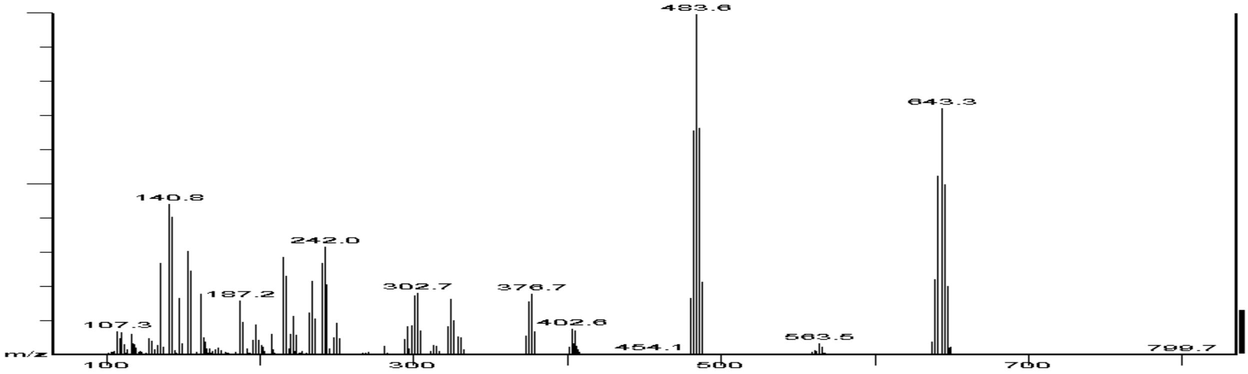


Fig. 51: Mass spectrum of HexaBDE (EI-mode)

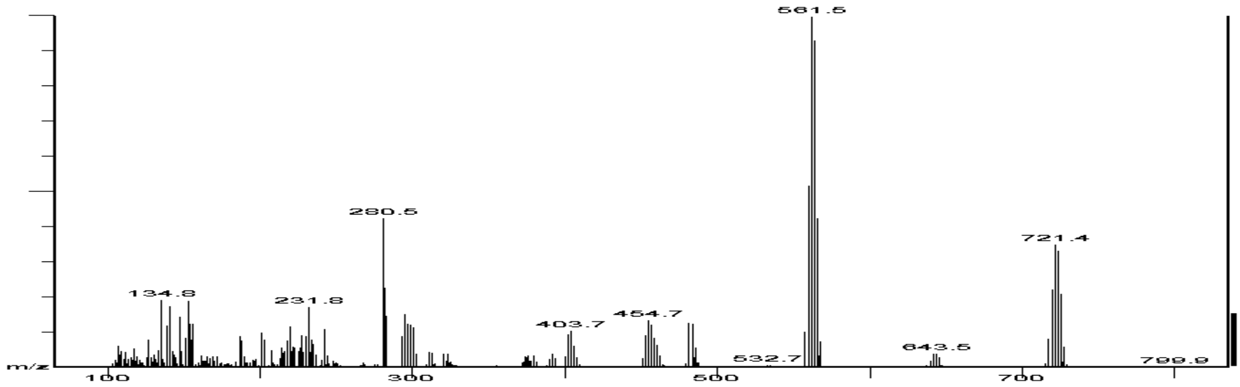


Fig. 52: of HeptaBDE (EI-mode)

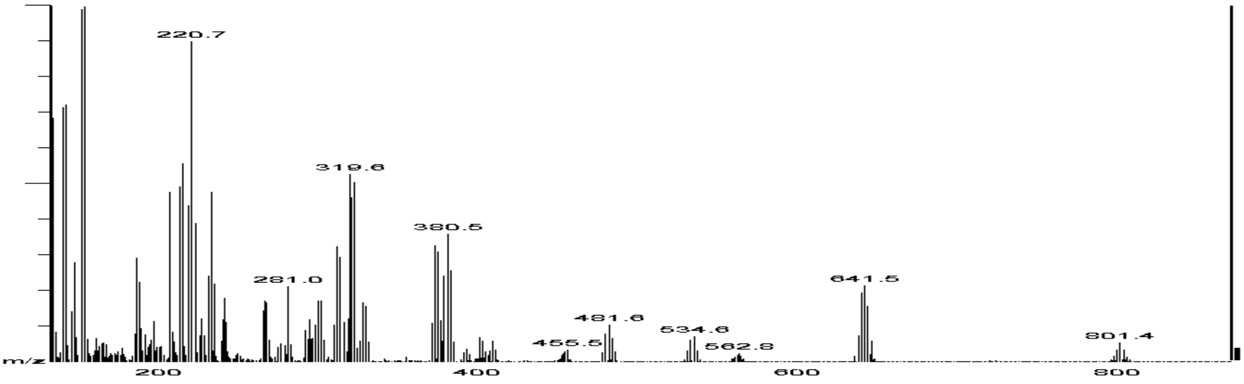


Fig. 53: Mass spectrum of OctaBDE (EI-mode)

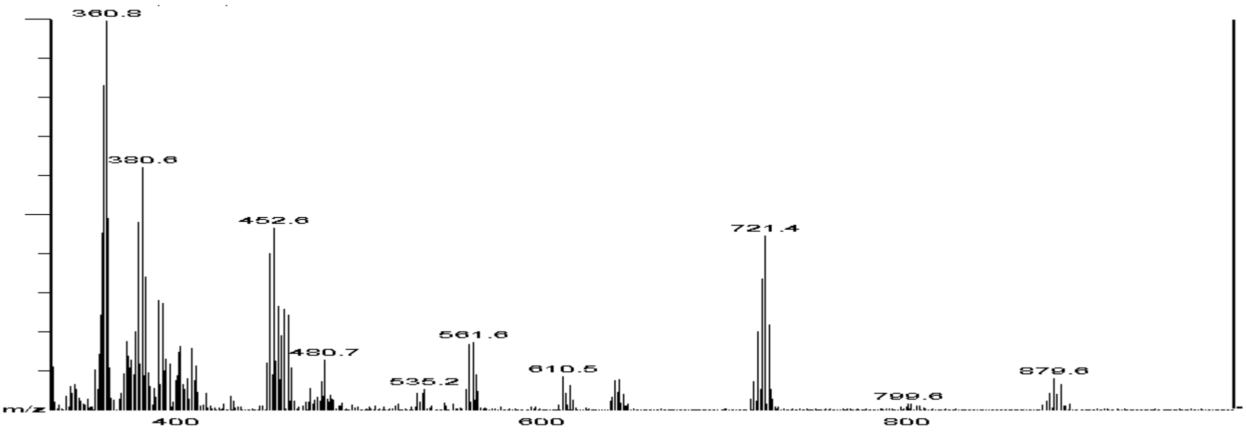


Fig. 54: Mass spectrum of NonaBDE (EI-mode)

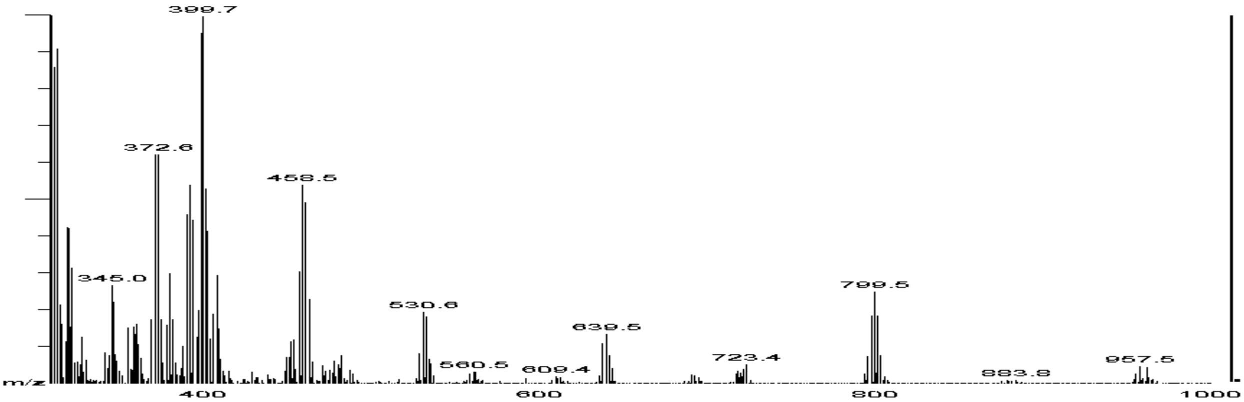


Fig. 55: Mass spectrum of DecaBDE (EI-mode

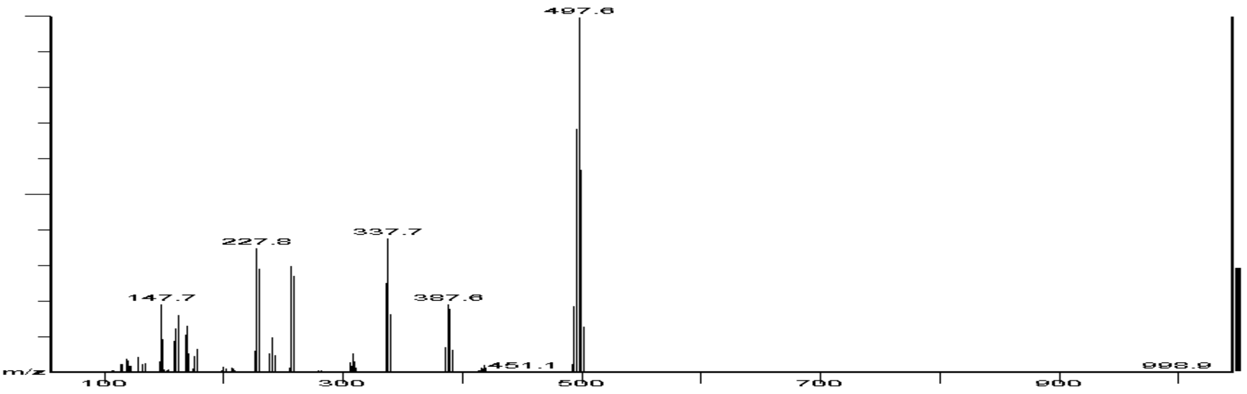


Fig. 56: Mass spectrum of $^{13}C_{12}$-TetraBDE (NCI-mode)

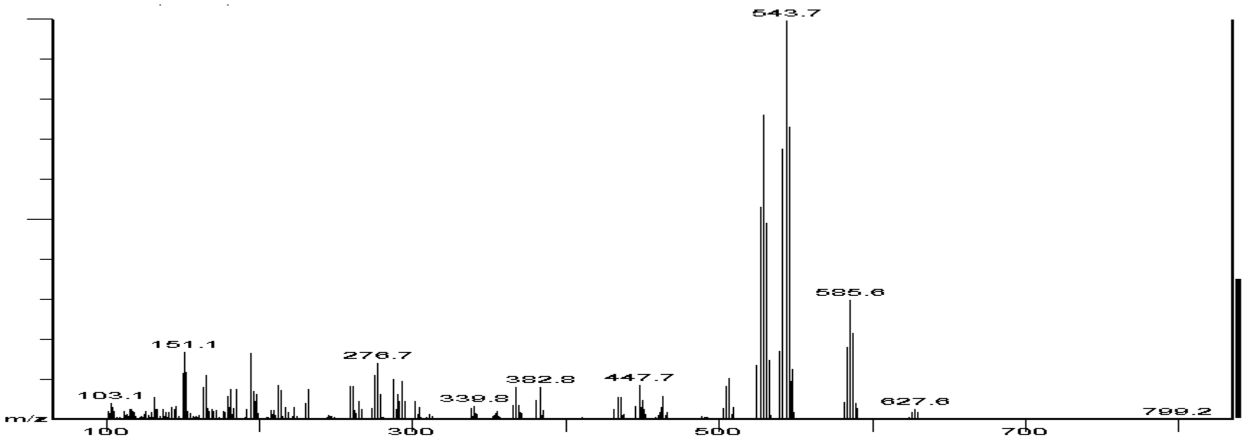


Fig. 57: Mass spectrum of Diacetyl-TBBPA (EI-mode)

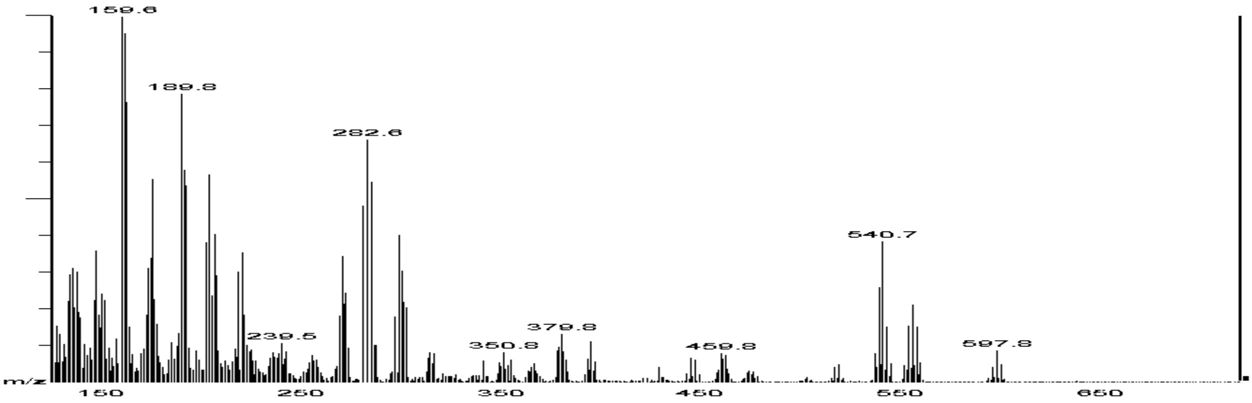


Fig. 58: Mass spectrum of Diacetyl-TBBPA-13C_{12}-ring (EI-mode)

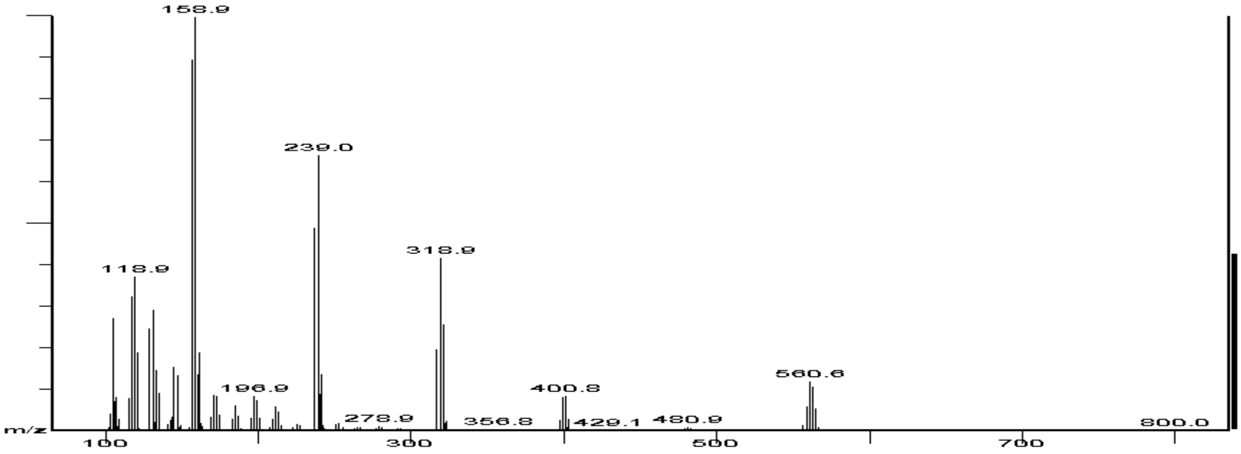


Fig. 59: Mass spectrum of HBCD (EI-mode)

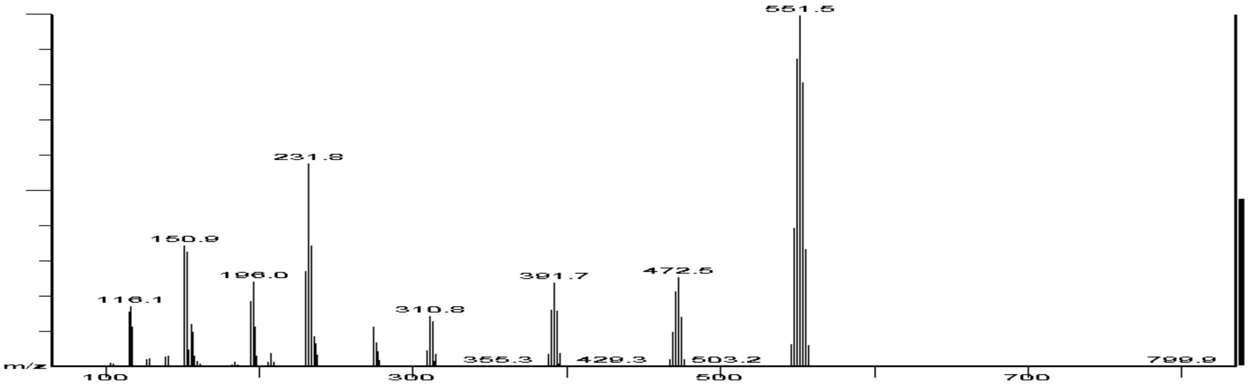


Fig. 60: Mass spectrum of HB (EI-mode)

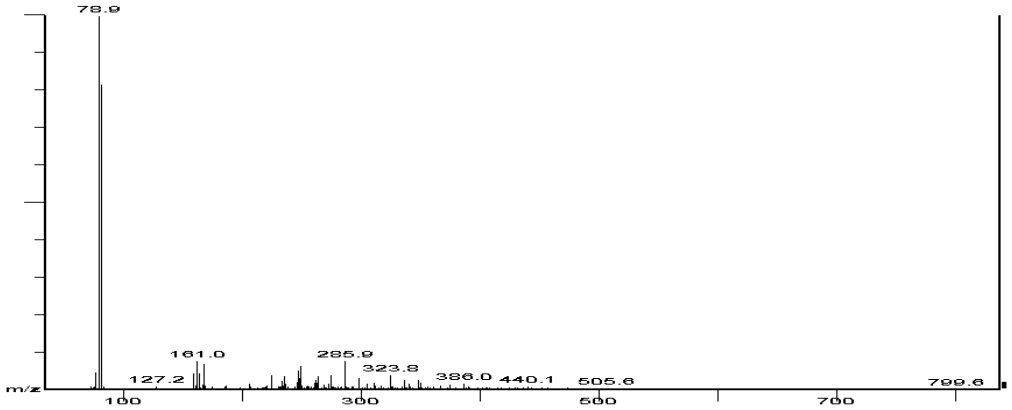


Fig. 61: Mass spectrum of DiBDE (NCI-mode)

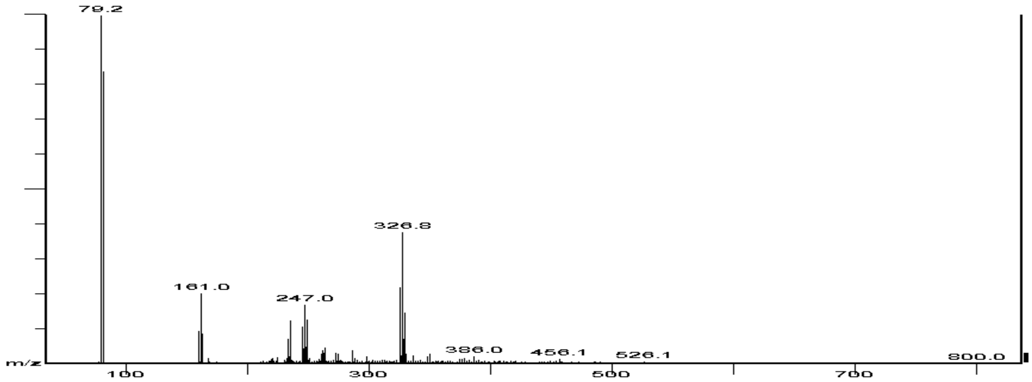


Fig. 62: Mass spectrum of TriBDE (NCI-mode)

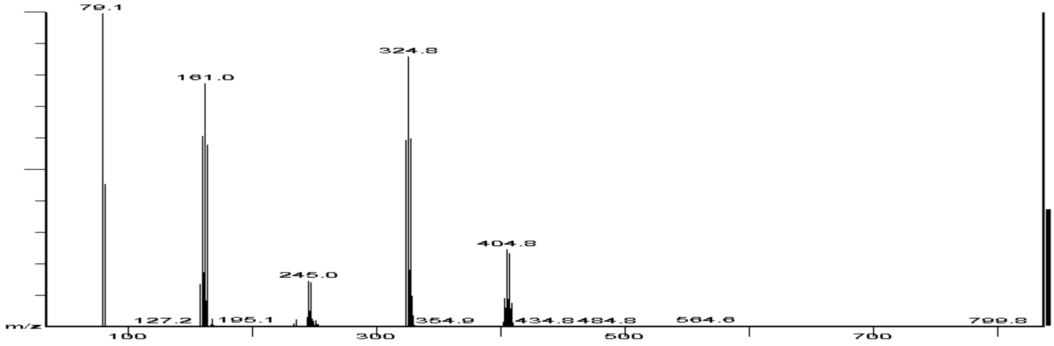


Fig. 63: Mass spectrum of TetraBDE (NCI-mode)

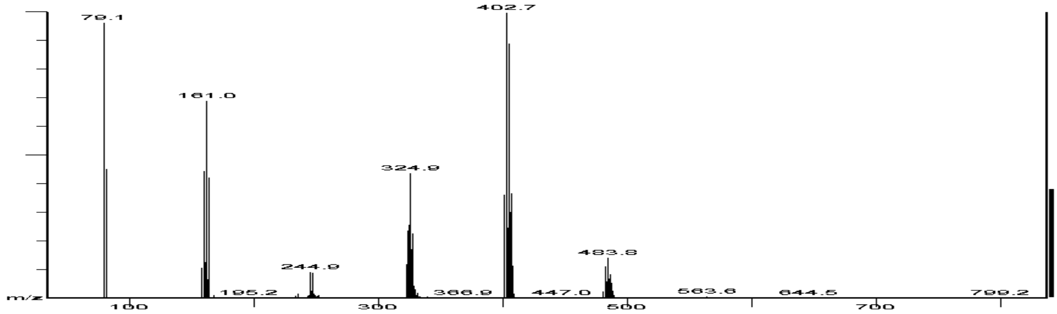


Fig. 64: Mass spectrum of PentaBDE (NCI-mode)

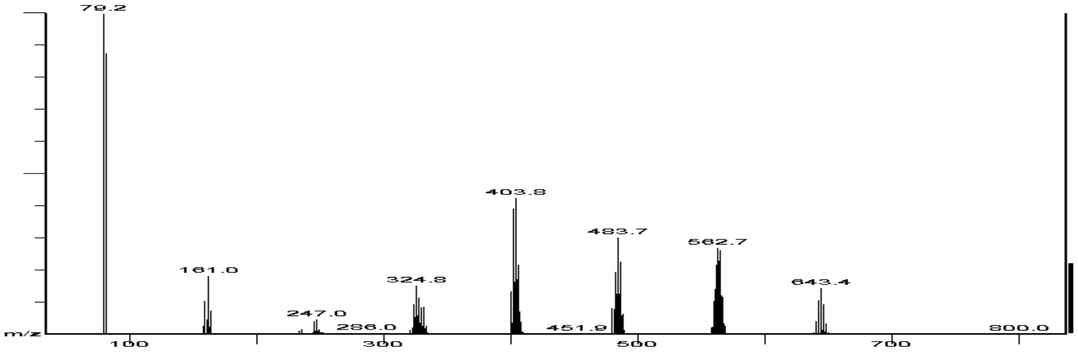


Fig. 65: Mass spectrum of HexaBDE (NCI-mode)

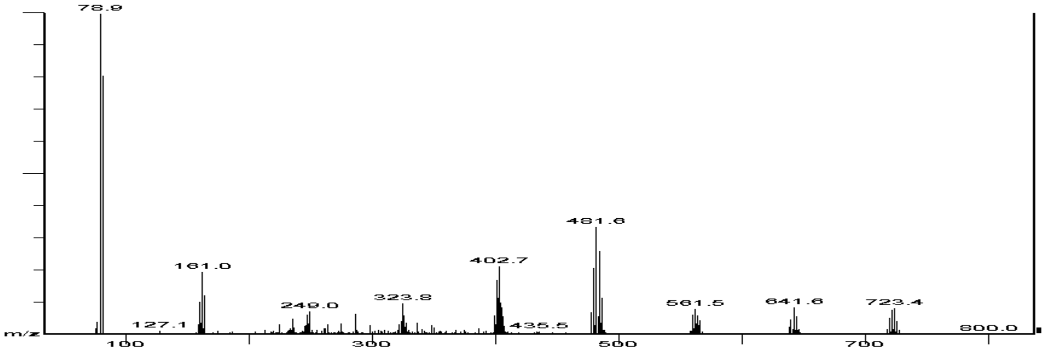


Fig. 66: Mass spectrum of HeptaBDE (NCI-mode)

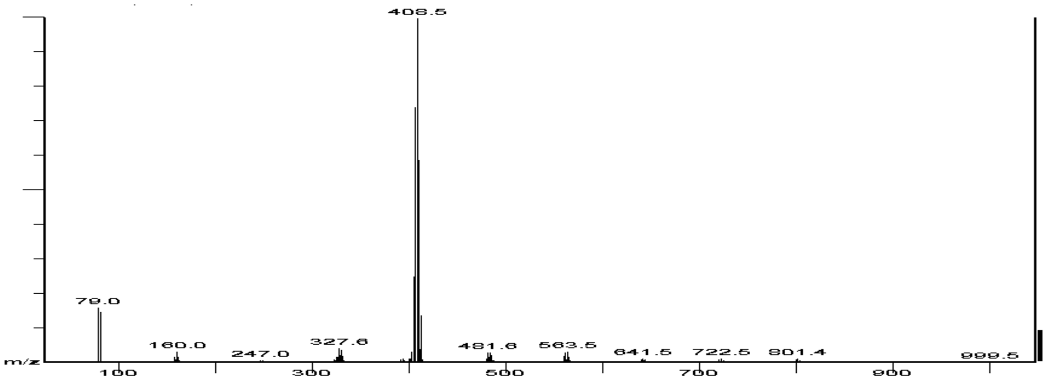


Fig. 67: Mass spectrum of OctaBDE (NCI-mode)

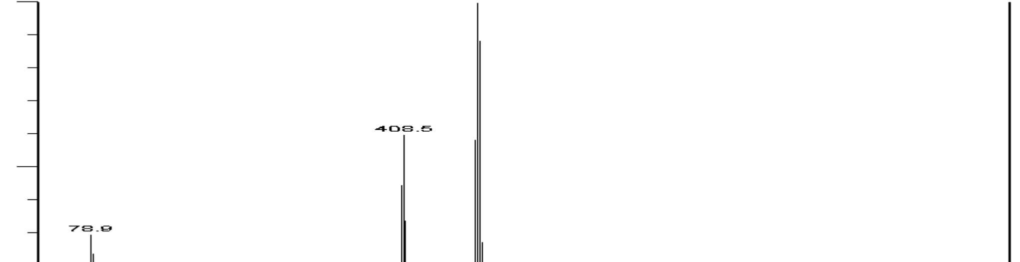


Fig. 68: Mass spectrum of NonaBDE (NCI-mode)

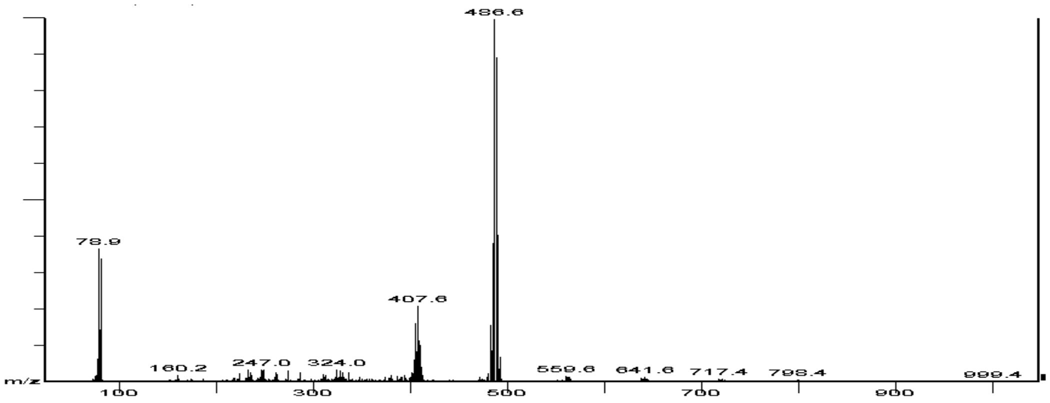


Fig. 69: Mass spectrum of DecaBDE (NCI-mode)

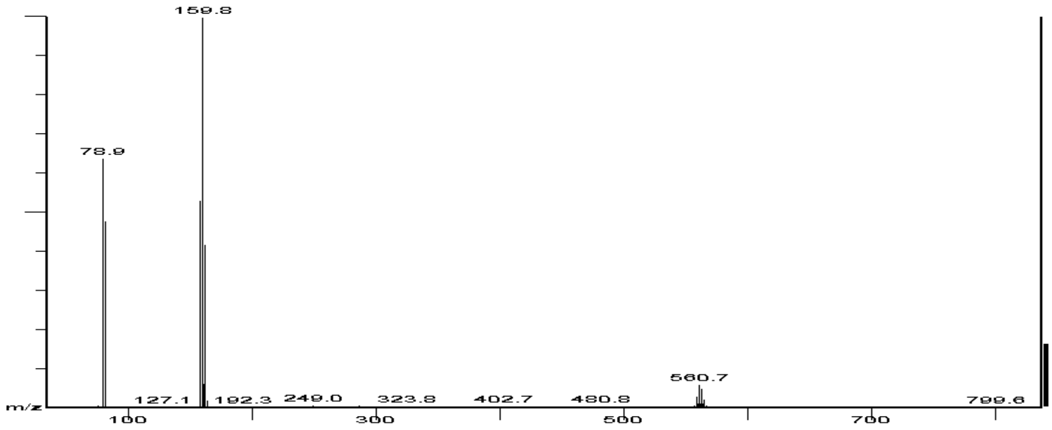


Fig. 70: Mass spectrum of HBCD (NCI-mode)

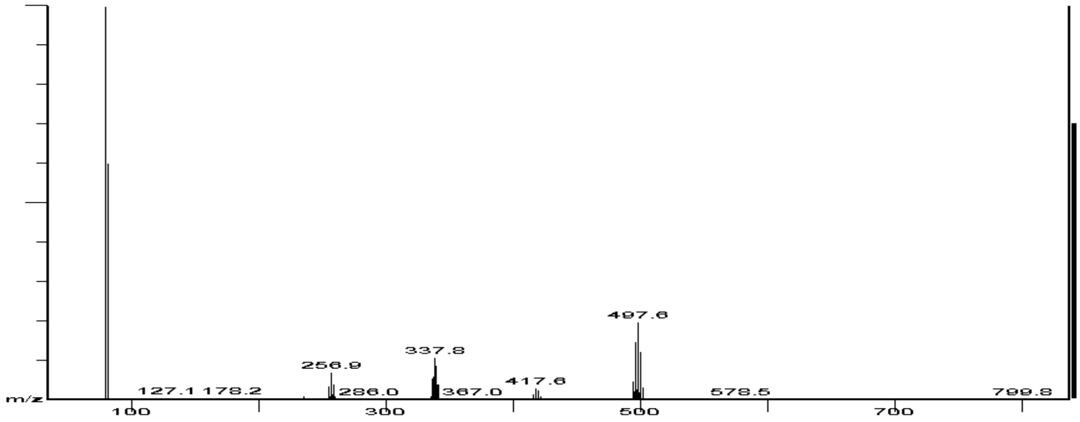


Fig. 71: Mass spectrum of $^{13}C_{12}$-TetraBDE (NCI-mode)

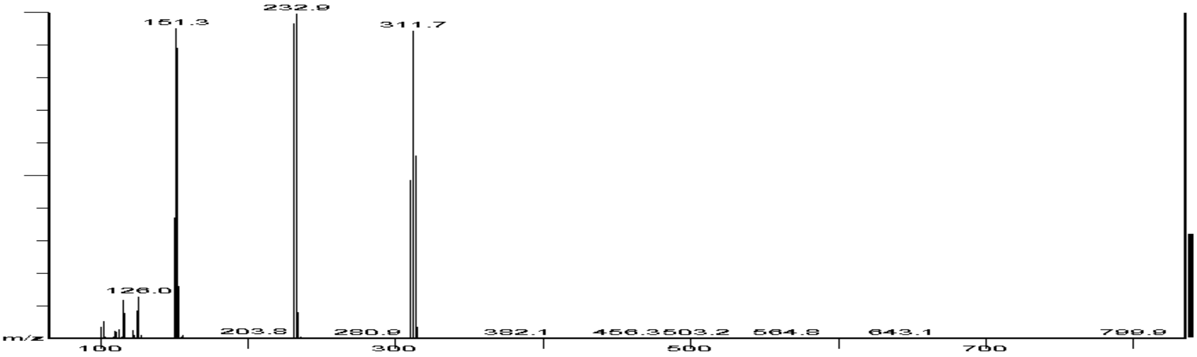


Fig.72: Mass spectrum of DiBB (EI-Mode)

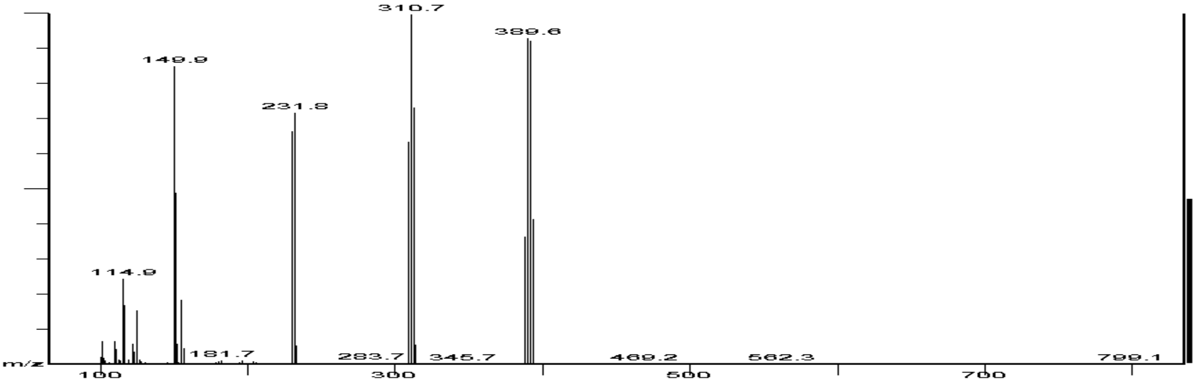


Fig. 73: Mass spectrum of TriBB (EI-Mode)

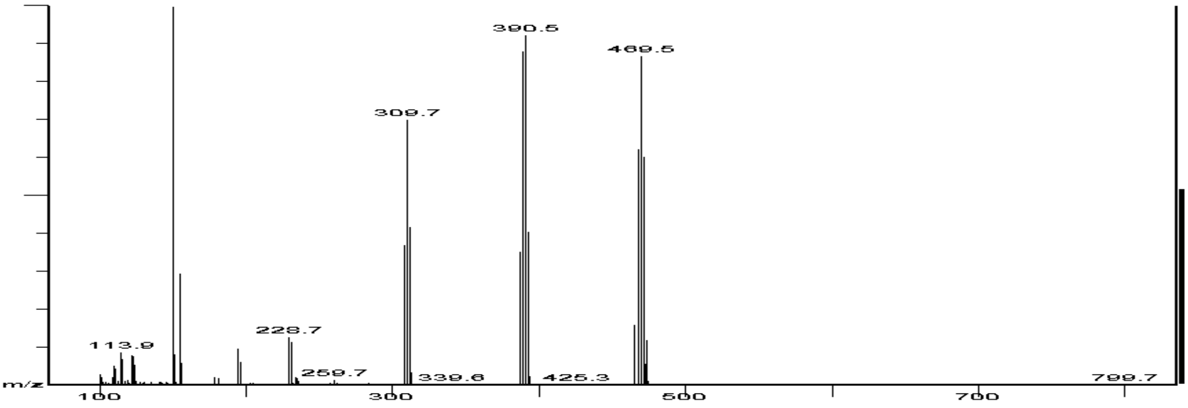


Fig. 74: Mass spectrum of TetraBB (EI-Mode)

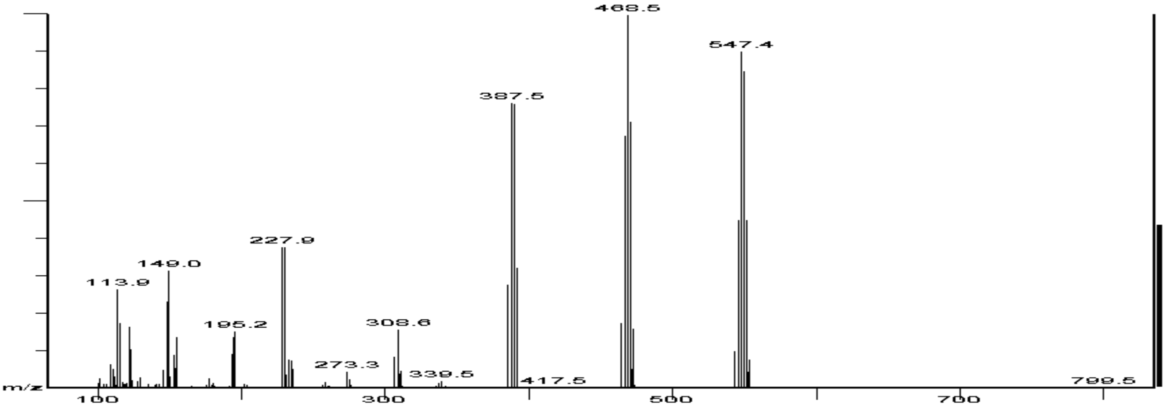


Fig. 75: Mass spectrum of PentaBB (EI-Mode)

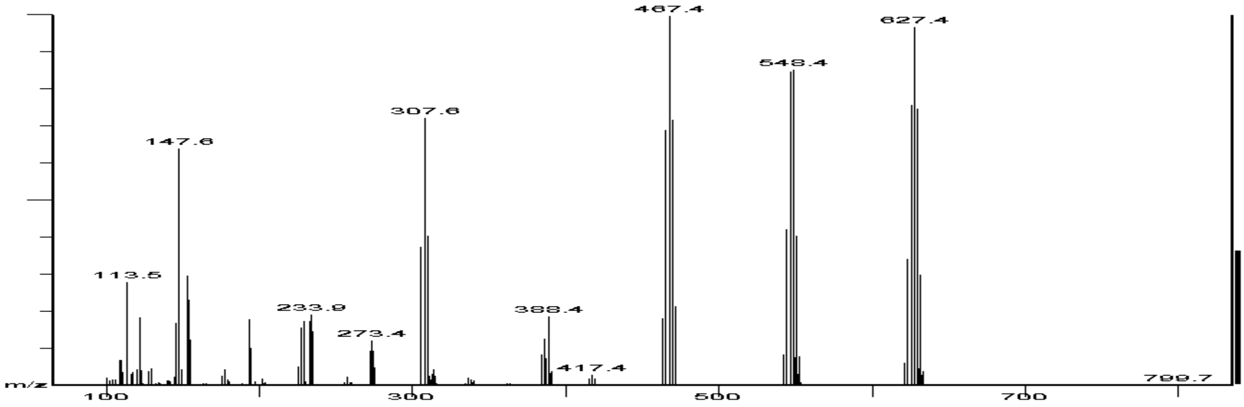


Fig. 76: Mass spectrum of HexaBB (EI-Mode)

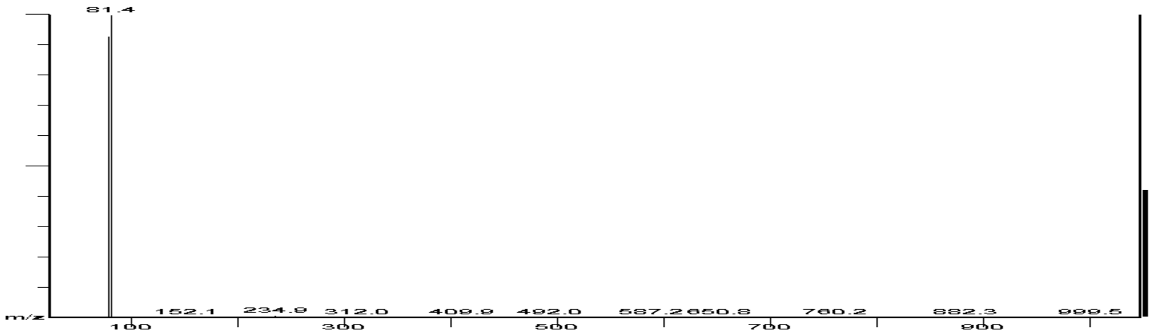


Fig. 77: Mass spectrum of DiBB (NCI-Mode)

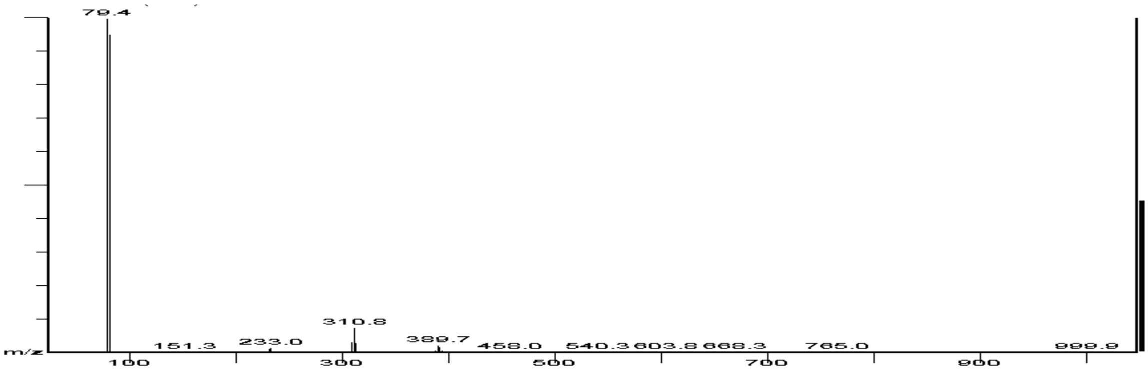


Fig. 78: Mass spectrum of TriBB (NCI-Mode)

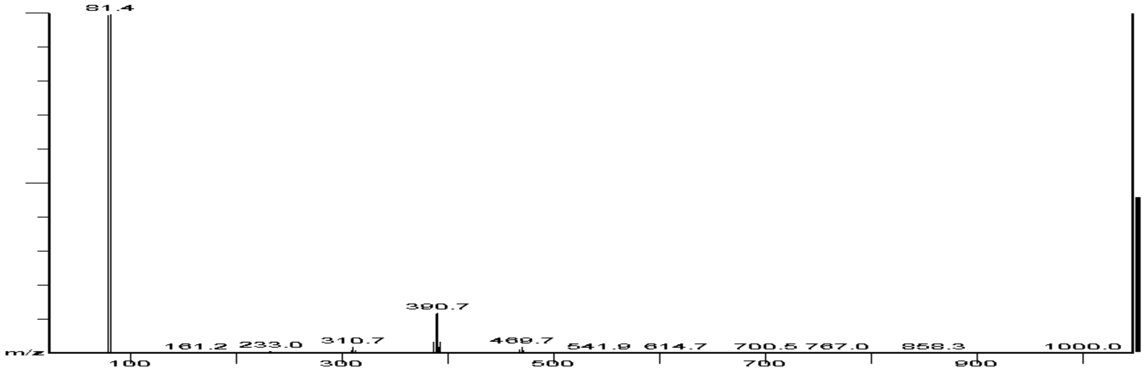


Fig. 79: Mass spectrum of TetraBB (NCI-Mode)

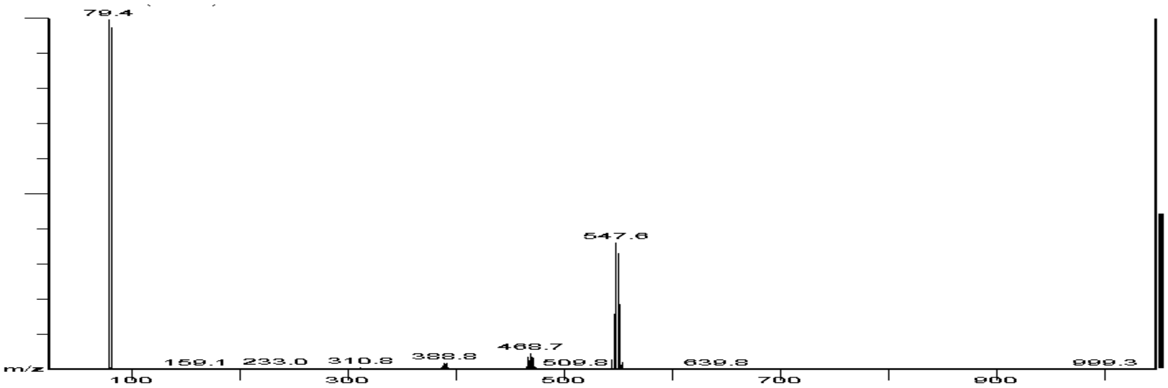


Fig. 80: Mass spectrum of PentaBB (NCI-Mode)

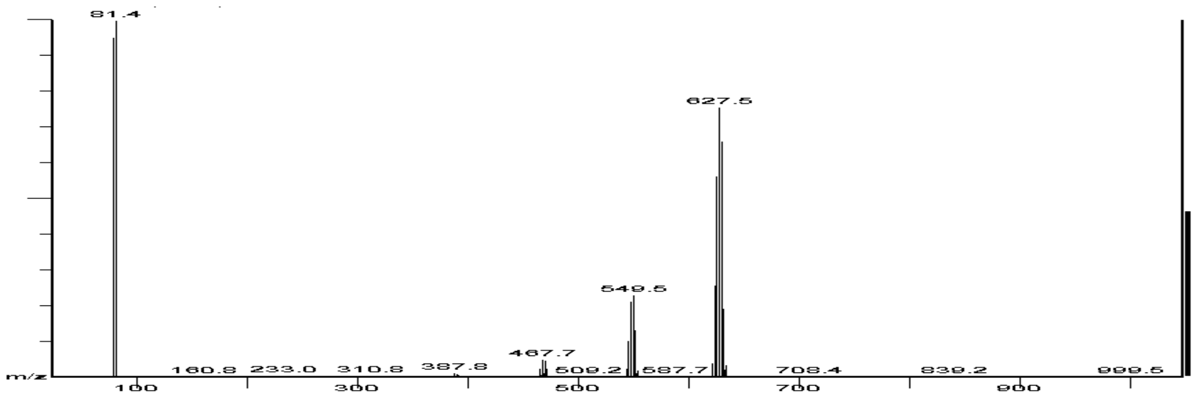


Fig. 81: Mass spectrum of HexaBB (NCI-Mode)

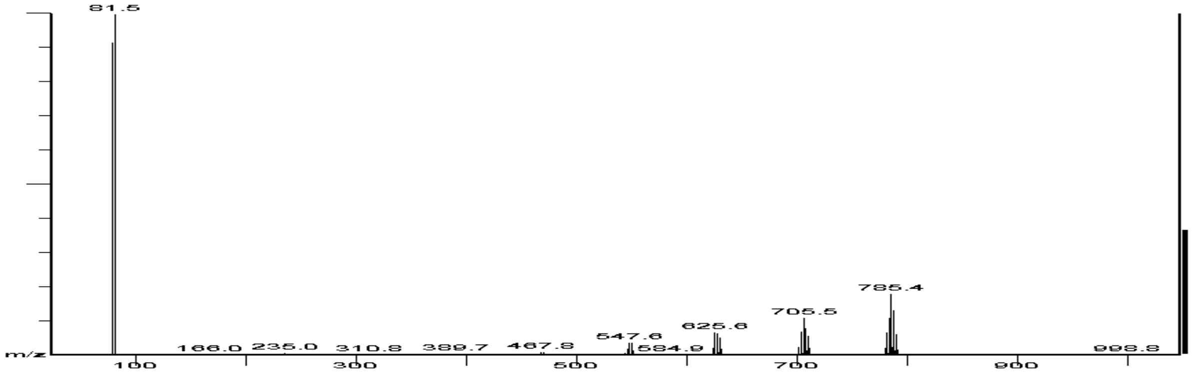


Fig. 82: Mass spectrum of HeptaBB (NCI-Mode)

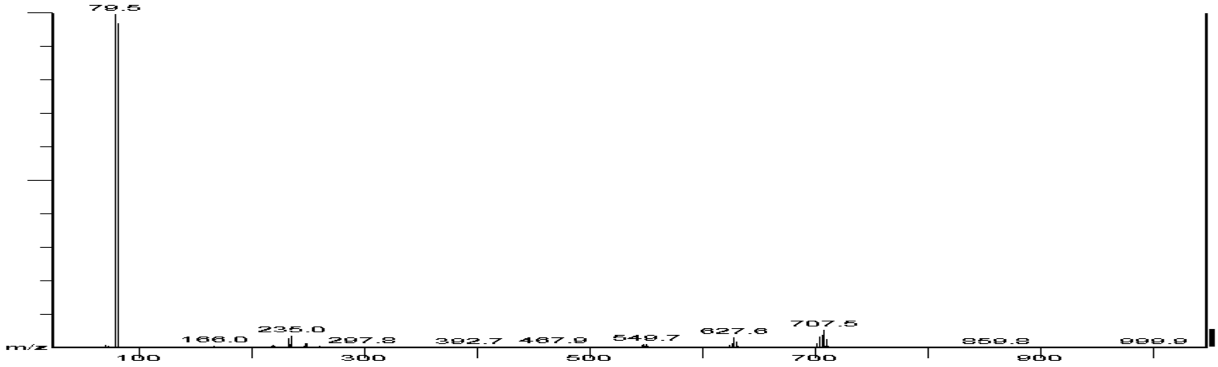


Fig. 83: Mass spectrum of OctaBB (NCI-Mode)

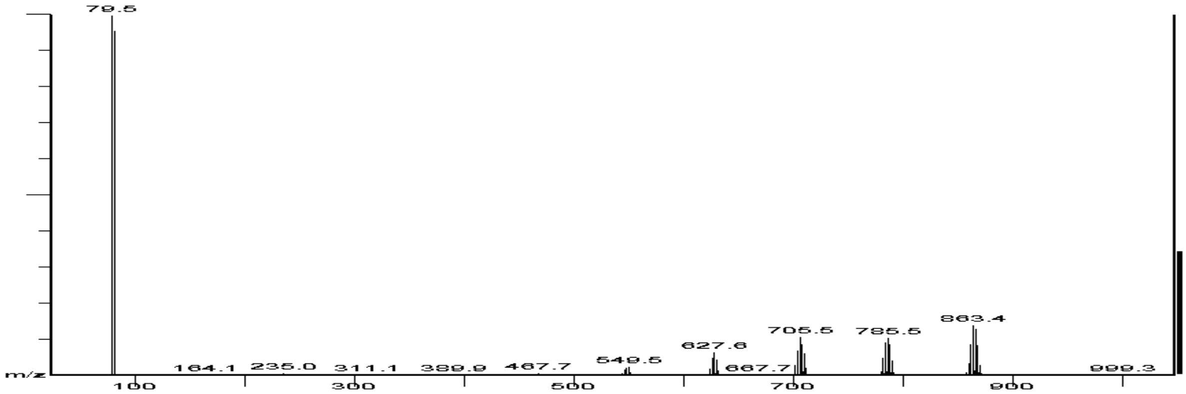


Fig. 84: Mass spectrum of NonaBB (NCI-Mode)

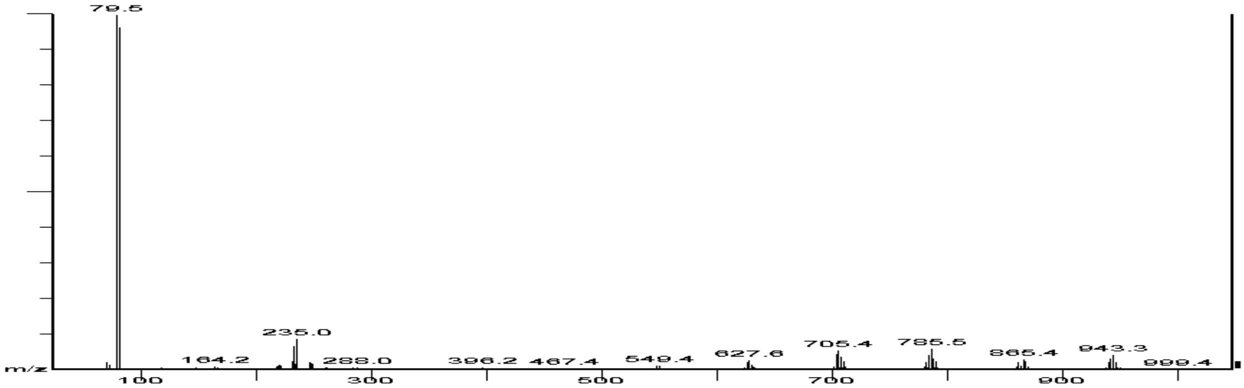


Fig. 85: Mass spectrum of DecaBB (NCI-Mode)

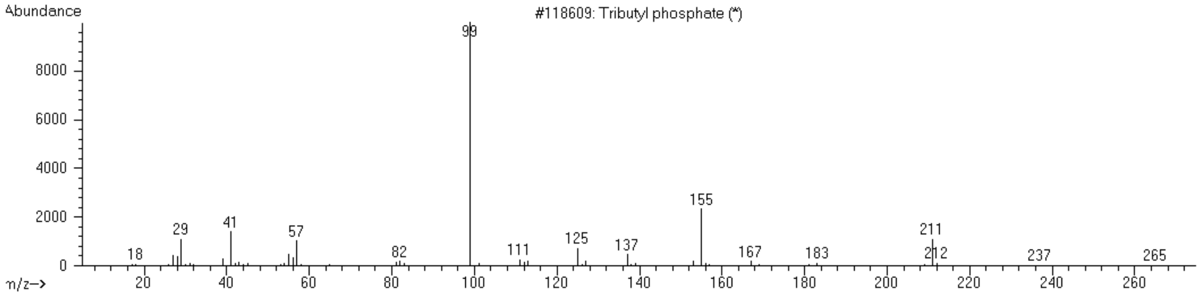


Fig. 86: Mass spectrum of TBP (EI-Mode)

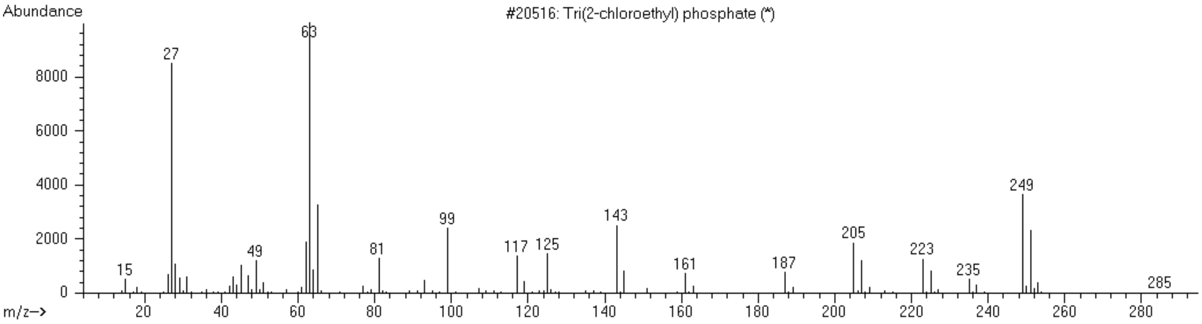


Fig. 87: Mass spectrum of TCEP (EI-Mode)

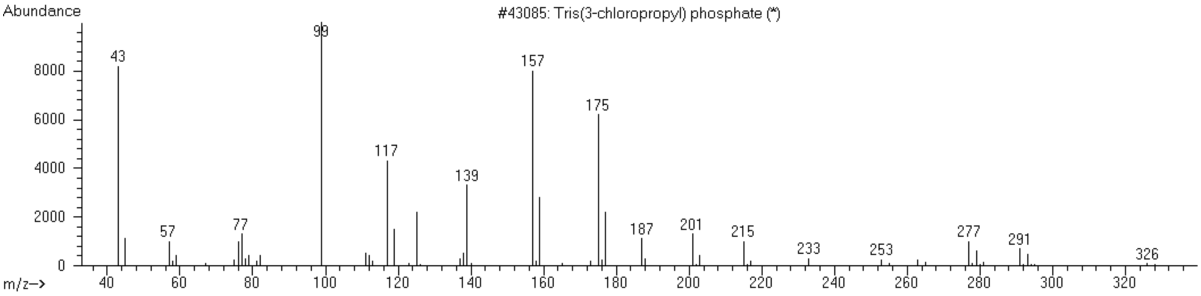


Fig. 88: Mass spectrum of TCPP (EI-Mode)

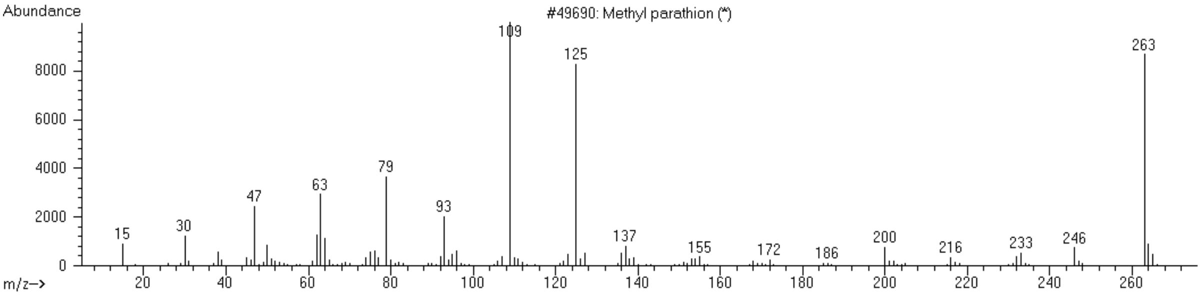


Fig. 89: Mass spectrum of ISTD (EI-Mode)

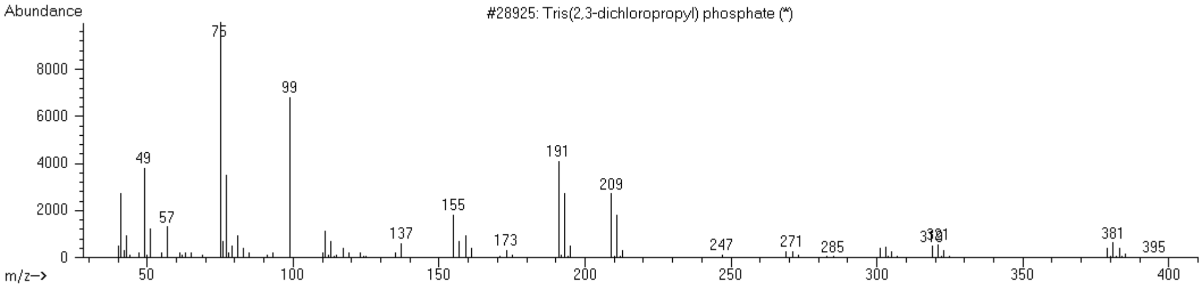


Fig. 90: Mass spectrum of TDCP (EI-Mode)

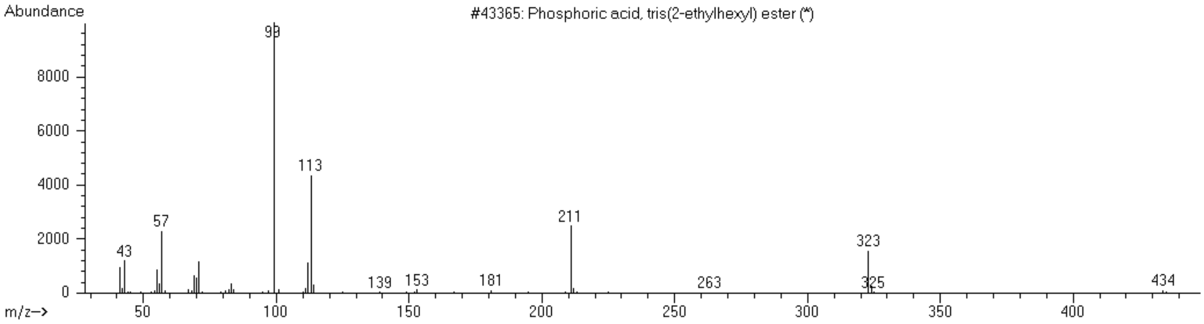


Fig. 91: Mass spectrum of TEHP (EI-Mode)

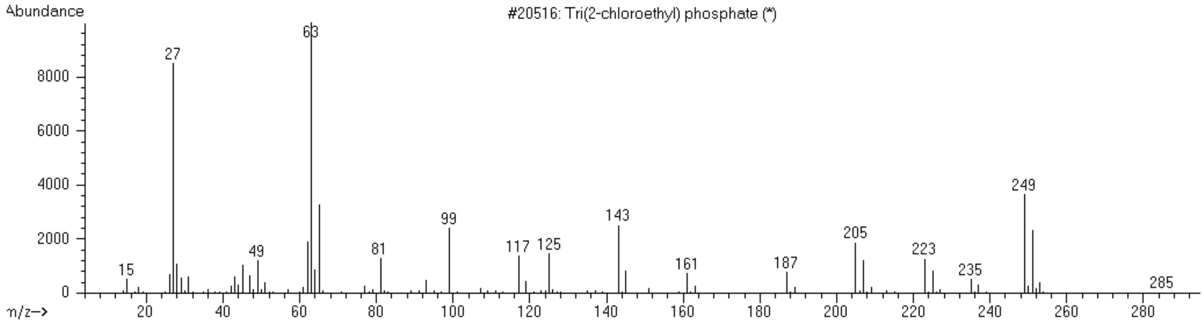


Fig. 92: Mass spectrum of TBEP (EI-Mode)

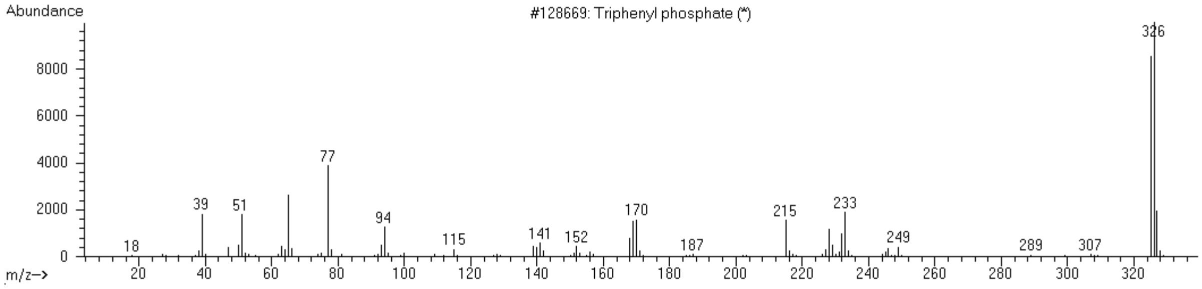


Fig. 93: Mass spectrum of TPP (EI-Mode)

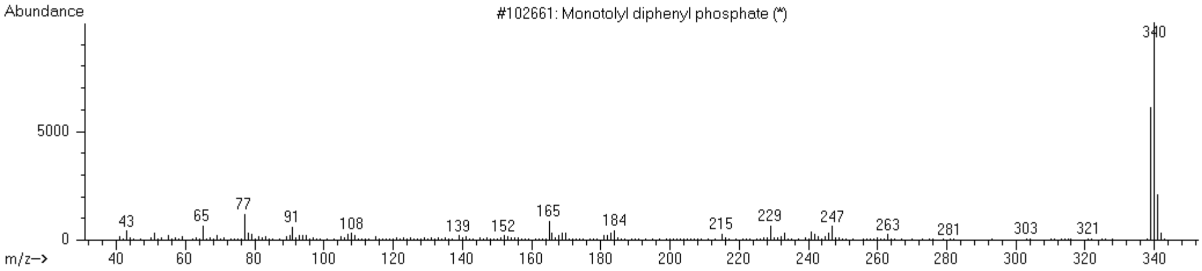


Fig. 94: Mass spectrum of DPK (EI-Mode)

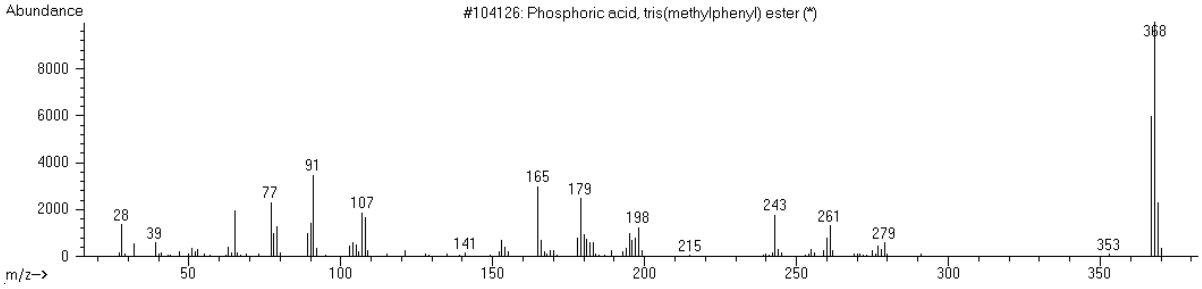


Fig. 95: Mass spectrum of TMTP (EI-Mode)

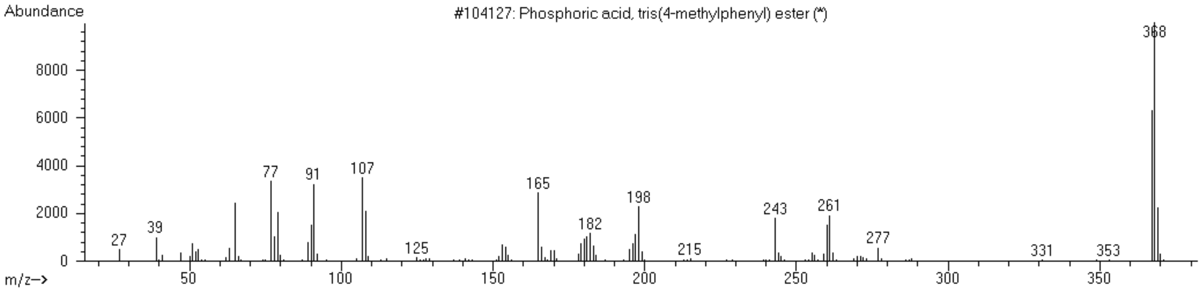


Fig. 96: Mass spectrum of TPTP (EI-Mode)

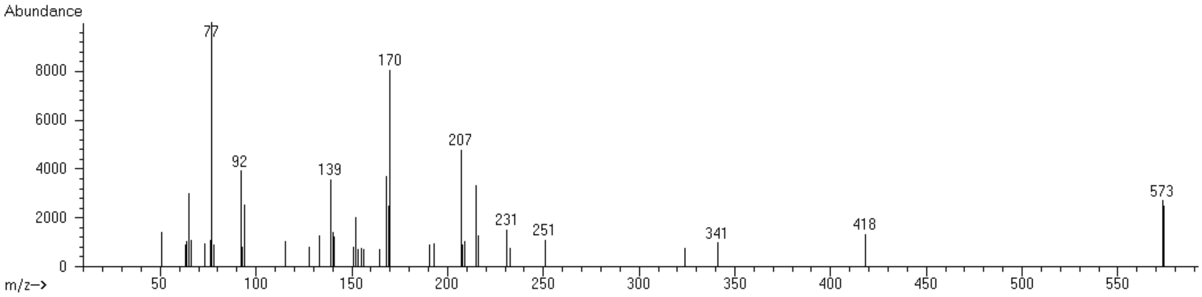


Fig. 97: Mass spectrum of RDP (EI-Mode)

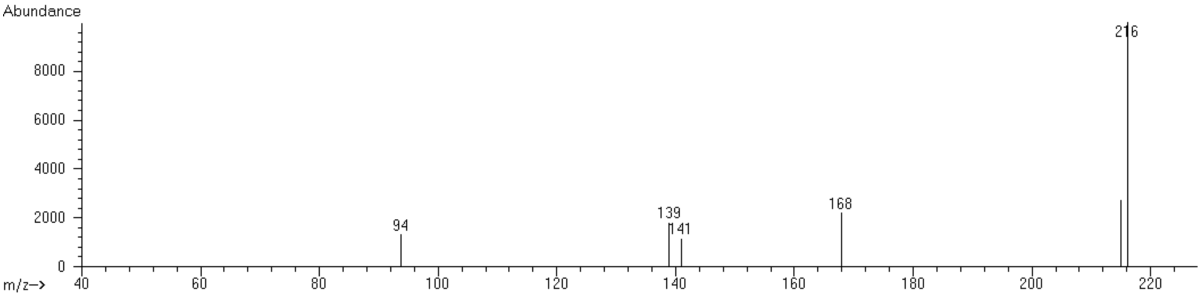


Fig. 98: Mass spectrum of DOPO (EI-Mode)

Appendix 3

Physicochemical Properties

Polybrominated Flame Retardants (BFR)

1.) Polybrominated Diphenylethers (PBDE)

Table 1: Composition of commercial PBDEs /13/.

product	composition							
	TriBDE	TetraBDE	PentaBDE	HexaBDE	HeptaBDE	OctaBDE	NonaBDE	DecaBDE
DecaBDE							0.3-3%	97-98%
OctaBDE				10-12%	43-44%	31-35%	9-11%	0-1%
PentaBDE	0-1 %	24-38%	50-62%	4-8%				

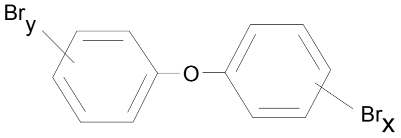


Fig. 1: Basic structure of PBDEs; Σ x,y: 1-10

Tribromo diphenylether

CAS-Nr.:	49690-94-0 /13/
Vapour pressure:	$1{,}45 \cdot 10^{-4}$ Pa (25 °C) /39/
	4,70-4,95 Pa (25 °C) /13/
Molar weight:	407 g mol^{-1}
Molecular formula:	$C_{12}H_7Br_3O$

Tetrabromo diphenylether

CAS-Nr.:	40088-47-9 /13/
Melting point:	80,5 °C /42/
Vapour pressure:	$1{,}45 \cdot 10^{-5}$ Pa (25 °C) /39/
	$2{,}9 \cdot 10^{-4}$ Pa (25 °C)
Solubility in water:	$1{,}1 \cdot 10^{-2}$ mg L^{-1} (25 °C) /42/
Molar weight:	486 g mol^{-1}
Molecular formula:	$C_{12}H_6Br_4O$

Pentabromo diphenylether

CAS-Nr.:	32534-81-9
Melting point:	(-7) - (-3) °C /13/
	93,2 °C /42/
Boiling point:	> 200 °C /13/
Vapour pressure:	2,2-5,5 * 10^{-7} mm Hg (25 °C) /38/
	5,11 * 10^{-5} Pa (25 °C) /42/
	7,76 * 10^{-6} Pa (25 °C) /38/
	9,3 mm Hg (22 °C) /16/
	6,26-6,66 Torr (25 °C) /16/
	4,69 10^{-5} Pa (21 °C) (commercial product) /41/
	1240 Pa (22 °C) /43/
Solubility in water:	13,3 µg L^{-1} (25 °C) (commercial product) /41/
	$9*10^{-7}$ mg L^{-1} (20 °C) /16/
	2,4 * 10^{-3} mg L^{-1} (25 °C) /42/
Molar weight:	565 g mol^{-1}
Molecular formula:	$C_{12}H_5Br_5O$

Hexabromo diphenylether

CAS-Nr.:	36483-60-0 /40/
Vapour pressure:	0,95-0,99 kPa (25 °C)
Molar weight:	644 g mol^{-1}
Molecular formula:	$C_{12}H_4Br_6O$

Heptabromo diphenylether

CAS-Nr.:	68928-80-3
Melting point:	70-150 °C /13/
Vapour pressure:	9,55 * 10^{-8} Pa (25 °C) /39/
Molar weight:	722 g mol^{-1}
Molecular formula:	$C_{12}H_3Br_7O$

Octabromo diphenylether

CAS-Nr.:	32536-52-0
Melting point:	200 °C /16/
	167-257 °C /16/
Vapour pressure:	1-1,7 * 10^{-9} mm Hg (25 °C) /38/
	8,78-9,04 Torr (25 °C) /16/
	< 13,3 Pa (20 °C) /13/
Solubility in water:	< 1 g L^{-1} (25 °C) /40/
Molar weight:	801 g mol^{-1}
Molecular formula:	$C_{12}H_2Br_8O$

Nonabromo diphenylether

CAS-Nr.:	63936-56-1
Molar weight:	880 g mol^{-1}
Molecular formula:	$C_{12}HBr_9O$

Decabromo diphenylether

CAS-Nr.:	1163-19-5 /13/
Melting point:	300 °C /42/ 290-306 °C /13/ 300-310 °C /73/
Boiling point:	425 °C /16/
Vapour pressure:	2,03 mm Hg (278 °C) /38/ < 10^{-6} mm Hg (20 °C) /13/ 4,63 10^{-6} Pa (20 °C) /40/ 4,63 10^{-6} Pa (21 °C) /73/
Solubility in water:	25-30 µg L^{-1} (25 °C) /13/
Molar weight:	959 g mol^{-1}
Molecular formula:	$C_{12}Br_{10}O$

2.) Polybrominated biphenyls (PBB)

Table 2: Composition of commercial PBBs /14/.

product	composition						
	TetraBB	PentaBB	HexaBB	HeptaBB	OctaBB	NonaBB	DecaBB
DecaBB					0.3%	3%	97%
OctaBB				1%	31%	49%	8%
HexaBB	2 %	11%	63%	14%			

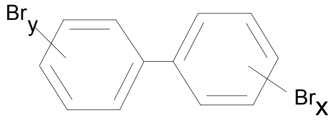


Fig.2: Basic structure of PBBs; Σ x,y: 1-10

Tetrabromo biphenyl

CAS-Nr.:	60044-24-8 /40/

Molar weight: 470 g mol^{-1}
Molecular formula: $C_{12}H_6Br_4$

Pentabromo biphenyl
CAS-Nr.: 67888-96-18X /40/
Molar weight: 549 g mol^{-1}
Molecular formula: $C_{12}H_5Br_5$

Hexabromo biphenyl
CAS-Nr.: 59536-65-1 (67774-32-7) /16/
Melting point: 72 °C /14/
Vapour pressure: $6*10^{-8}$ mm Hg (25 °C) /38/
Solubility in water: 0,06-610 µg L^{-1} (25 °C) /14/
Molar weight: 626 g mol^{-1}
Molecular formula: $C_{12}H_4Br_6$

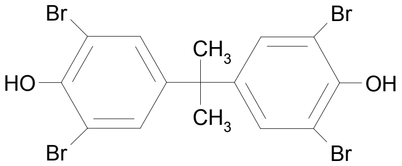
Heptabromo biphenyl
Molar weight: 706 g mol^{-1}
Molecular formula: $C_{12}H_3Br_7$

Octabromo biphenyl
CAS-Nr.: 61288-13-9
Melting point: 200-250 °C /14/
Solubility in water: 20-30 µg L^{-1} (25 °C) /14/
Molar weight: 786 g mol^{-1}
Molecular formula: $C_{12}H_2Br_8$

Nonabromo biphenyl
Molar weight: 864 g mol^{-1}
Molecular formula: $C_{12}HBr_9$

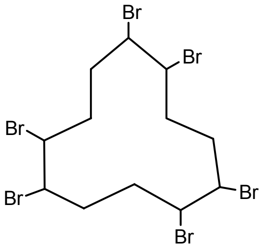
Decabromo biphenyl
CAS-Nr.: 13654-09-6 /13/
Melting point: 380-386 °C /14/
360-380 °C /16/
Vapour pressure: $1*10^{-11}$ mm Hg (25 °C) /38/
Solubility in water: < 30 µg L^{-1} (25 °C) /14/
Molar weight: 943 g mol^{-1}
Molecular formula: $C_{12}Br_{10}$

3.) Tetrabromo bisphenol A (TBBPA)



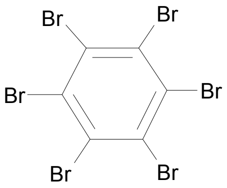
Chemical name:	2,2-Bis-(4-hydroxyphenyl)-propan
	4,4'-Isopropyliden-*bis*-(2,6-dibromphenol) /15/
CAS-Nr.:	79-94-7 /16/
Melting point:	181-182 °C /13/
	181-182 °C /15/
	178-180 °C /16/
Boiling point:	316 °C /15/
Vapour pressure:	<1,3 hPa (20 °C) /40/
Solubility in water:	0,72 mg L^{-1} (15 °C) /37/
	4,16 mg L^{-1} (25 °C) /15/
Molar weight:	544 g mol^{-1}
Molecular formula:	$C_{15}H_{12}Br_4O_2$

4.) Hexabromocyclododecane (HBCD)



Chemical name:	1,2,5,6,9,10-Hexabromocyclododecane
CAS-Nr.:	25637-99-4 /16/
	3194-55-6 /16/
Melting point:	170-180 °C /16/
	190 °C /40/
Vapour pressure:	6,4 * 10^{-6} Pa (10 °C) /10/
	6,27 10^{-5} Pa (20 °C) /40/
	1,7 * 10^{-4} Pa (50 °C) /10/
	< 133 Pa (20 °C) /16/
Solubility in water:	0,12 mg L^{-1} (23 °C) /10/
	3,4 µg L^{-1} (25 °C) /13/
Molar weight:	642 g mol^{-1}
Molecular formula:	$C_{12}H_{18}Br_6$

5.) Hexabromobenzene (HB)



Chemical name:	Hexabromobenzene
CAS-Nr.:	87-82-1 /16/
Melting point:	326 °C /37/
Molar weight:	552 g mol^{-1}
Molecular formula:	C_6Br_6

Organophosphorus Compounds (OPC)

1.) TEP

Chemical name: Triethylphosphate
CAS-Nr.: 78-40-0 /44/
Chemical group: alkylated phosphoric acid ester
Effect: additive FR
Melting point: -56 °C /44/
Boiling point: 215,6 °C (101,3 kPa) /44/
Vapour pressure 39 Pa (20 °C) /44/
Molar weight: 182 g mol^{-1}
Molecular formula: $C_6H_{15}O_4P$

2.) TBP

Chemical name: Tri(n-butyl)phosphate
CAS-Nr.: 126-73-8
Chemical group: alkylated phosphoric acid ester
Effect: additive FR, plasticizer
Melting point: -80 °C /45/
Boiling point: 289 °C (decomposition), 177-178 °C (3,6 kPa),
150 °C (1,33 kPa) /84/
Vapour pressure: 66,7 kPa (200 °C), 973 Pa (150 °C),
9 Pa (25 °C) /84/
13,7 mm Hg (20 °C) /46/
Solubility in water: 0,422 mg L^{-1} (25 °C) /84/
Molar weight: 266 g mol^{-1}
Molecular formula: $C_{12}H_{27}O_4P$

3.) TBEP

Chemical name: Tris (2-butoxyethyl) phosphate
CAS-Nr.: 78-51-3
Chemical group: alkylated phosphoric acid ester
Effect: additive FR, plasticizer
Melting point: -70 °C /12/
Boiling point at 5-5,3 hPa: 200 - 230 °C /79/
Vapour pressure: 2,8 10^{-7} hPa (25 °C), 0,33 hPa (150 °C) /79/
Solubility in water: 1,1 - 1,3 g L^{-1} (20 °C) /12/
Molar weight: 398 g mol^{-1}
Molecular formula: $C_{18}H_{39}O_7P$

4.) TEHP
Chemical name: Tris (2-ethylhexyl) phosphate
CAS-Nr.: 78-42-2
Chemical group: alkylated phosphoric acid ester
Effect: additive FR, plasticizer
Melting point: -74 °C /12/
Boiling point: 220 °C (6,67 hPa), 210 °C (5 hPa) /79/
Vapour pressure: < 0,1 hPa (20 °C) /79/
Solubility in water: <0,1 g L^{-1} (20 °C) /79/
Molar weight: 435 g mol^{-1}
Molecular formula: $C_{24}H_{51}O_4P$

5.) TCPP
Chemical name: Tris (1-chloro-2-propyl) phosphate
CAS-Nr.: 13674-84-5
Chemical group: halogenated alkylated phosphoric acid ester
Effect: additive FR
Melting point: -42 °C /5/
Boiling point at 101,3 kPa: 341,5 °C, 235-248 °C, degraded /78/
Vapour pressure: 100 Pa (20 °C) /60/
40 mm Hg (110 °C) /76/
< 2 mm Hg (25 °C) /76/
Solubility in water: 1,6 g L^{-1} (20 °C) /86/
Molar weight: 328 g mol^{-1}
Molecular formula: $C_9H_{18}Cl_3O_4P$

6.) TDCPP
Chemical name: Tris (1,3-dichlor-2-propyl) phosphate
CAS-Nr.: 13674-87-8
Chemical group: halogenated alkylated phosphoric acid ester
Effect: additive FR
Boiling point : 236 - 237 °C (5 mm Hg) /78/
Vapour pressure: 1,33 Pa (30 °C) /78, 85/
Solubility in water: 0,1 g L^{-1} (30 °C) /86/
Molar weight: 431 g mol^{-1}
Molecular formula: $C_9H_{15}Cl_6O_4P$

7.) TPP
Chemical name: Triphenylphosphate
CAS-Nr.: 115-86-6
Chemical group: arylated phosphoric acid ester

Effect: additive FR
Melting point: 50-51 °C /8/
Boiling point: 220 °C (101,3 kPa) /87/
245 °C (11 mm Hg) /8/
Vapour pressure: 20 Pa (150 °C) /87/
1 mm Hg (193,5 °C) /87/
Solubility in water: 0,73-2,1 mg L^{-1} /84/,
0,025-1,9 mg L^{-1} /87/
Molar weight: 326 g mol^{-1}
Molecular formula: $C_{18}H_{15}O_4P$

8.) DPC

Chemical name: Diphenylcresylphosphate
CAS-Nr.: 26444-49-5
Chemical group: arylated phosphoric acid ester
Effect: additive FR
Melting point: -38 °C
Boiling point: 253 °C (10 mm Hg)
Vapour pressure: 0,08 mm Hg (150 °C)
Molar weight: 340 g mol^{-1}
Molecular formula: $C_{19}H_{17}O_4P$

9.) TMTP

Chemical name: Tris(m-tolyl)phosphate
CAS-Nr.: 563-04-2
Chemical group: arylated phosphoric acid ester
Effect: additive FR
Molar weight: 368 g mol^{-1}
Molecular formula: $C_{21}H_{21}O_4P$

10.) TPTP

Chemical name: Tris(p-tolyl)phosphate
CAS-Nr.: 78-32-0
Chemical group: arylated phosphoric acid ester
Effect: additive FR
Molar weight: 368 g mol^{-1}
Molecular formula: $C_{21}H_{21}O_4P$

11.) RDP

Chemical name: Resorcinol-bis-(diphenylphosphate)
CAS-Nr.: 57583-54-7

Chemical group: arylated phosphoric acid ester
Effect: additive FR, plasticizer /6/
Boiling point at 101,3 kPa: approx. 300 °C /60/
Vapour pressure: 138 Pa (38 °C) /60/ lower volatility compared to other arylated POC /77/
Solubility in water: insoluble, low solubility in water /60/
Molar weight: (n = 1-7), n = 1: 574,6 g mol^{-1}
Molecular formula: $C_{30}H_{24}P_2O_8$ (n = 1)

12.) BDP

Chemical name: Bisphenol-A-bisdiphenylphosphate
CAS-Nr.: 5945-33-5
Chemical group: arylated phosphoric acid ester
Effect: additive FR
Molar weight: 820 g mol^{-1}
Molecular formula: $C_{39}H_{34}O_8P_2$

13.) DOPO

Chemical name: 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide
CAS-Nr.: 35948-25-5
Effect: reactive FR
Molar weight: 216 g mol^{-1}
Molecular formula: $C_{12}H_9O_2P$

Appendix 4

Project-related Working Group and Workshop

A project-related working group was organised at the beginning of the project to provide technical support, which was then extended to a workshop at the end of the project.

The project's subject was discussed and suggestions were given for its direction in this project-related working group.

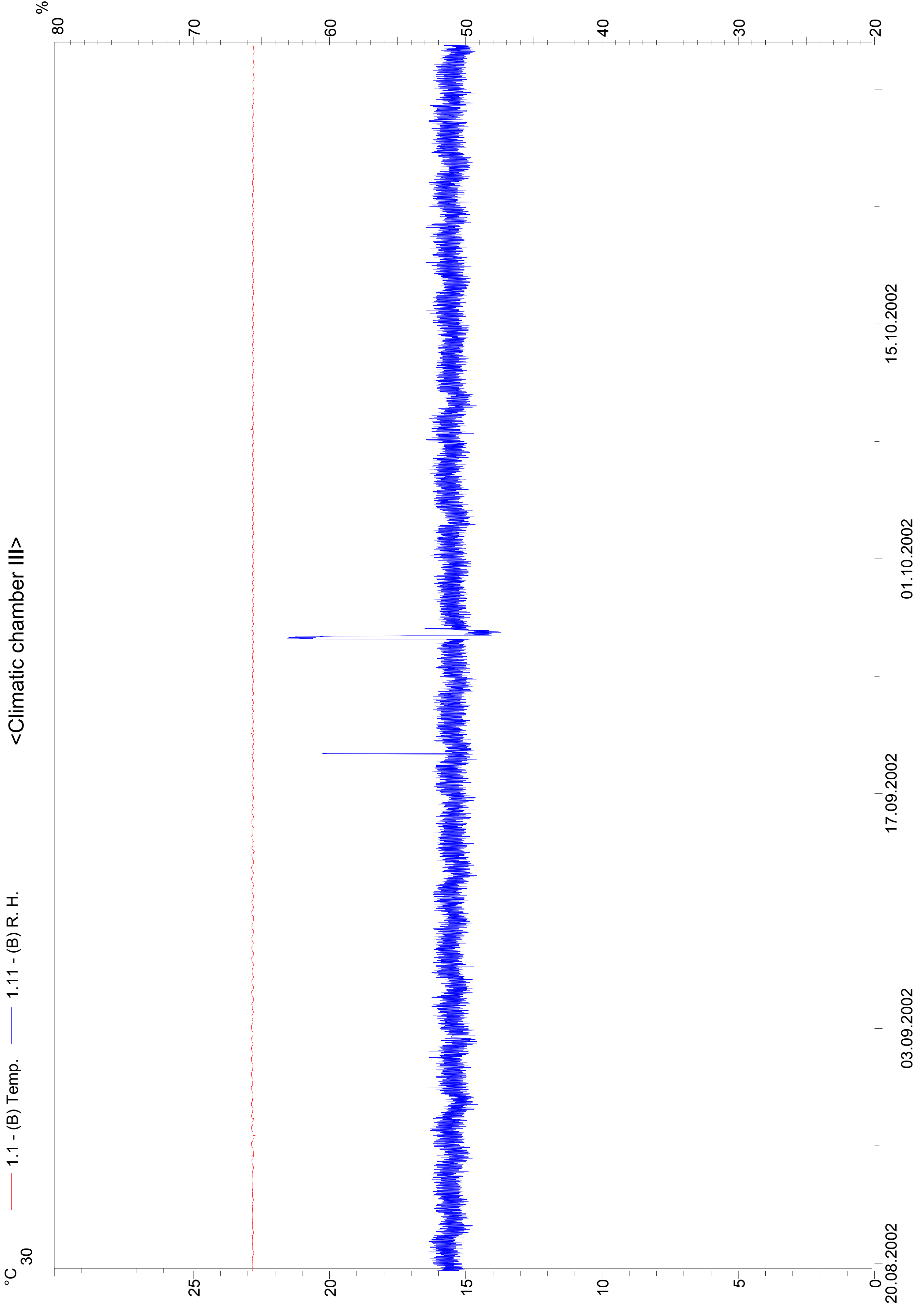
The participants of the project-related working group were selected so as to facilitate sample provision and information exchange on the relevant substance groups. Experts and manufacturers from the insulation material (polyuretane, polyisocyanurate, polystyrene, polyethylene, polybutadiene) producing and processing industry, upholstered furniture and mattress production, computer industry, assembly foam production and flame retardant industry were invited to attend the workshop.

In addition to presenting and discussing the project itself, issues of product selection, in particular sampling and sample preparation, as well as background issues to the usa of flame retardants were discussed.

The aim was to organise support in the form of a working group and workshop to integrate expert opinion and expert knowledge into the implementation of the project at an as early stage as possible.

The constructive and helpful contribution of all those who participated is once again gratefully acknowledged.

Appendix 5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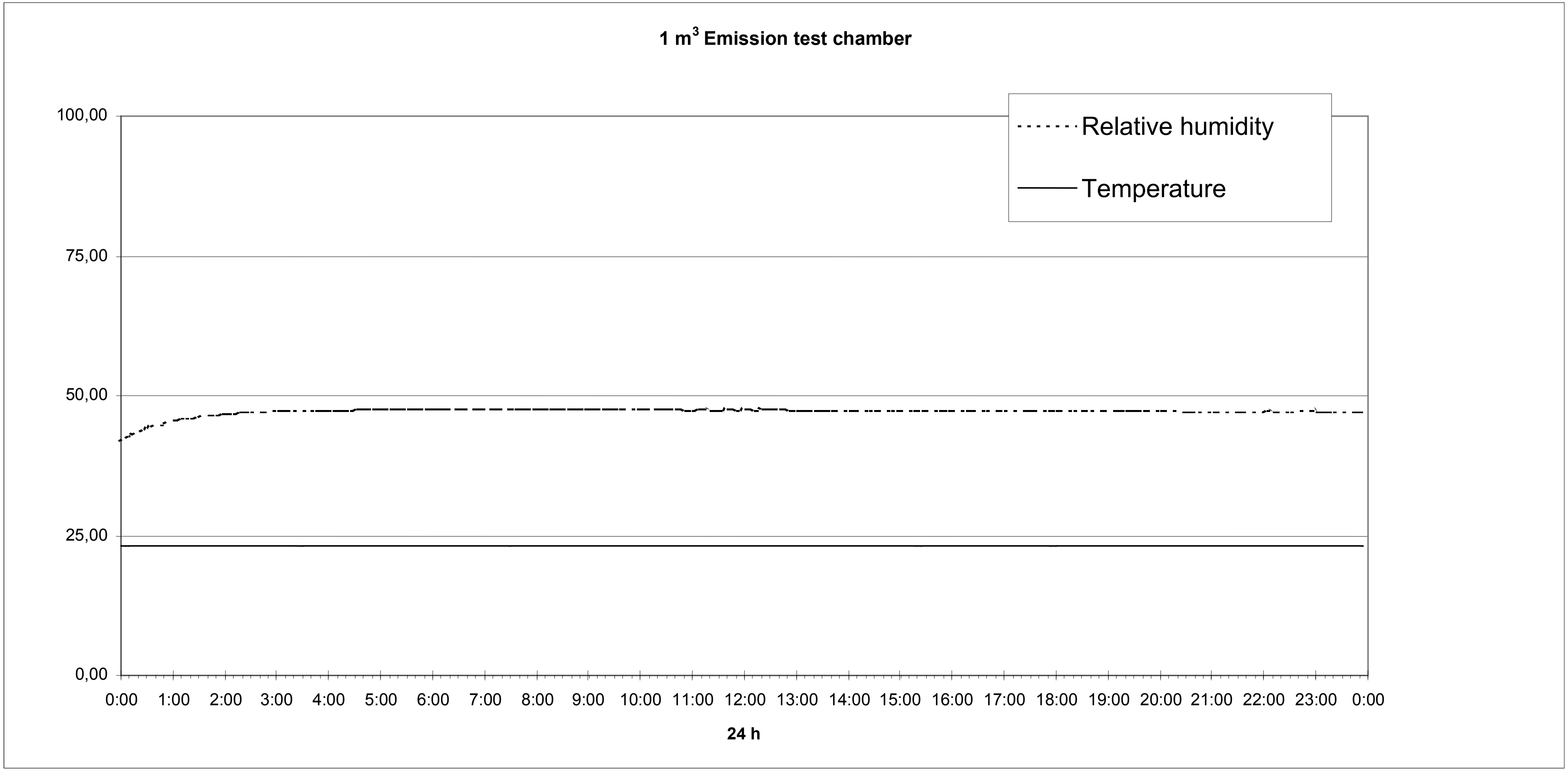
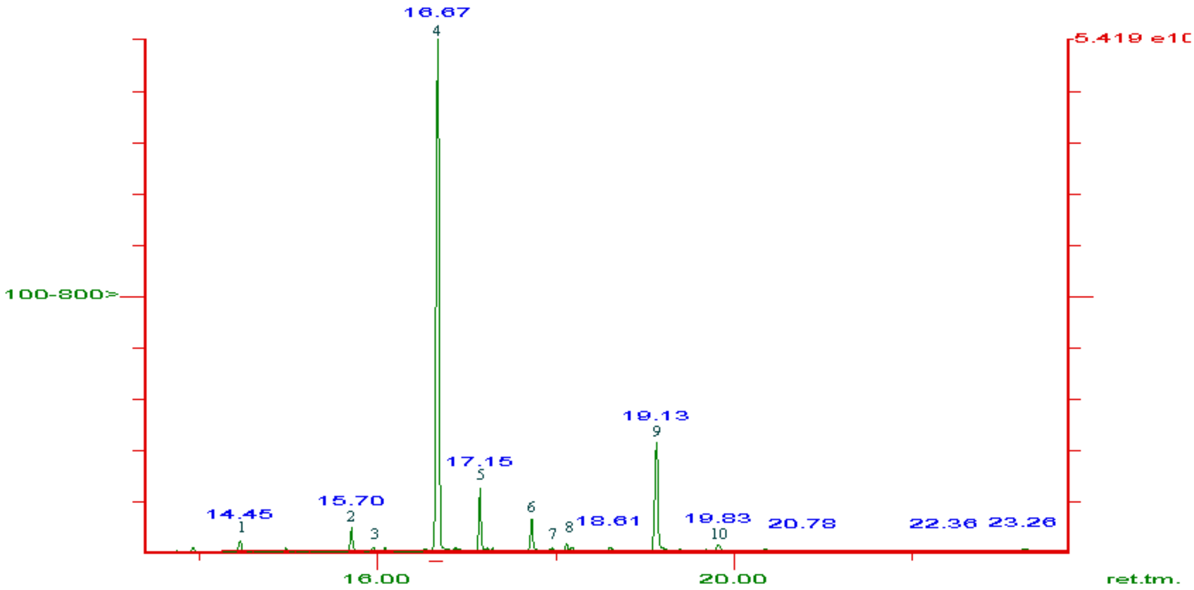
%H
80
70
60
50
40
30
20
°C
30
25
20
15
10
5
0
1.1 - (B) Temp.
1.11 - (B) R. H.
20.08.2002
03.09.2002
17.09.2002
01.10.2002
15.10.2002


1 m³ Emission test chamber
Relative humidity
Temperature
100,00
75,00
50,00
25,00
0,00
0:00
1:00
2:00
3:00
4:00
5:00
6:00
7:00
8:00
9:00
10:00
11:00
12:00
13:00
14:00
15:00
16:00
17:00
18:00
19:00
20:00
21:00
22:00
23:00
0:00
24 h

Appendix 1

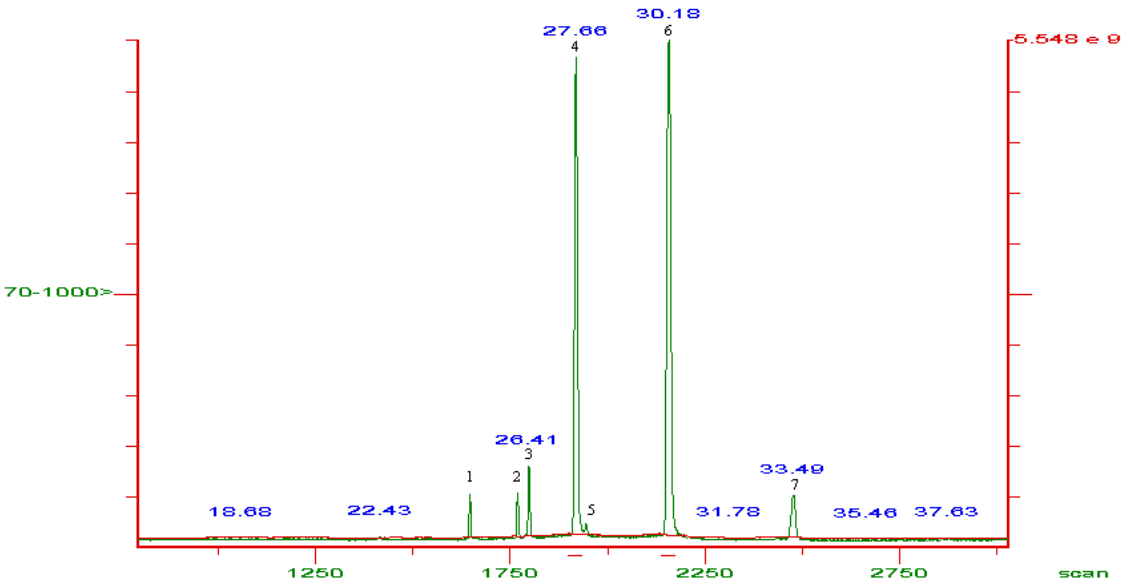
Chromatogram and composition of the technical PBDE and PBB

Hexabromobiphenyl (Firemaster BP-6)



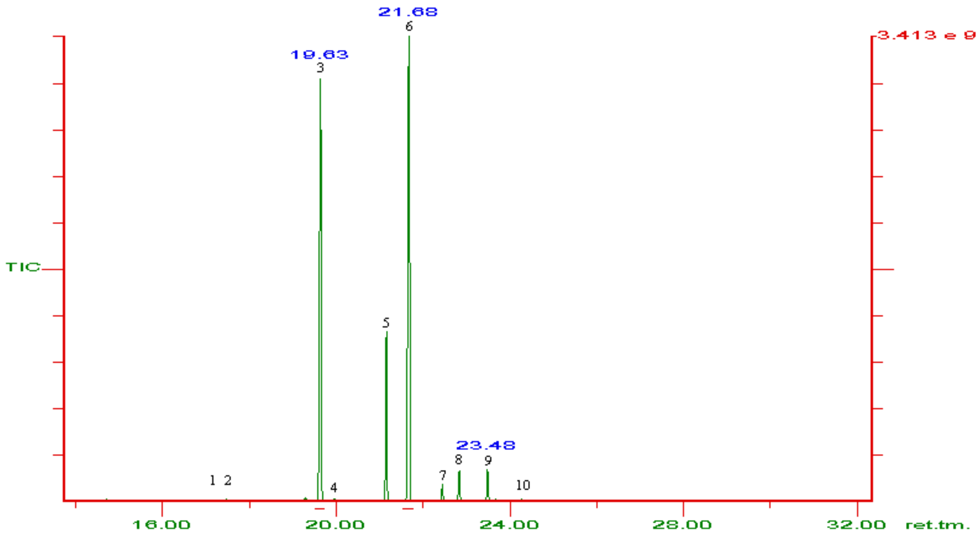
	Ballschmitter Nr.		*Weight-% /19/*
1	101	2,2',4,5,5'-PentaBB	1,76
2	118	2,3',4,4',5-PentaBB	3,51
3	149	2,2',3,4',5,6-HexaBB	0,72
	132	2,2',3,3',4,6'-HexaBB	0,41
4	153	2,2',4,4',5,5'-HexaBB	54,33
		HexaBB	0,82
		HexaBB	0,34
5	138	2,2',3,4,4',5'-HexaBB	8,2
		HexaBB	0,68
6	167	2,3',4,4',5,5'-HexaBB	4,82
7	178	2,2',3,3',5',5,6-HeptaBB	0,90
8	187	2,2',3,4',5,5',6-HeptaBB	1,3
8	156	2,3,3,4,4'5'HexaBB	2,44
8	157	2,3,3',4,4',5'HexaBB	1,14
9	180	2,2',3,4,4',5,5'HeptaBB	19,23
	169	3,3',4,4',5,5'HexaBBoder	
	172	2,2',3,3',4,5,5'HeptaBB	0,39
10	170	2,2',3,3',4,4',5HeptaBB	1,8

Octabromobiphenyl (FR 250 13 A Dow Chemical)



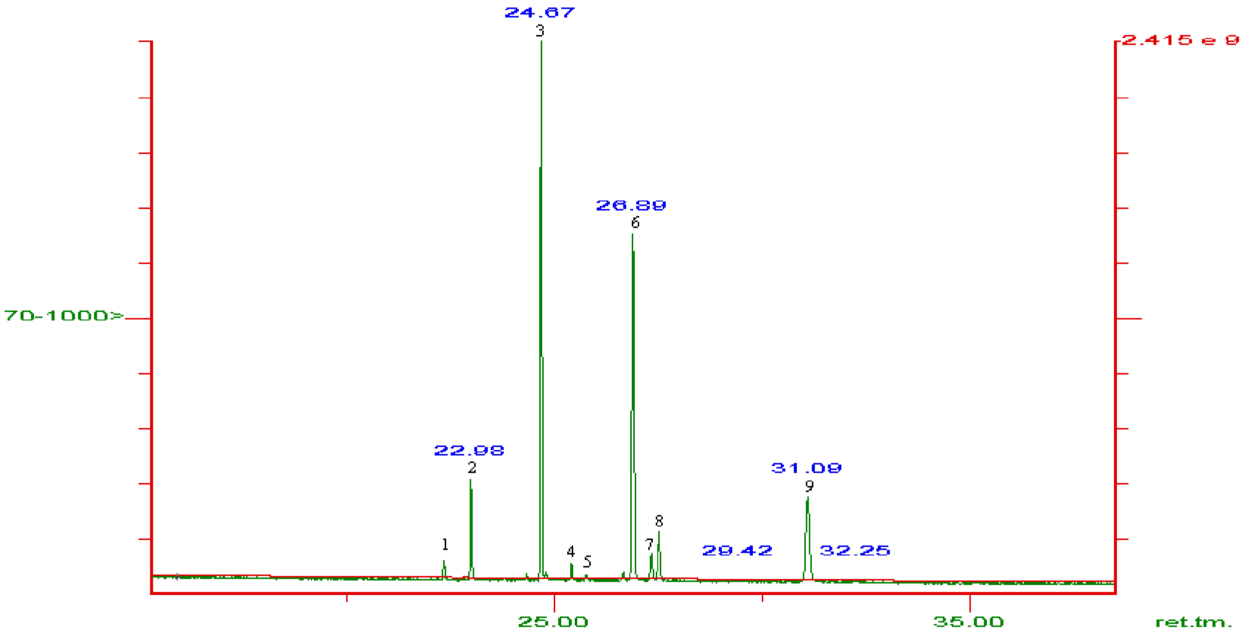
	Ballschmitter Nr.		Weight-% /19/
1	180	2,2’,3,4,4’,5,5’-HeptaBB	1,03
2	198	2,2’,3,3’,4,5,5’,6-OctaBB	1,31
3	203 od. 196	2,2’3,4,4’,5,5’,6-OctaBB 2,2’,3,3’,4,4’,5,6’.OctaBB	2,5
4	194	2,2’,3,3’,4,4’,5,5’-OctaBB	32,84
5	208	2,2’,3,3’,4,5,5’,6,6’-NonaBB	0,77
6	206	2,2’,3,3’,4,4’,5,5’,6-NonaBB	53,64
7	209	2,2’,3,3’,4,4’,5,5’,6,6’-DecaBB	7,91

Pentabromodiphenylether (DE-71-Great Lakes)



	Ballschmitter Nr.		Weight-% /19/
1	17	2,2,4’-TriBDE	0,067
2	28	2,4,4’-TriBDE	0,22
3	47	2,2’,4,4’-TeBDE	32,96
4	66	2,3’,4,4’-TeBDE	0,77
5	100	2,2’,4,4’,6-PeBDE	9,96
6	99	2,2’4,4’,5-PeBDE	42,03
7	85	2,2’,3,4,4’-PeBDE	1,82
8	154	2,2’,4,4’,5,6’-PeBDE	4,15
9	153	2,2’,4,4’,5,5’-PeBDE	4,77
		HxBDE	0,70
10	138	2,2’,3,4,4’,5’-HxBDE	0,46

Octabromodiphenylether (DE-79-Great Lakes)



	Ballschmitter Nr.		Weight-% /19/
1	154	2,2’,4,4’,5,6’-HexaBDE	1,19
2	153	2,2’,4,4’,5,5’-HexaBDE	8,10
3		HeptaBDE	40,17
4		HeptaBDE	2,01
5	190	2,3,3’,4,4’,5,6-HeptaBDE	0,84
6		OctaBDE	21,42
7		OctaBDE	5,51
8		OctaBDE	8,27
9		NonaBDE	12,49

Appendix 2

Mass spectrum of BFRs and OPCs

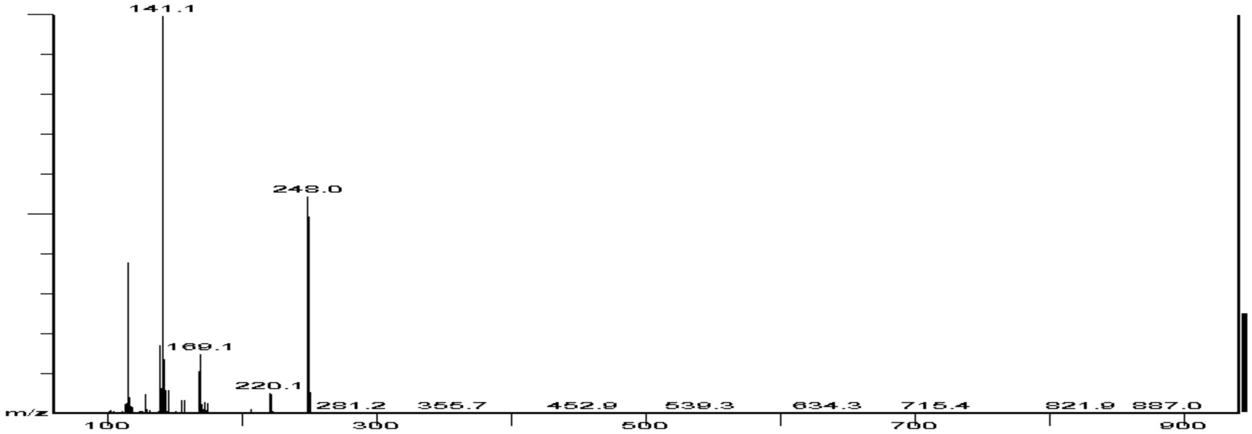


Fig.46: Mass spectrum of MonoBDE (EI-mode)

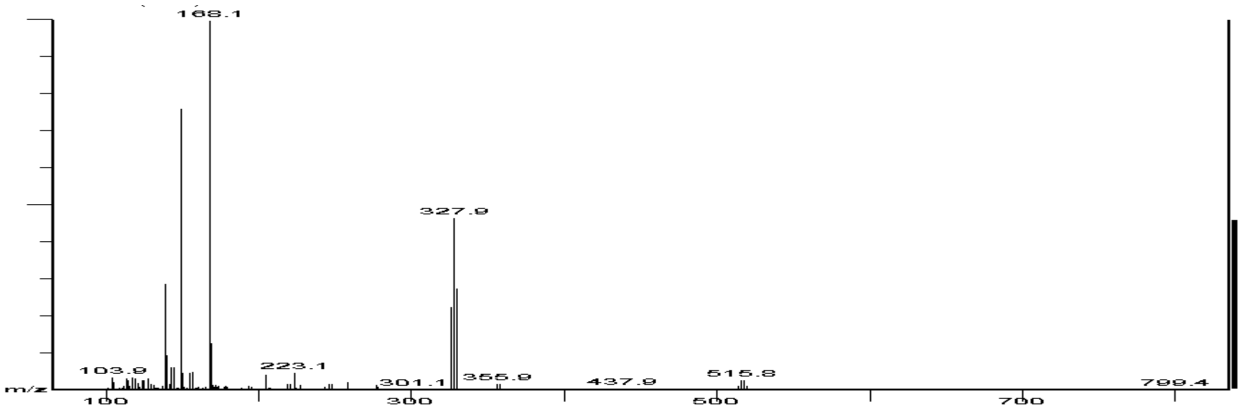


Fig. 47: Mass spectrum of DiBDE (EI-mode)

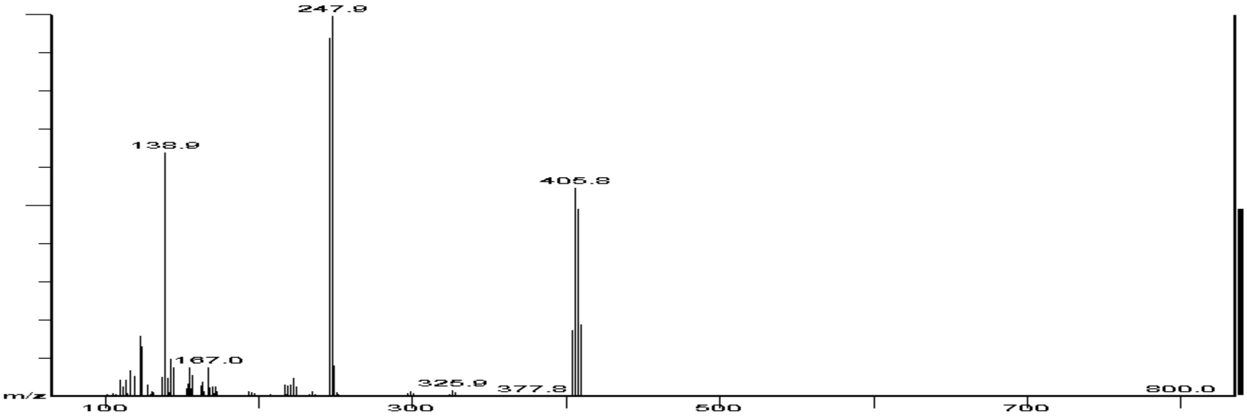


Fig.48: Mass spectrum of TriBDE (EI-mode)

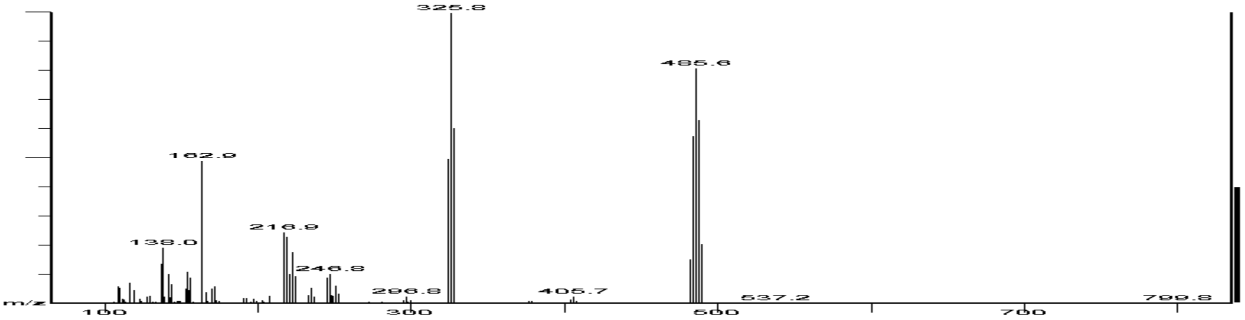


Fig.49: Mass spectrum of TetraBDE (EI-mode

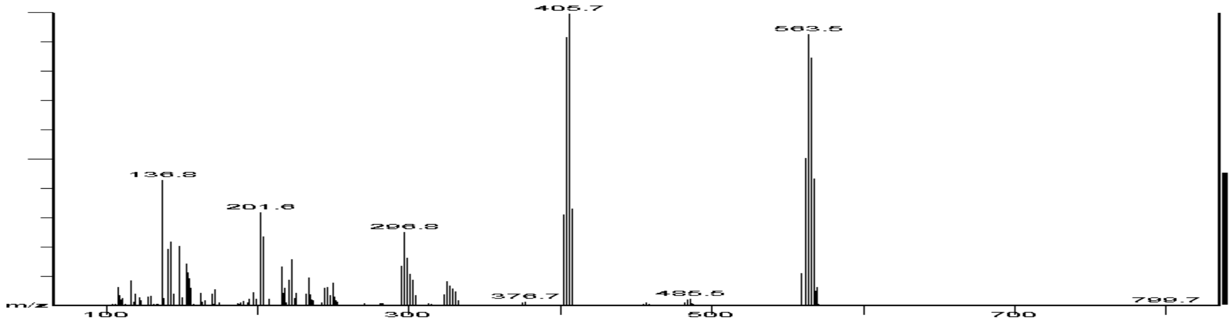


Fig. 50: Mass spectrum of PentaBDE (EI-mode)

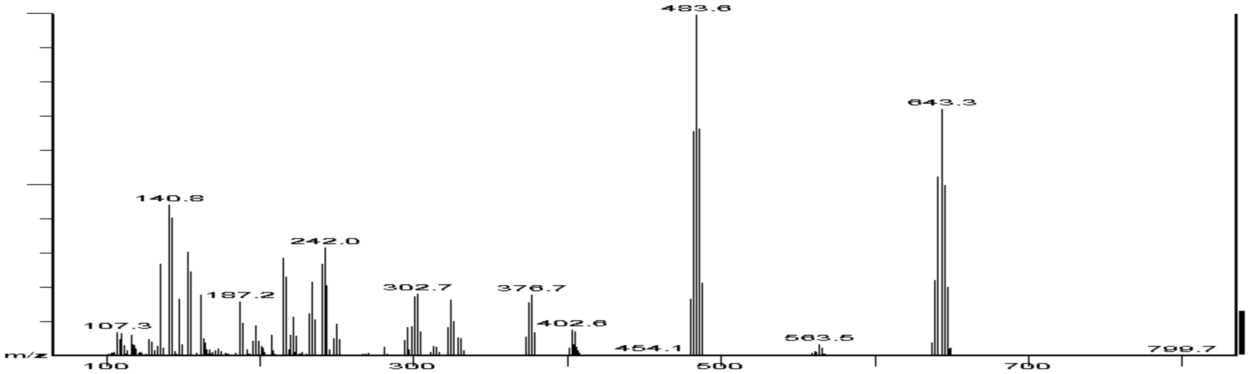


Fig. 51: Mass spectrum of HexaBDE (EI-mode)

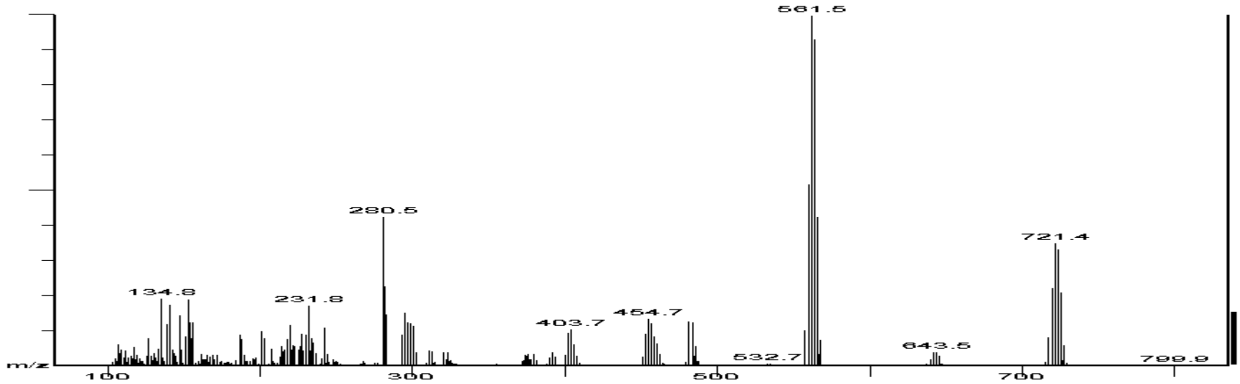


Fig. 52: of HeptaBDE (EI-mode)

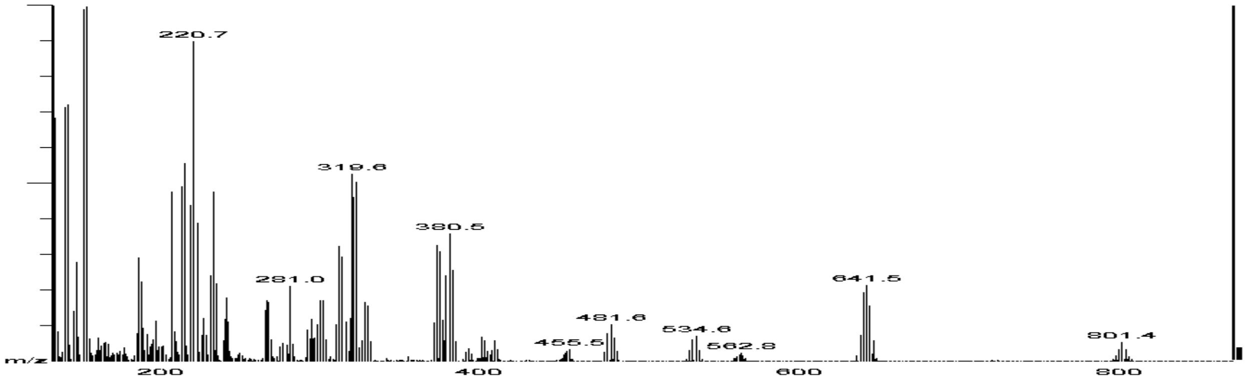


Fig. 53: Mass spectrum of OctaBDE (EI-mode)

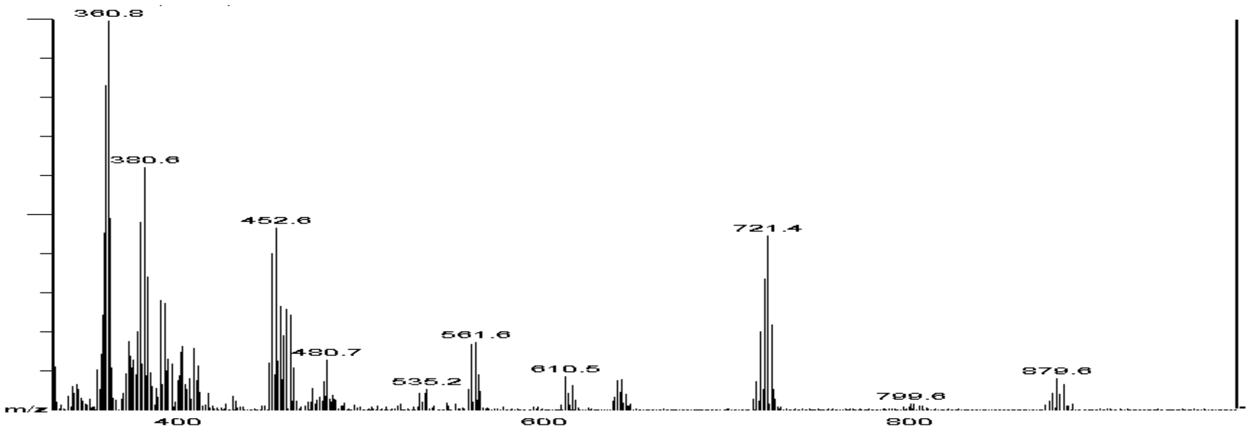


Fig. 54: Mass spectrum of NonaBDE (EI-mode)

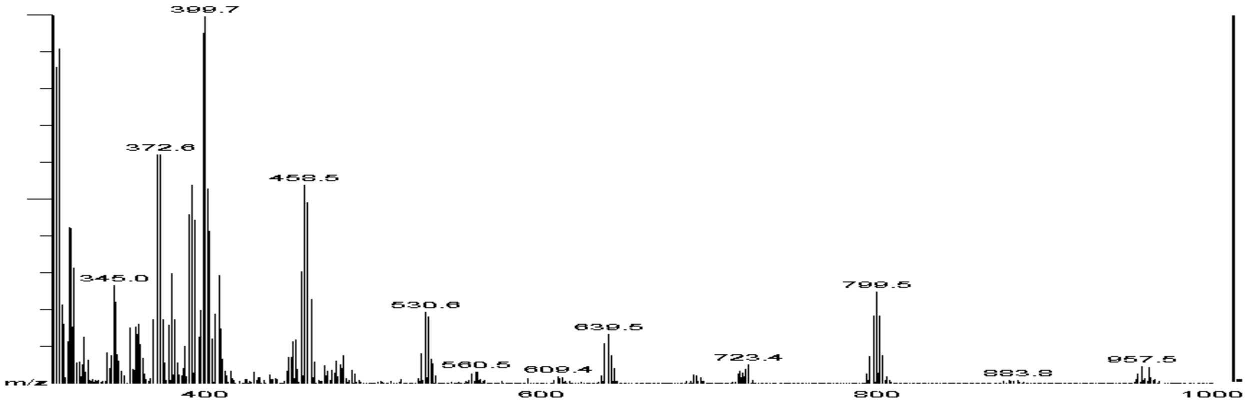


Fig. 55: Mass spectrum of DecaBDE (EI-mode

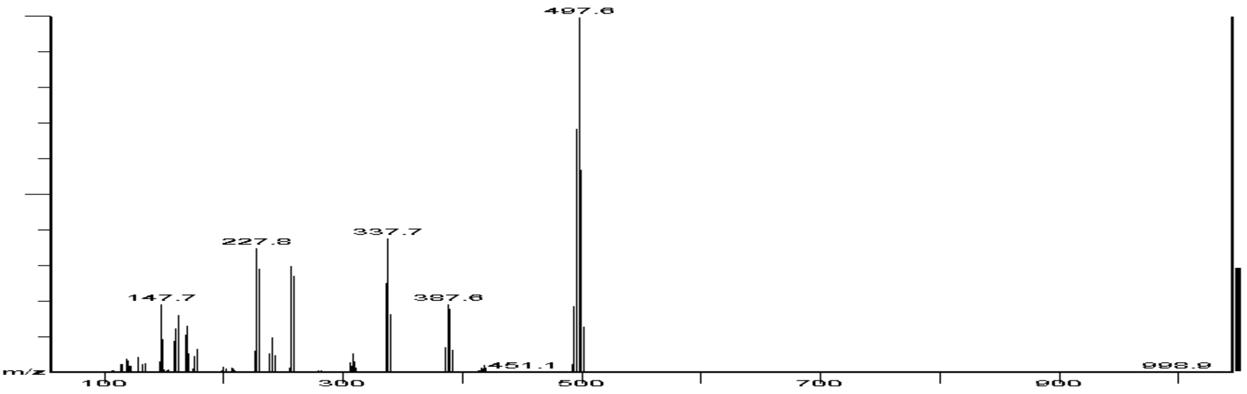


Fig. 56: Mass spectrum of $^{13}C_{12}$-TetraBDE (NCI-mode)

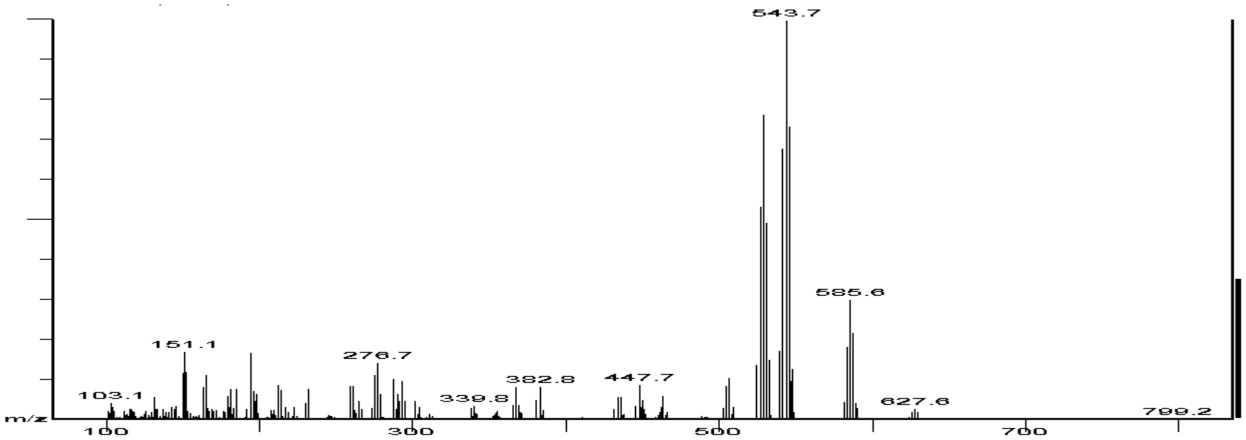


Fig. 57: Mass spectrum of Diacetyl-TBBPA (EI-mode)

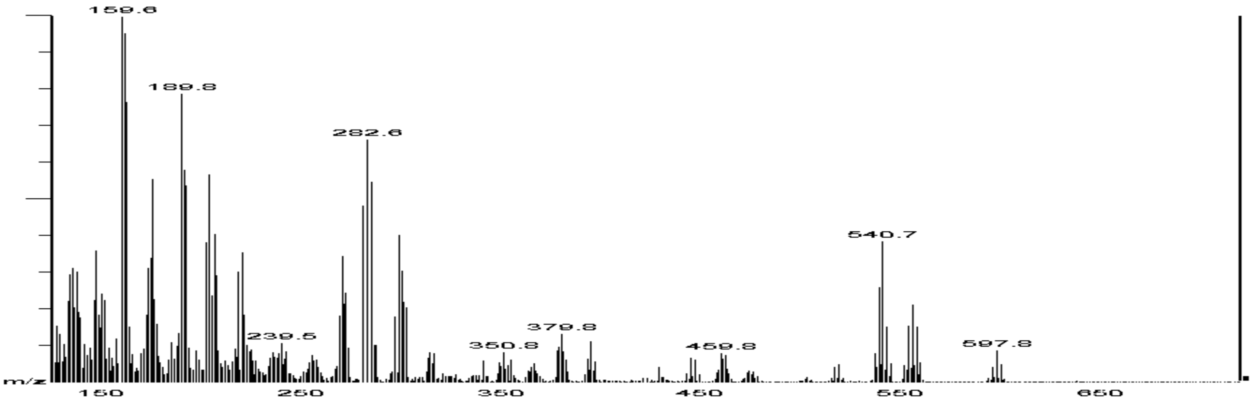


Fig. 58: Mass spectrum of Diacetyl-TBBPA-13C_{12}-ring (EI-mode)

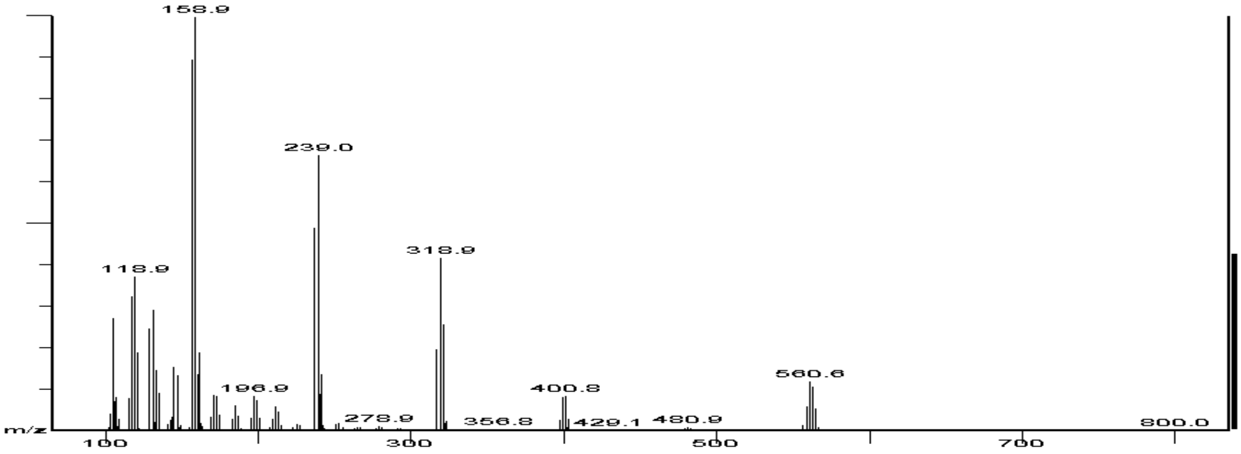


Fig. 59: Mass spectrum of HBCD (EI-mode)

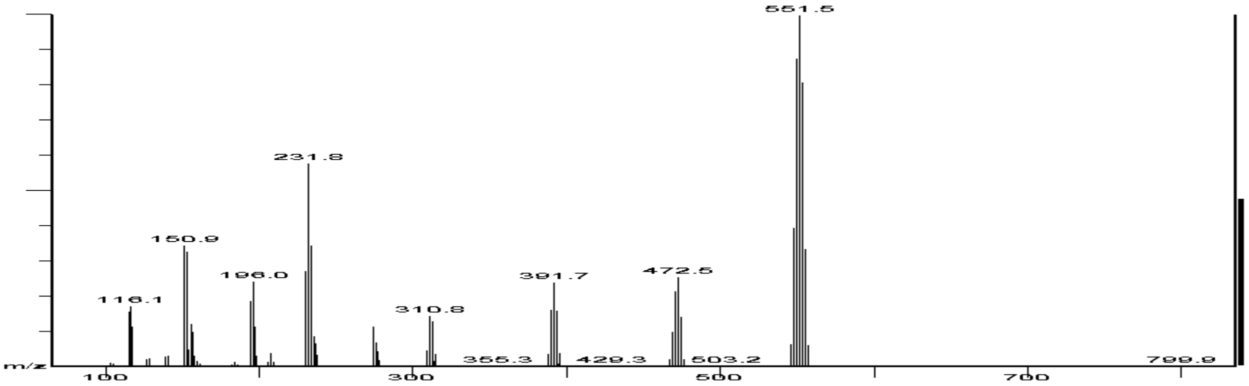


Fig. 60: Mass spectrum of HB (EI-mode)

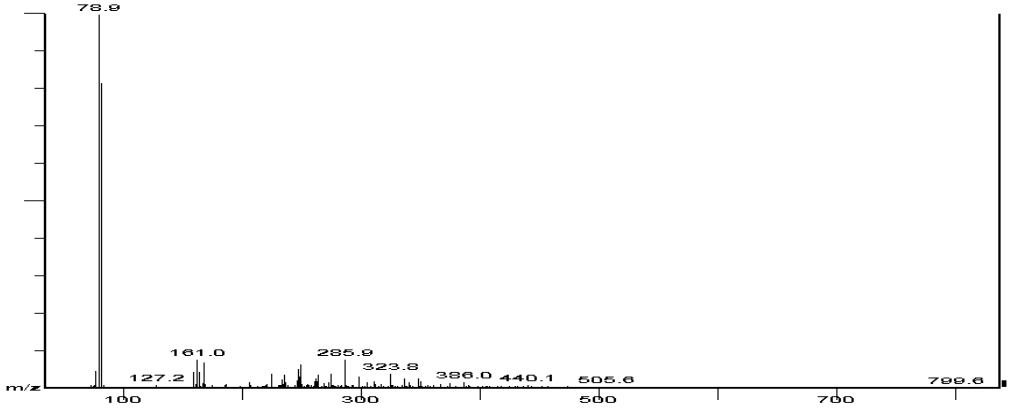


Fig. 61: Mass spectrum of DiBDE (NCI-mode)

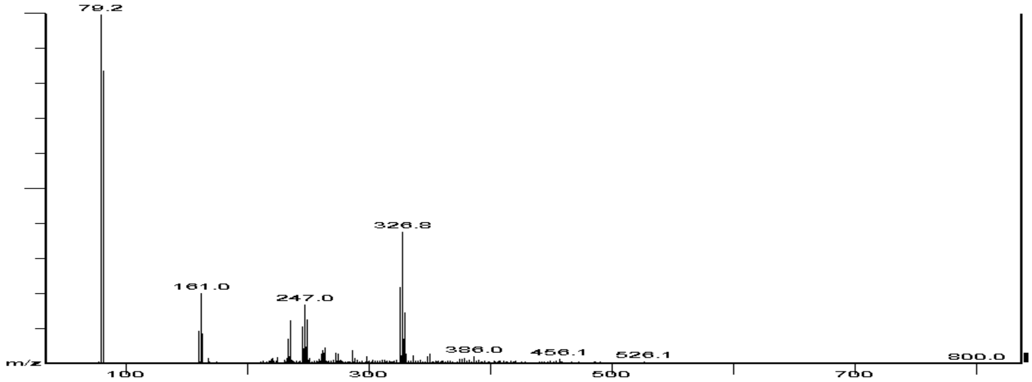


Fig. 62: Mass spectrum of TriBDE (NCI-mode)

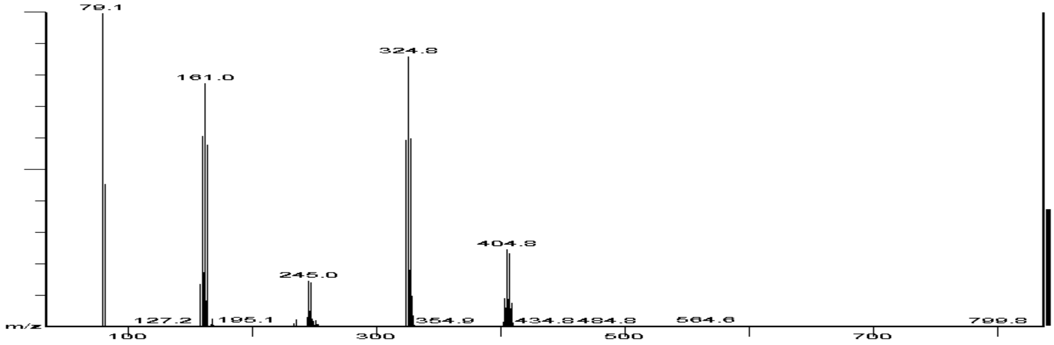


Fig. 63: Mass spectrum of TetraBDE (NCI-mode)

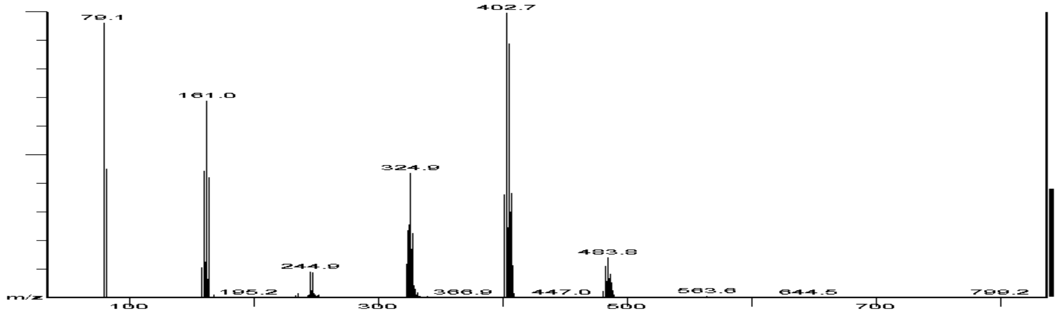


Fig. 64: Mass spectrum of PentaBDE (NCI-mode)

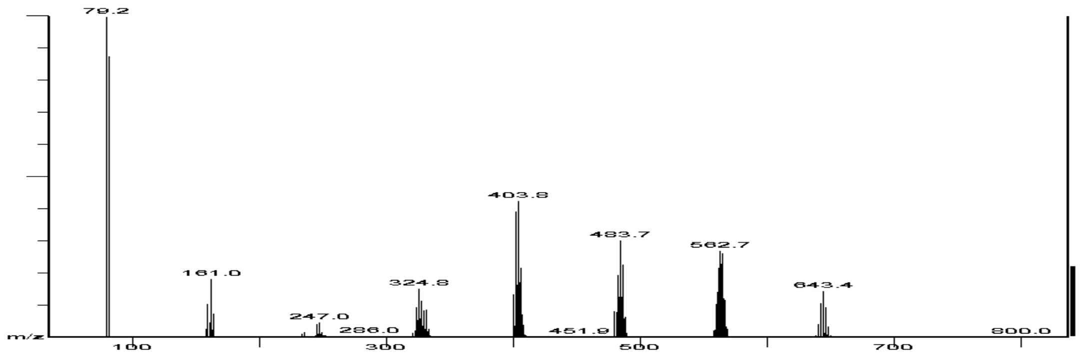


Fig. 65: Mass spectrum of HexaBDE (NCI-mode)

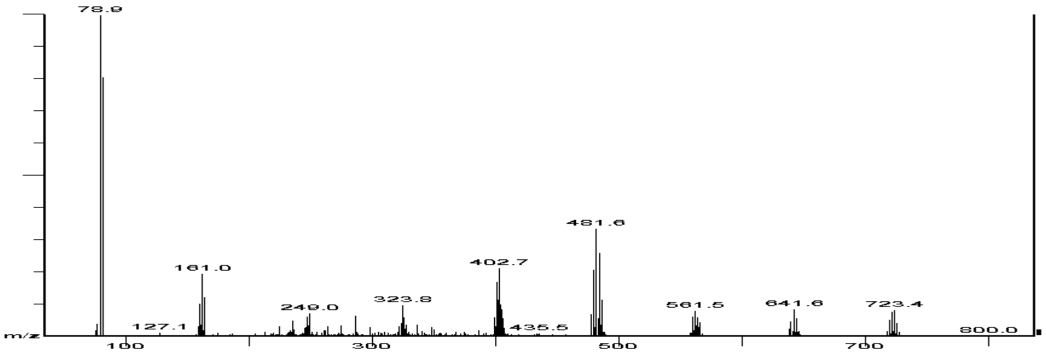


Fig. 66: Mass spectrum of HeptaBDE (NCI-mode)

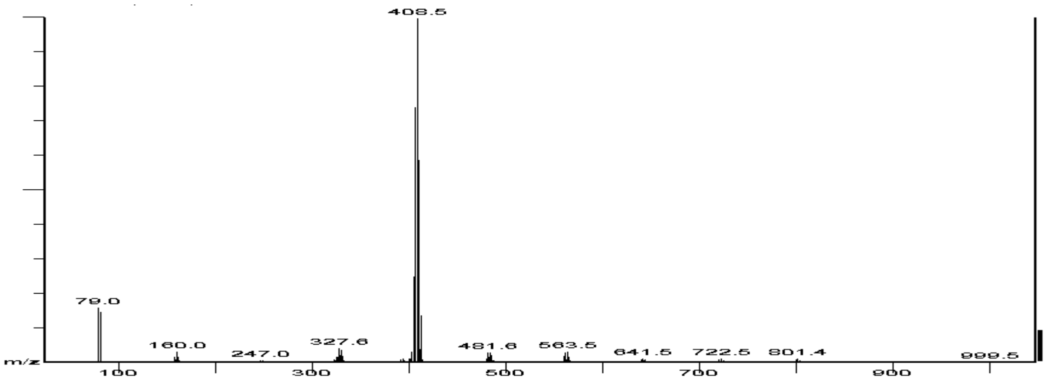


Fig. 67: Mass spectrum of OctaBDE (NCI-mode)

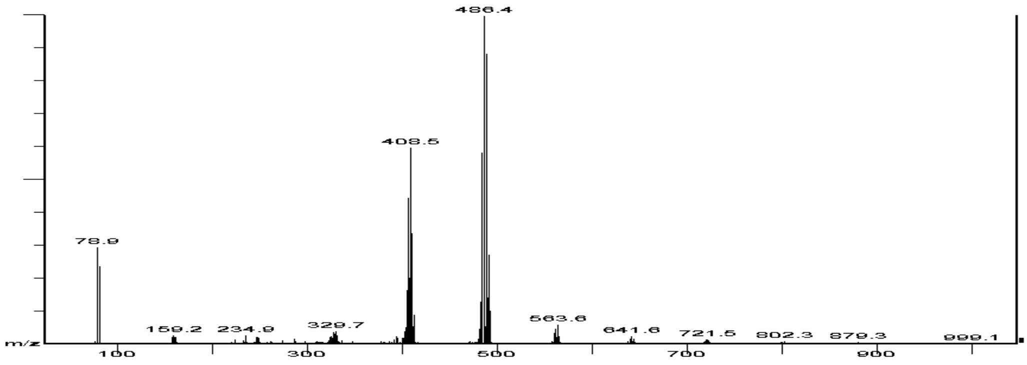


Fig. 68: Mass spectrum of NonaBDE (NCI-mode)

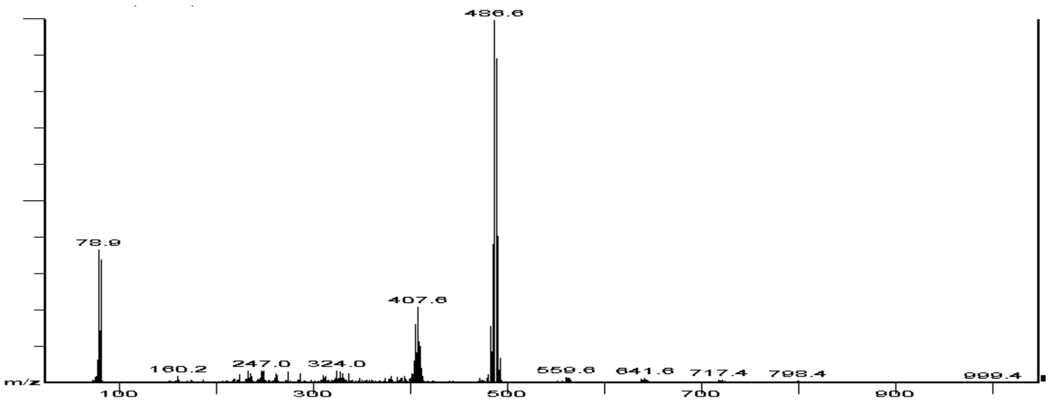


Fig. 69: Mass spectrum of DecaBDE (NCI-mode)

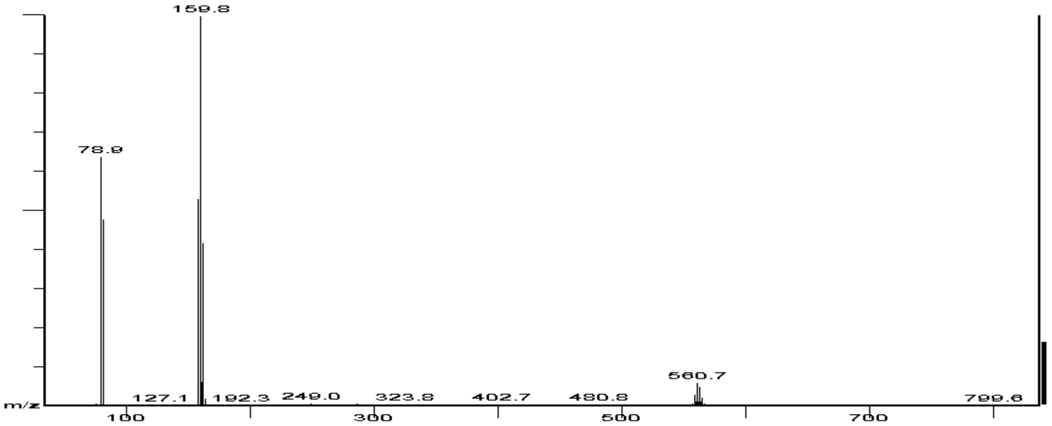


Fig. 70: Mass spectrum of HBCD (NCI-mode)

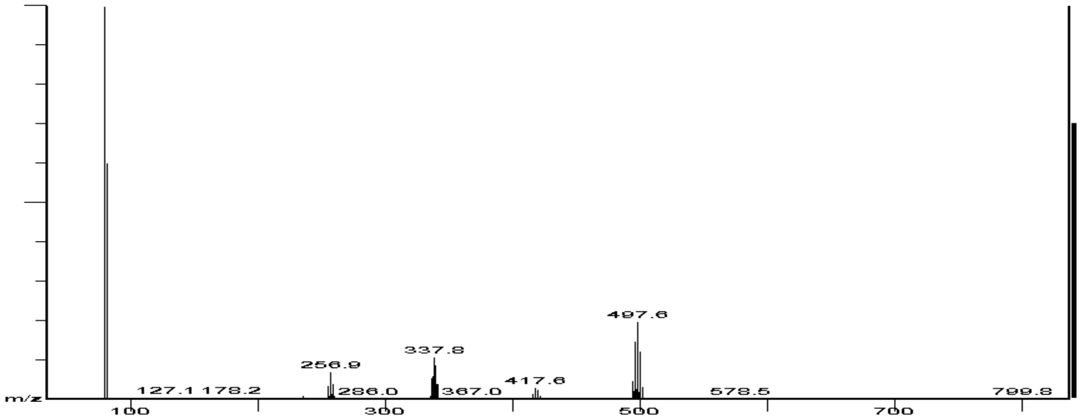


Fig. 71: Mass spectrum of $^{13}C_{12}$-TetraBDE (NCI-mode)

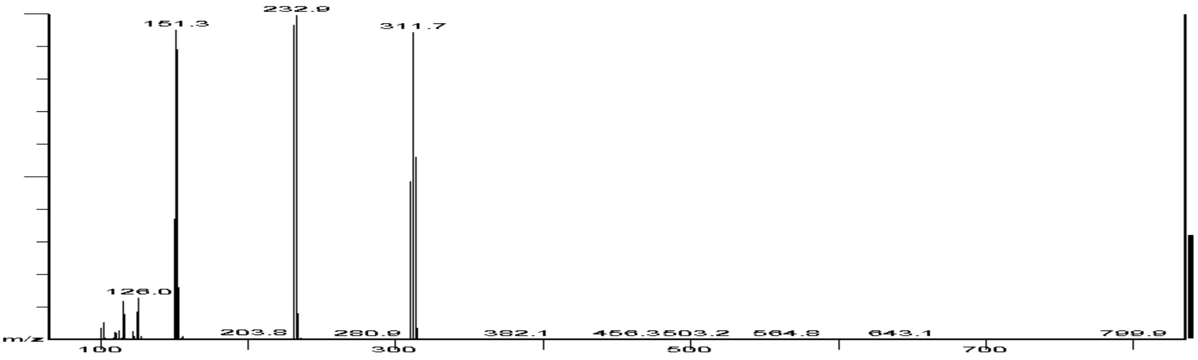


Fig.72: Mass spectrum of DiBB (EI-Mode)

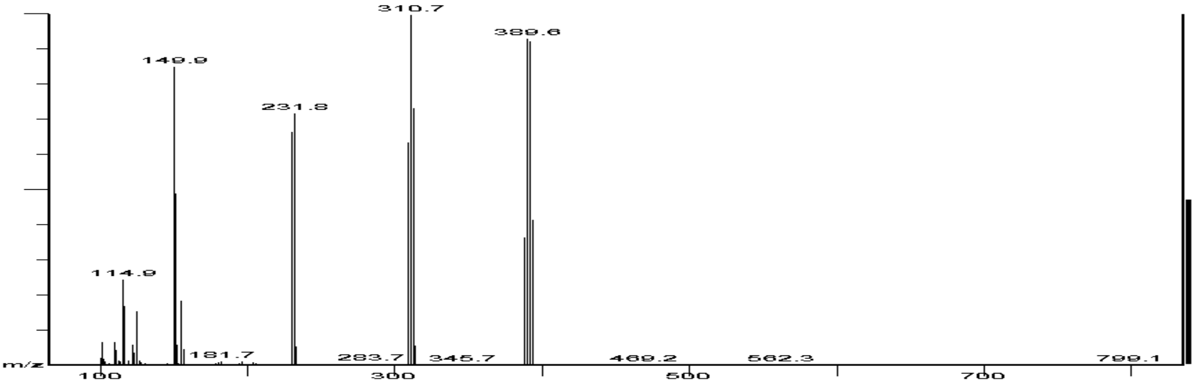


Fig. 73: Mass spectrum of TriBB (EI-Mode)

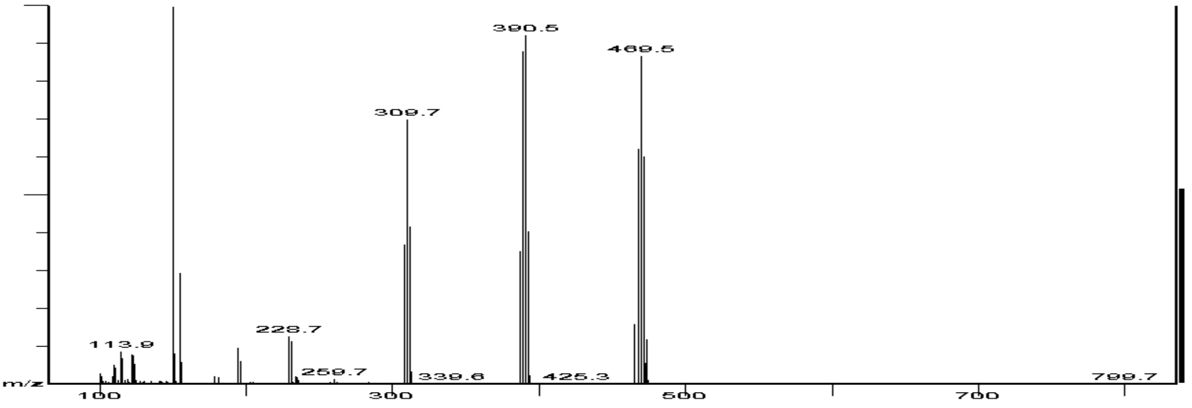


Fig. 74: Mass spectrum of TetraBB (EI-Mode)

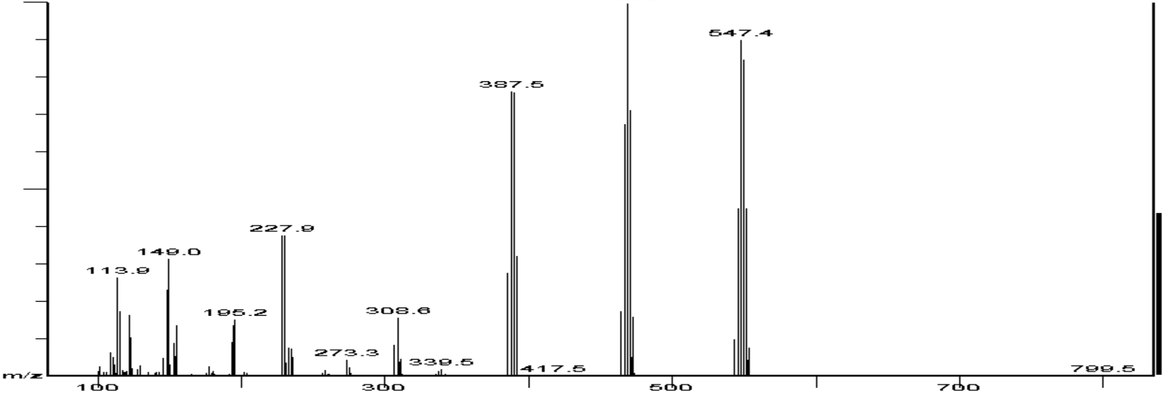


Fig. 75: Mass spectrum of PentaBB (EI-Mode)

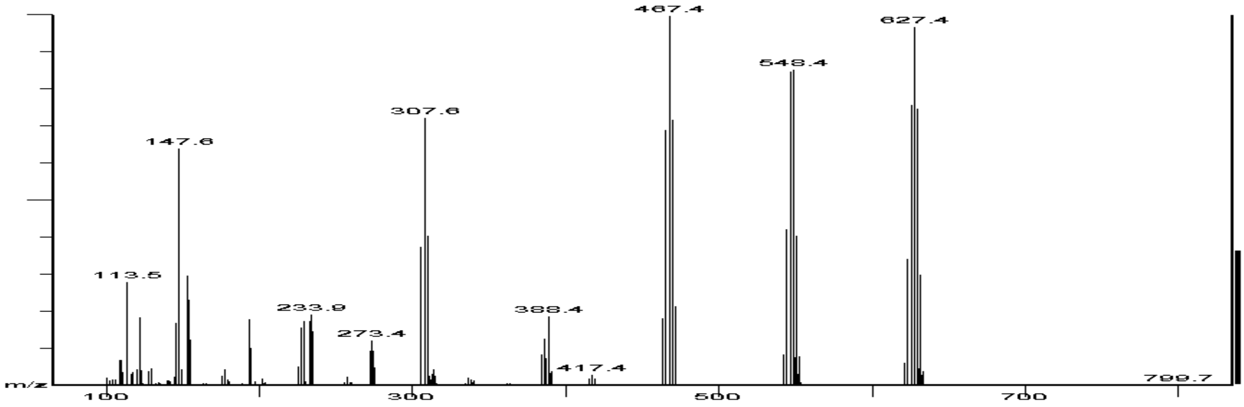


Fig. 76: Mass spectrum of HexaBB (EI-Mode)

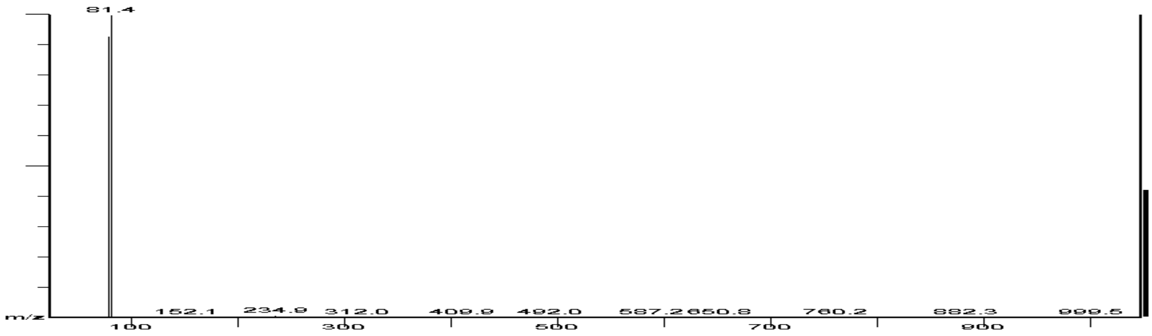


Fig. 77: Mass spectrum of DiBB (NCI-Mode)

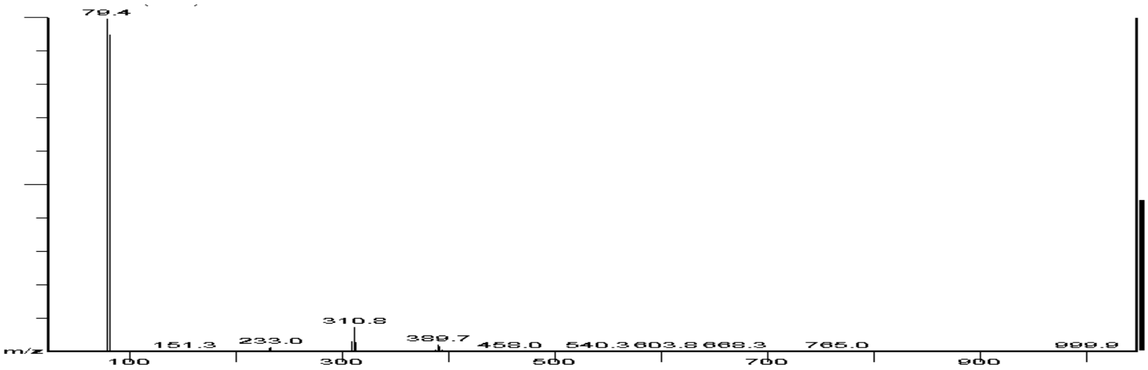


Fig. 78: Mass spectrum of TriBB (NCI-Mode)

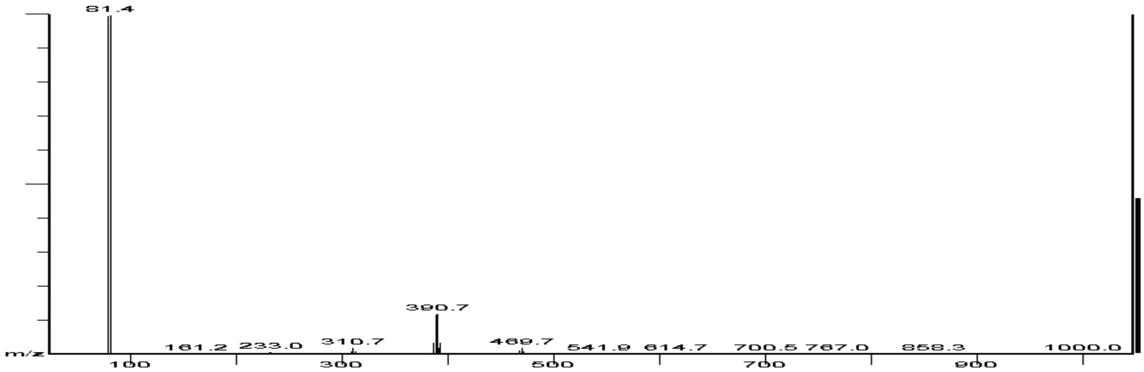


Fig. 79: Mass spectrum of TetraBB (NCI-Mode)

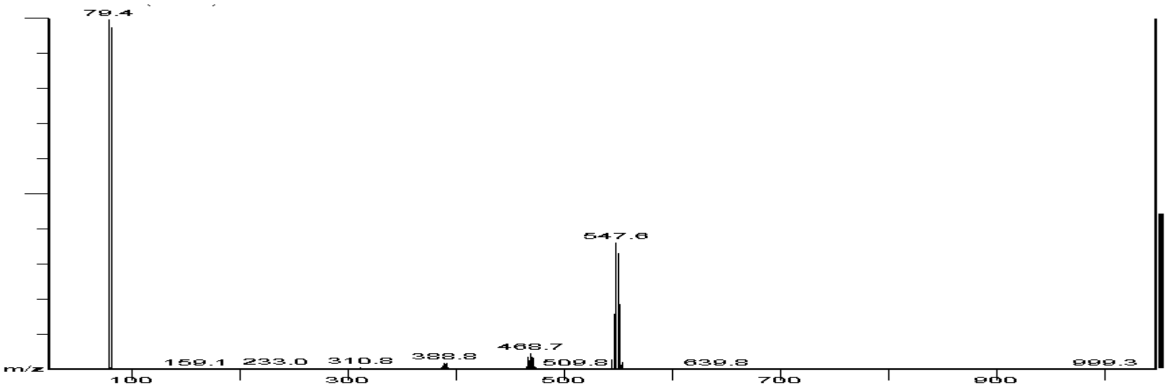


Fig. 80: Mass spectrum of PentaBB (NCI-Mode)

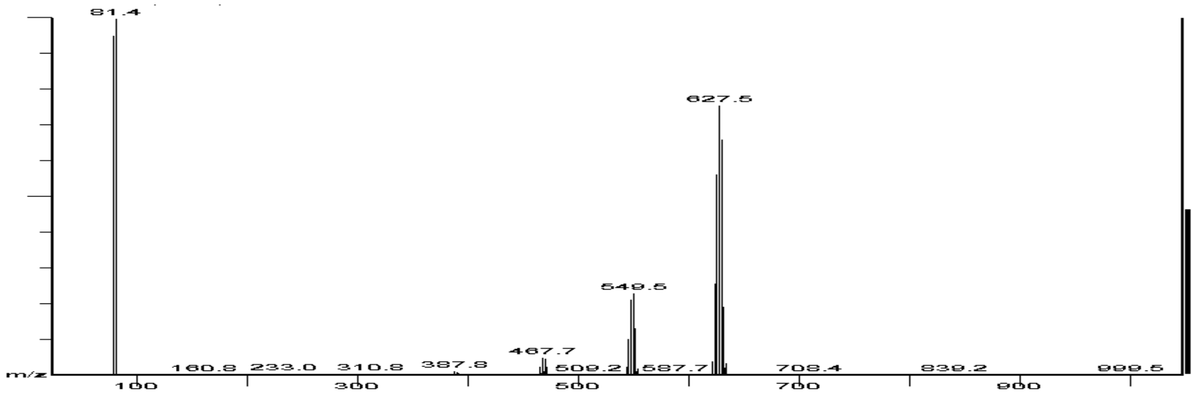


Fig. 81: Mass spectrum of HexaBB (NCI-Mode)

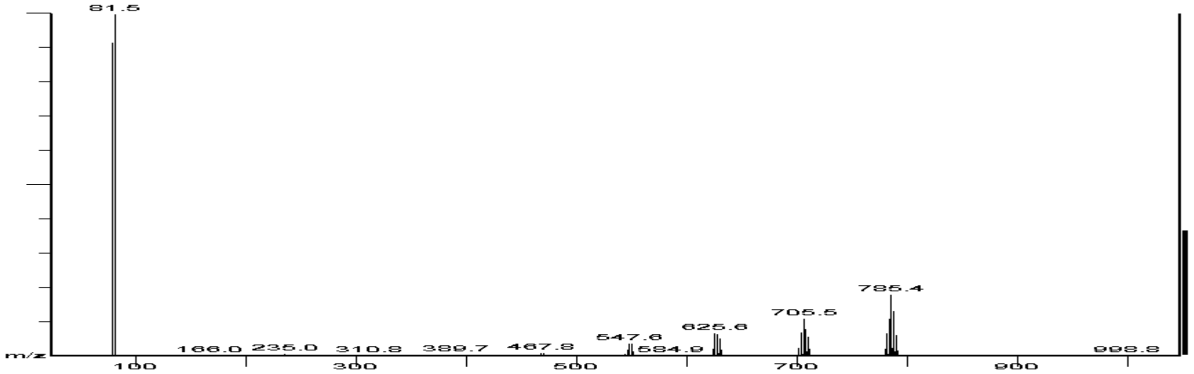


Fig. 82: Mass spectrum of HeptaBB (NCI-Mode)

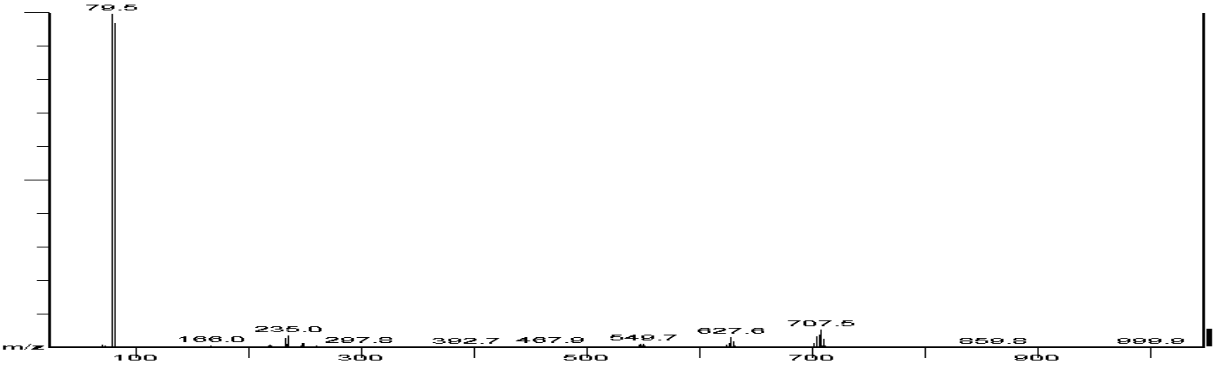


Fig. 83: Mass spectrum of OctaBB (NCI-Mode)

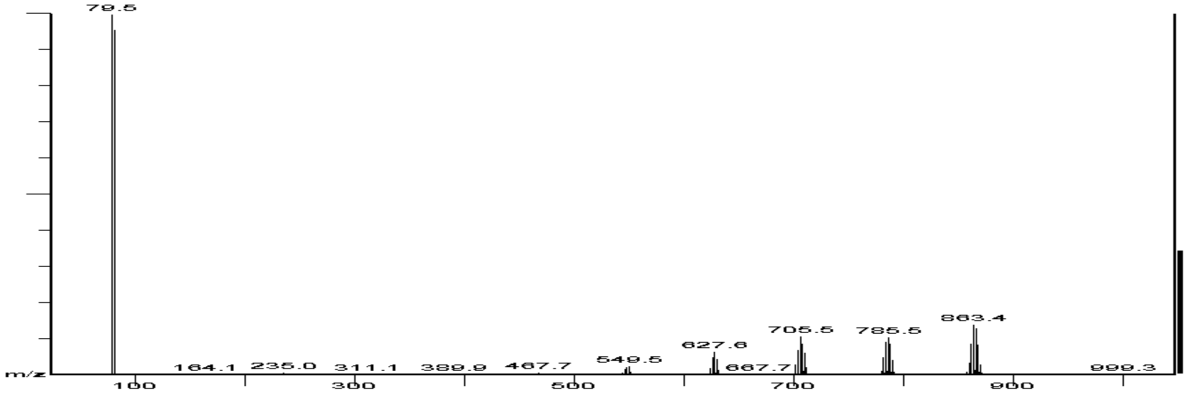


Fig. 84: Mass spectrum of NonaBB (NCI-Mode)

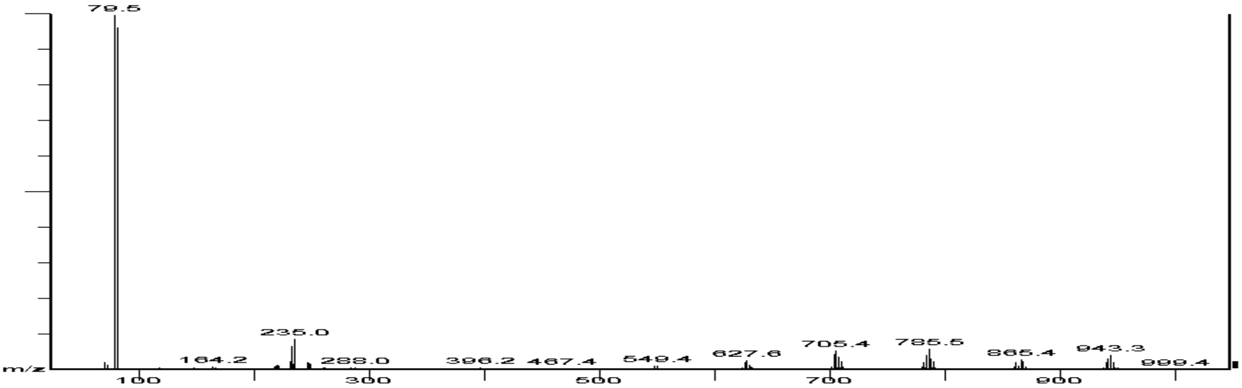


Fig. 85: Mass spectrum of DecaBB (NCI-Mode)

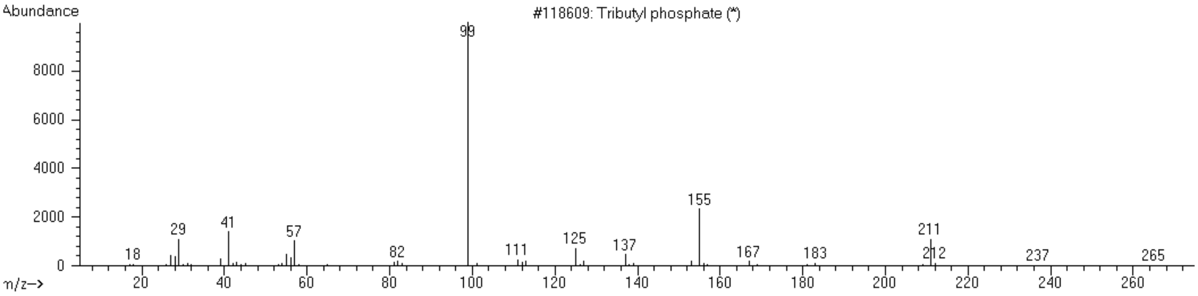


Fig. 86: Mass spectrum of TBP (EI-Mode)

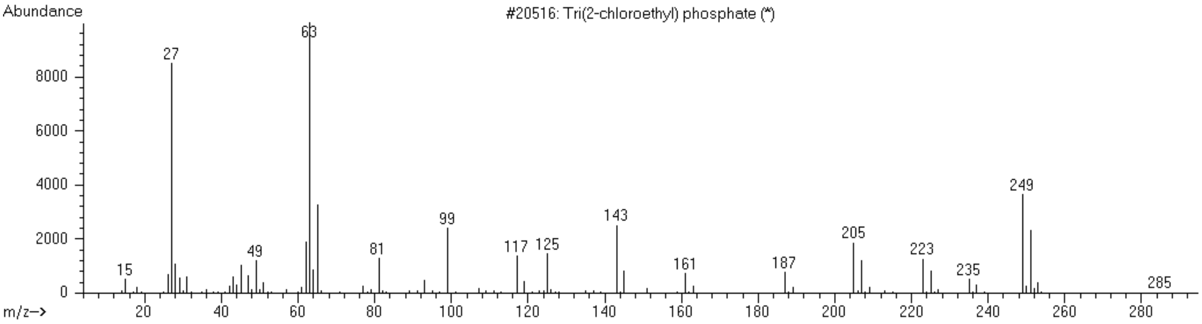


Fig. 87: Mass spectrum of TCEP (EI-Mode)

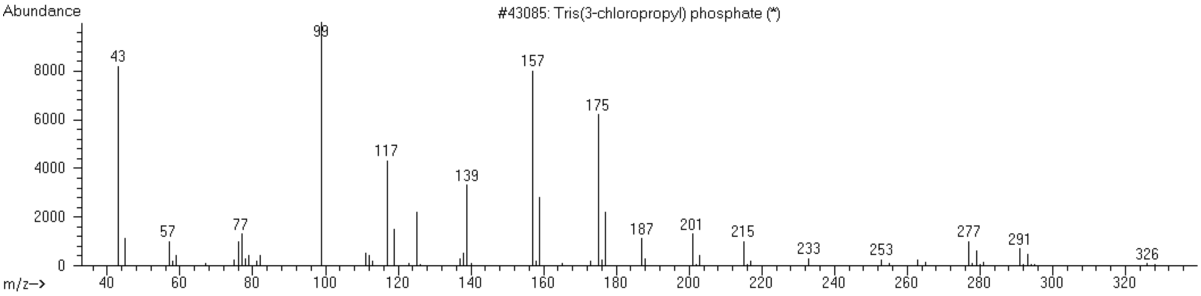


Fig. 88: Mass spectrum of TCPP (EI-Mode)

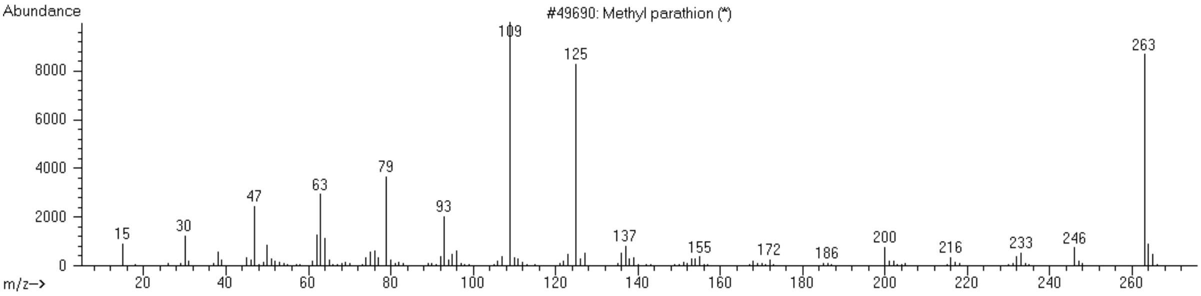


Fig. 89: Mass spectrum of ISTD (EI-Mode)

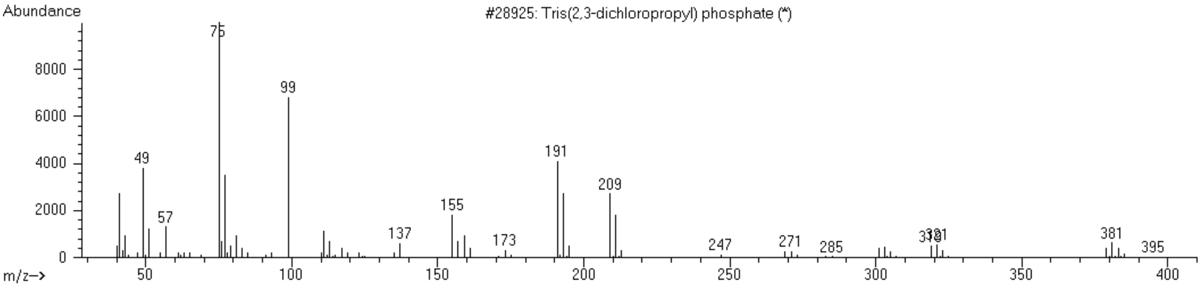


Fig. 90: Mass spectrum of TDCP (EI-Mode)

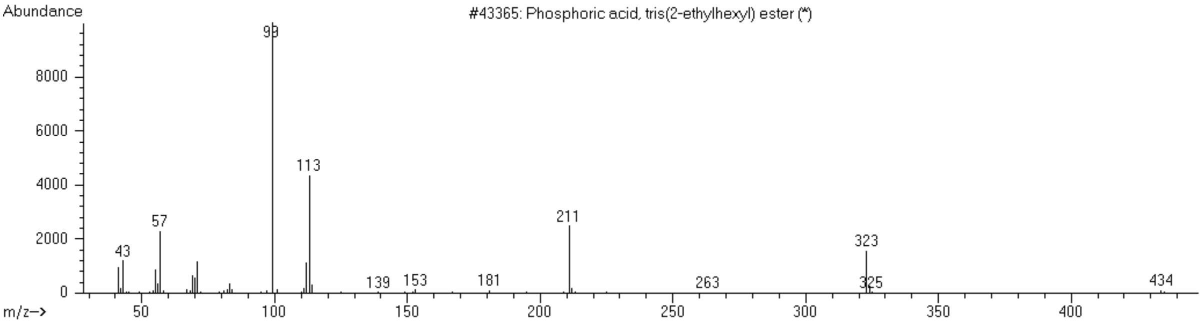


Fig. 91: Mass spectrum of TEHP (EI-Mode)

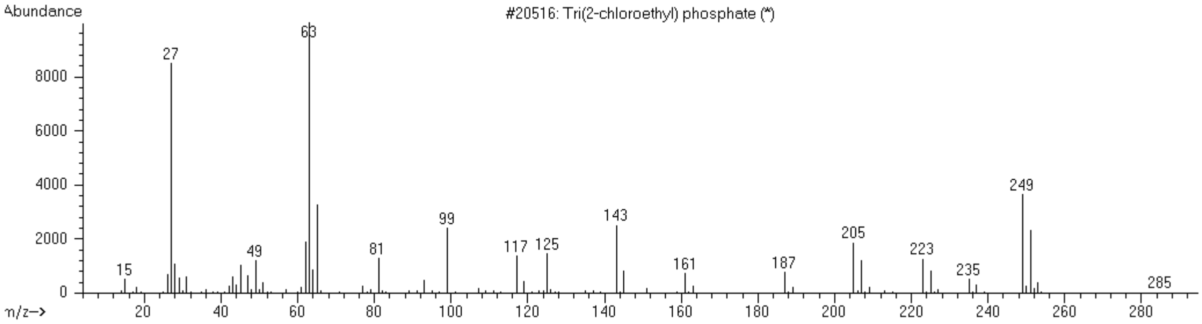


Fig. 92: Mass spectrum of TBEP (EI-Mode)

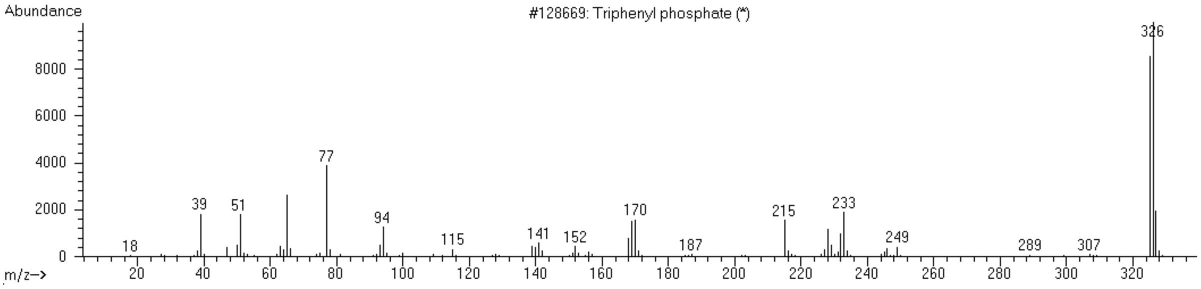


Fig. 93: Mass spectrum of TPP (EI-Mode)

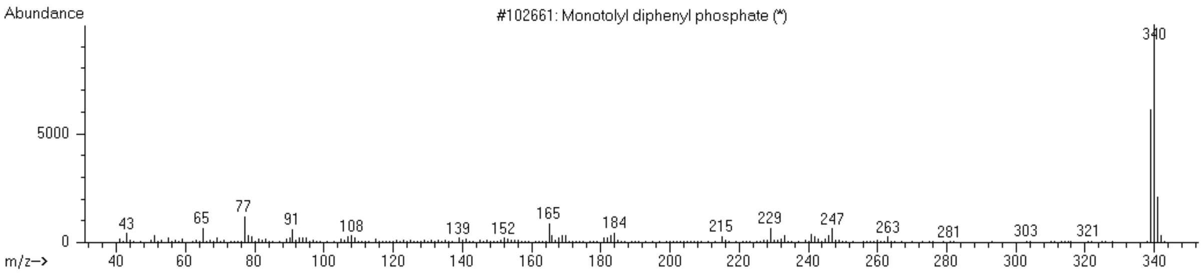


Fig. 94: Mass spectrum of DPK (EI-Mode)

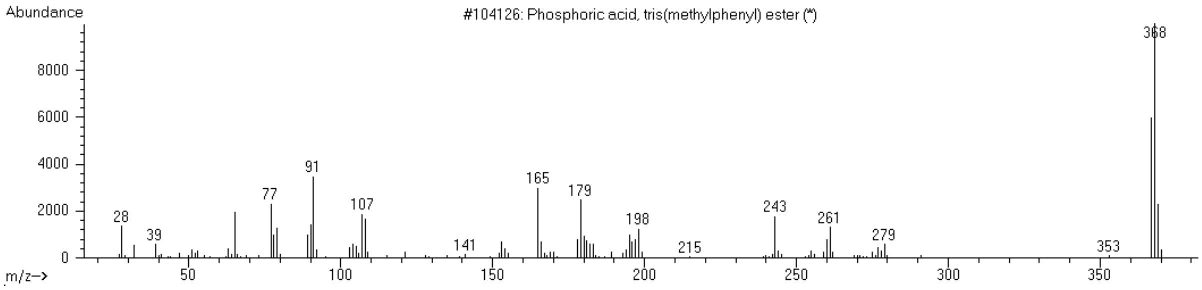


Fig. 95: Mass spectrum of TMTP (EI-Mode)

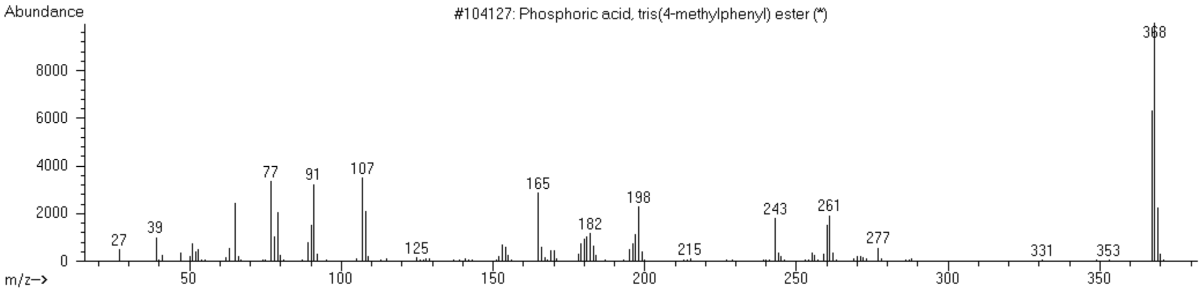


Fig. 96: Mass spectrum of TPTP (EI-Mode)

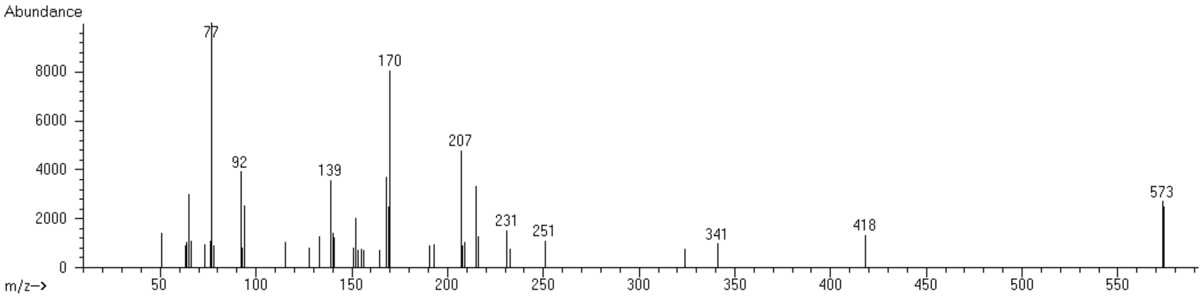


Fig. 97: Mass spectrum of RDP (EI-Mode)

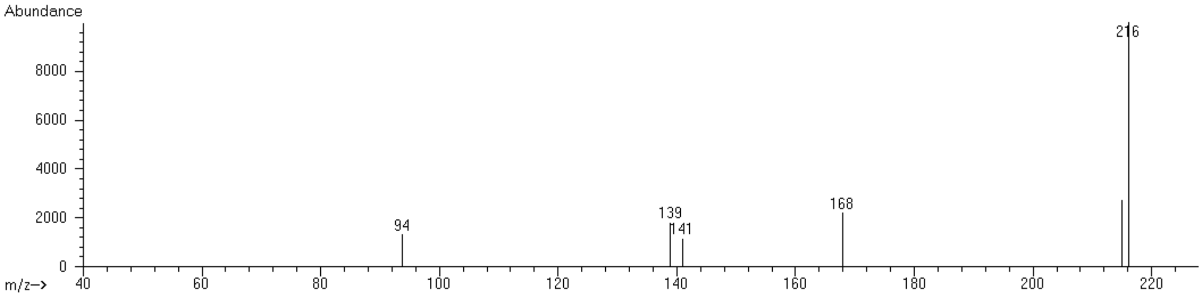


Fig. 98: Mass spectrum of DOPO (EI-Mode)

Appendix 3

Physicochemical Properties

Polybrominated Flame Retardants (BFR)

1.) Polybrominated Diphenylethers (PBDE)

Table 1: Composition of commercial PBDEs /13/.

product	composition							
	TriBDE	TetraBDE	PentaBDE	HexaBDE	HeptaBDE	OctaBDE	NonaBDE	DecaBDE
DecaBDE							0.3-3%	97-98%
OctaBDE				10-12%	43-44%	31-35%	9-11%	0-1%
PentaBDE	0-1 %	24-38%	50-62%	4-8%				

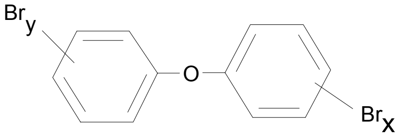


Fig. 1: Basic structure of PBDEs; Σ x,y: 1-10

Tribromo diphenylether

CAS-Nr.:	49690-94-0 /13/
Vapour pressure:	1,45 * 10^{-4} Pa (25 °C) /39/ 4,70-4,95 Pa (25 °C) /13/
Molar weight:	407 g mol^{-1}
Molecular formula:	$C_{12}H_7Br_3O$

Tetrabromo diphenylether

CAS-Nr.:	40088-47-9 /13/
Melting point:	80,5 °C /42/
Vapour pressure:	1,45 * 10^{-5} Pa (25 °C) /39/ 2,9 * 10^{-4} Pa (25 °C)
Solubility in water:	1,1 * 10^{-2} mg L^{-1} (25 °C) /42/
Molar weight:	486 g mol^{-1}
Molecular formula:	$C_{12}H_6Br_4O$

Pentabromo diphenylether

CAS-Nr.: 32534-81-9
Melting point: (-7) - (-3) °C /13/
93,2 °C /42/
Boiling point: > 200 °C /13/
Vapour pressure: 2,2-5,5 * 10^{-7} mm Hg (25 °C) /38/
5,11 * 10^{-5} Pa (25 °C) /42/
7,76 * 10^{-6} Pa (25 °C) /38/
9,3 mm Hg (22 °C) /16/
6,26-6,66 Torr (25 °C) /16/
4,69 10^{-5} Pa (21 °C) (commercial product) /41/
1240 Pa (22 °C) /43/
Solubility in water: 13,3 µg L^{-1} (25 °C) (commercial product) /41/
9*10^{-7} mg L^{-1} (20 °C) /16/
2,4 * 10^{-3} mg L^{-1} (25 °C) /42/
Molar weight: 565 g mol^{-1}
Molecular formula: $C_{12}H_5Br_5O$

Hexabromo diphenylether

CAS-Nr.: 36483-60-0 /40/
Vapour pressure: 0,95-0,99 kPa (25 °C)
Molar weight: 644 g mol^{-1}
Molecular formula: $C_{12}H_4Br_6O$

Heptabromo diphenylether

CAS-Nr.: 68928-80-3
Melting point: 70-150 °C /13/
Vapour pressure: 9,55 * 10^{-8} Pa (25 °C) /39/
Molar weight: 722 g mol^{-1}
Molecular formula: $C_{12}H_3Br_7O$

Octabromo diphenylether

CAS-Nr.: 32536-52-0
Melting point: 200 °C /16/
167-257 °C /16/
Vapour pressure: 1-1,7 * 10^{-9} mm Hg (25 °C) /38/
8,78-9,04 Torr (25 °C) /16/
< 13,3 Pa (20 °C) /13/
Solubility in water: < 1 g L^{-1} (25 °C) /40/
Molar weight: 801 g mol^{-1}
Molecular formula: $C_{12}H_2Br_8O$

Nonabromo diphenylether

CAS-Nr.:	63936-56-1
Molar weight:	880 g mol^{-1}
Molecular formula:	$C_{12}HBr_9O$

Decabromo diphenylether

CAS-Nr.:	1163-19-5 /13/
Melting point:	300 °C /42/ 290-306 °C /13/ 300-310 °C /73/
Boiling point:	425 °C /16/
Vapour pressure:	2,03 mm Hg (278 °C) /38/ $< 10^{-6}$ mm Hg (20 °C) /13/ 4,63 10^{-6} Pa (20 °C) /40/ 4,63 10^{-6} Pa (21 °C) /73/
Solubility in water:	25-30 µg L^{-1} (25 °C) /13/
Molar weight:	959 g mol^{-1}
Molecular formula:	$C_{12}Br_{10}O$

2.) Polybrominated biphenyls (PBB)

Table 2: Composition of commercial PBBs /14/.

product	composition						
	TetraBB	PentaBB	HexaBB	HeptaBB	OctaBB	NonaBB	DecaBB
DecaBB					0.3%	3%	97%
OctaBB				1%	31%	49%	8%
HexaBB	2 %	11%	63%	14%			

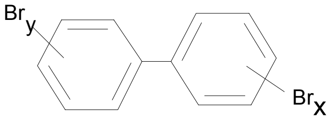


Fig.2: Basic structure of PBBs; Σ x,y: 1-10

Tetrabromo biphenyl

CAS-Nr.:	60044-24-8 /40/

Molar weight: 470 g mol^{-1}
Molecular formula: $C_{12}H_6Br_4$

Pentabromo biphenyl

CAS-Nr.: 67888-96-18X /40/
Molar weight: 549 g mol^{-1}
Molecular formula: $C_{12}H_5Br_5$

Hexabromo biphenyl

CAS-Nr.: 59536-65-1 (67774-32-7) /16/
Melting point: 72 °C /14/
Vapour pressure: $6*10^{-8}$ mm Hg (25 °C) /38/
Solubility in water: 0,06-610 µg L^{-1} (25 °C) /14/
Molar weight: 626 g mol^{-1}
Molecular formula: $C_{12}H_4Br_6$

Heptabromo biphenyl

Molar weight: 706 g mol^{-1}
Molecular formula: $C_{12}H_3Br_7$

Octabromo biphenyl

CAS-Nr.: 61288-13-9
Melting point: 200-250 °C /14/
Solubility in water: 20-30 µg L^{-1} (25 °C) /14/
Molar weight: 786 g mol^{-1}
Molecular formula: $C_{12}H_2Br_8$

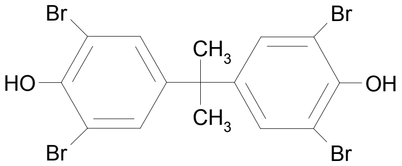
Nonabromo biphenyl

Molar weight: 864 g mol^{-1}
Molecular formula: $C_{12}HBr_9$

Decabromo biphenyl

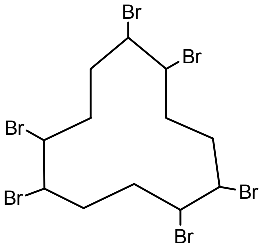
CAS-Nr.: 13654-09-6 /13/
Melting point: 380-386 °C /14/
360-380 °C /16/
Vapour pressure: $1*10^{-11}$ mm Hg (25 °C) /38/
Solubility in water: < 30 µg L^{-1} (25 °C) /14/
Molar weight: 943 g mol^{-1}
Molecular formula: $C_{12}Br_{10}$

3.) Tetrabromo bisphenol A (TBBPA)



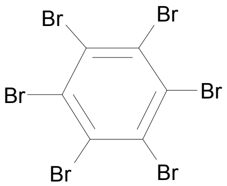
Chemical name: 2,2-Bis-(4-hydroxyphenyl)-propan
4,4'-Isopropyliden-*bis*-(2,6-dibromphenol) /15/
CAS-Nr.: 79-94-7 /16/
Melting point: 181-182 °C /13/
181-182 °C /15/
178-180 °C /16/
Boiling point: 316 °C /15/
Vapour pressure: <1,3 hPa (20 °C) /40/
Solubility in water: 0,72 mg L^{-1} (15 °C) /37/
4,16 mg L^{-1} (25 °C) /15/
Molar weight: 544 g mol^{-1}
Molecular formula: $C_{15}H_{12}Br_4O_2$

4.) Hexabromocyclododecane (HBCD)



Chemical name: 1,2,5,6,9,10-Hexabromocyclododecane
CAS-Nr.: 25637-99-4 /16/
3194-55-6 /16/
Melting point: 170-180 °C /16/
190 °C /40/
Vapour pressure: $6,4 * 10^{-6}$ Pa (10 °C) /10/
$6,27\ 10^{-5}$ Pa (20 °C) /40/
$1,7 * 10^{-4}$ Pa (50 °C) /10/
< 133 Pa (20 °C) /16/
Solubility in water: 0,12 mg L^{-1} (23 °C) /10/
3,4 µg L^{-1} (25 °C) /13/
Molar weight: 642 g mol^{-1}
Molecular formula: $C_{12}H_{18}Br_6$

5.) Hexabromobenzene (HB)



Chemical name:	Hexabromobenzene
CAS-Nr.:	87-82-1 /16/
Melting point:	326 °C /37/
Molar weight:	552 g mol^{-1}
Molecular formula:	C_6Br_6

Organophosphorus Compounds (OPC)

1.) TEP

Chemical name:	Triethylphosphate
CAS-Nr.:	78-40-0 /44/
Chemical group:	alkylated phosphoric acid ester
Effect:	additive FR
Melting point:	-56 °C /44/
Boiling point:	215,6 °C (101,3 kPa) /44/
Vapour pressure	39 Pa (20 °C) /44/
Molar weight:	182 g mol^{-1}
Molecular formula:	$C_6H_{15}O_4P$

2.) TBP

Chemical name:	Tri(n-butyl)phosphate
CAS-Nr.:	126-73-8
Chemical group:	alkylated phosphoric acid ester
Effect:	additive FR, plasticizer
Melting point:	-80 °C /45/
Boiling point:	289 °C (decomposition), 177-178 °C (3,6 kPa), 150 °C (1,33 kPa) /84/
Vapour pressure:	66,7 kPa (200 °C), 973 Pa (150 °C), 9 Pa (25 °C) /84/ 13,7 mm Hg (20 °C) /46/
Solubility in water:	0,422 mg L^{-1} (25 °C) /84/
Molar weight:	266 g mol^{-1}
Molecular formula:	$C_{12}H_{27}O_4P$

3.) TBEP

Chemical name:	Tris (2-butoxyethyl) phosphate
CAS-Nr.:	78-51-3
Chemical group:	alkylated phosphoric acid ester
Effect:	additive FR, plasticizer
Melting point:	-70 °C /12/
Boiling point at 5-5,3 hPa:	200 - 230 °C /79/
Vapour pressure:	2,8 10^{-7} hPa (25 °C), 0,33 hPa (150 °C) /79/
Solubility in water:	1,1 - 1,3 g L^{-1} (20 °C) /12/
Molar weight:	398 g mol^{-1}
Molecular formula:	$C_{18}H_{39}O_7P$

4.) TEHP

Chemical name: Tris (2-ethylhexyl) phosphate
CAS-Nr.: 78-42-2
Chemical group: alkylated phosphoric acid ester
Effect: additive FR, plasticizer
Melting point: -74 °C /12/
Boiling point: 220 °C (6,67 hPa), 210 °C (5 hPa) /79/
Vapour pressure: < 0,1 hPa (20 °C) /79/
Solubility in water: <0,1 g L^{-1} (20 °C) /79/
Molar weight: 435 g mol^{-1}
Molecular formula: $C_{24}H_{51}O_4P$

5.) TCPP

Chemical name: Tris (1-chloro-2-propyl) phosphate
CAS-Nr.: 13674-84-5
Chemical group: halogenated alkylated phosphoric acid ester
Effect: additive FR
Melting point: -42 °C /5/
Boiling point at 101,3 kPa: 341,5 °C, 235-248 °C, degraded /78/
Vapour pressure: 100 Pa (20 °C) /60/
40 mm Hg (110 °C) /76/
< 2 mm Hg (25 °C) /76/
Solubility in water: 1,6 g L^{-1} (20 °C) /86/
Molar weight: 328 g mol^{-1}
Molecular formula: $C_9H_{18}Cl_3O_4P$

6.) TDCPP

Chemical name: Tris (1,3-dichlor-2-propyl) phosphate
CAS-Nr.: 13674-87-8
Chemical group: halogenated alkylated phosphoric acid ester
Effect: additive FR
Boiling point : 236 - 237 °C (5 mm Hg) /78/
Vapour pressure: 1,33 Pa (30 °C) /78, 85/
Solubility in water: 0,1 g L^{-1} (30 °C) /86/
Molar weight: 431 g mol^{-1}
Molecular formula: $C_9H_{15}Cl_6O_4P$

7.) TPP

Chemical name: Triphenylphosphate
CAS-Nr.: 115-86-6
Chemical group: arylated phosphoric acid ester

Effect: additive FR
Melting point: 50-51 °C /8/
Boiling point: 220 °C (101,3 kPa) /87/
245 °C (11 mm Hg) /8/
Vapour pressure: 20 Pa (150 °C) /87/
1 mm Hg (193,5 °C) /87/
Solubility in water: 0,73-2,1 mg L^{-1} /84/,
0,025-1,9 mg L^{-1} /87/
Molar weight: 326 g mol^{-1}
Molecular formula: $C_{18}H_{15}O_4P$

8.) DPC

Chemical name: Diphenylcresylphosphate
CAS-Nr.: 26444-49-5
Chemical group: arylated phosphoric acid ester
Effect: additive FR
Melting point: -38 °C
Boiling point: 253 °C (10 mm Hg)
Vapour pressure: 0,08 mm Hg (150 °C)
Molar weight: 340 g mol^{-1}
Molecular formula: $C_{19}H_{17}O_4P$

9.) TMTP

Chemical name: Tris(m-tolyl)phosphate
CAS-Nr.: 563-04-2
Chemical group: arylated phosphoric acid ester
Effect: additive FR
Molar weight: 368 g mol^{-1}
Molecular formula: $C_{21}H_{21}O_4P$

10.) TPTP

Chemical name: Tris(p-tolyl)phosphate
CAS-Nr.: 78-32-0
Chemical group: arylated phosphoric acid ester
Effect: additive FR
Molar weight: 368 g mol^{-1}
Molecular formula: $C_{21}H_{21}O_4P$

11.) RDP

Chemical name: Resorcinol-bis-(diphenylphosphate)
CAS-Nr.: 57583-54-7

Chemical group: arylated phosphoric acid ester
Effect: additive FR, plasticizer /6/
Boiling point at 101,3 kPa: approx. 300 °C /60/
Vapour pressure: 138 Pa (38 °C) /60/ lower volatility compared to other arylated POC /77/
Solubility in water: insoluble, low solubility in water /60/
Molar weight: (n = 1-7), n = 1: 574,6 g mol^{-1}
Molecular formula: $C_{30}H_{24}P_2O_8$ (n = 1)

12.) BDP
Chemical name: Bisphenol-A-bisdiphenylphosphate
CAS-Nr.: 5945-33-5
Chemical group: arylated phosphoric acid ester
Effect: additive FR
Molar weight: 820 g mol^{-1}
Molecular formula: $C_{39}H_{34}O_8P_2$

13.) DOPO
Chemical name: 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide
CAS-Nr.: 35948-25-5
Effect: reactive FR
Molar weight: 216 g mol^{-1}
Molecular formula: $C_{12}H_9O_2P$

Appendix 4

Project-related Working Group and Workshop

A project-related working group was organised at the beginning of the project to provide technical support, which was then extended to a workshop at the end of the project.

The project's subject was discussed and suggestions were given for its direction in this project-related working group.

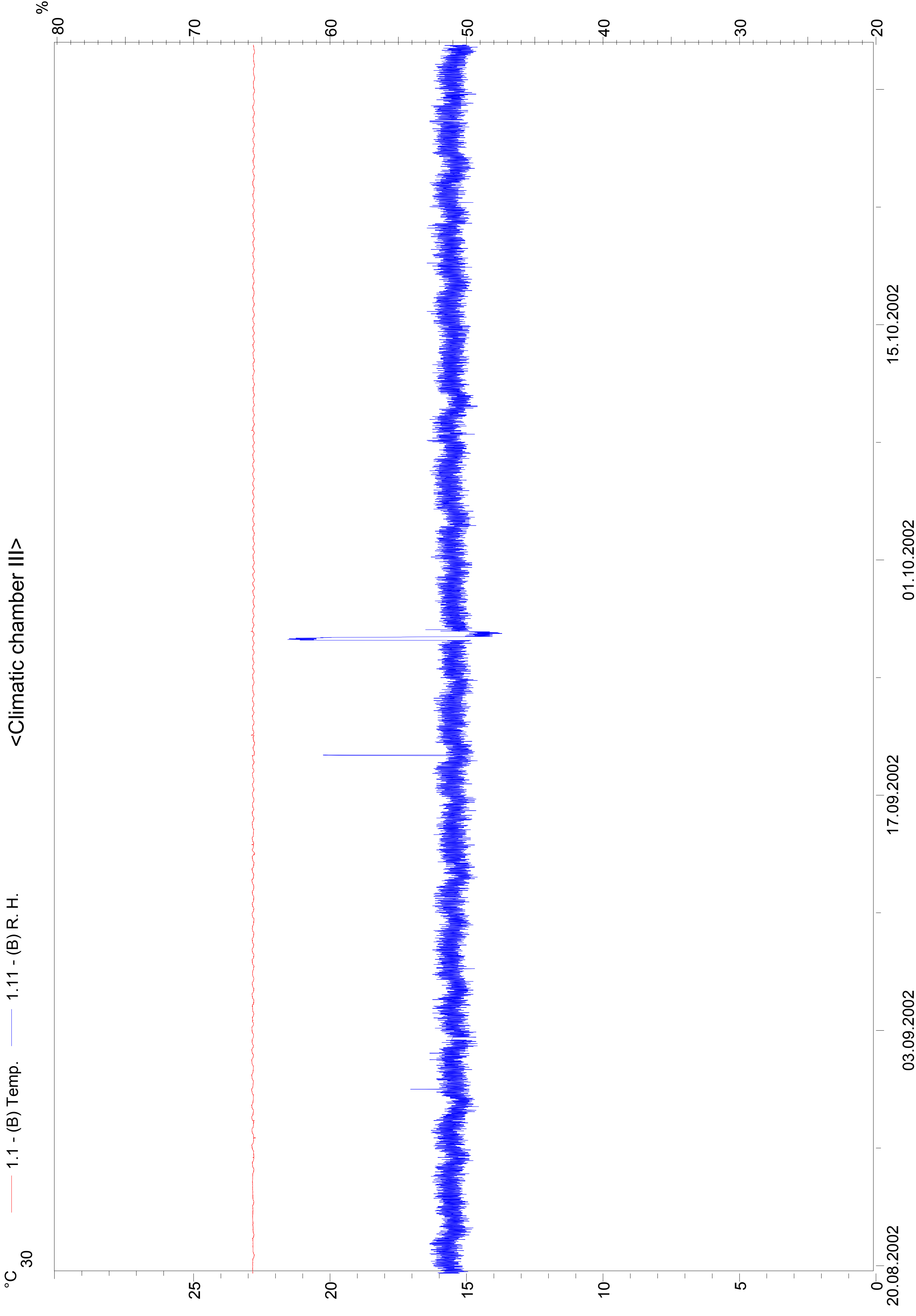
The participants of the project-related working group were selected so as to facilitate sample provision and information exchange on the relevant substance groups. Experts and manufacturers from the insulation material (polyuretane, polyisocyanurate, polystyrene, polyethylene, polybutadiene) producing and processing industry, upholstered furniture and mattress production, computer industry, assembly foam production and flame retardant industry were invited to attend the workshop.

In addition to presenting and discussing the project itself, issues of product selection, in particular sampling and sample preparation, as well as background issues to the usa of flame retardants were discussed.

The aim was to organise support in the form of a working group and workshop to integrate expert opinion and expert knowledge into the implementation of the project at an as early stage as possible.

The constructive and helpful contribution of all those who participated is once again gratefully acknowledged.

Appendix 5



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1.11 - (B) R. H.
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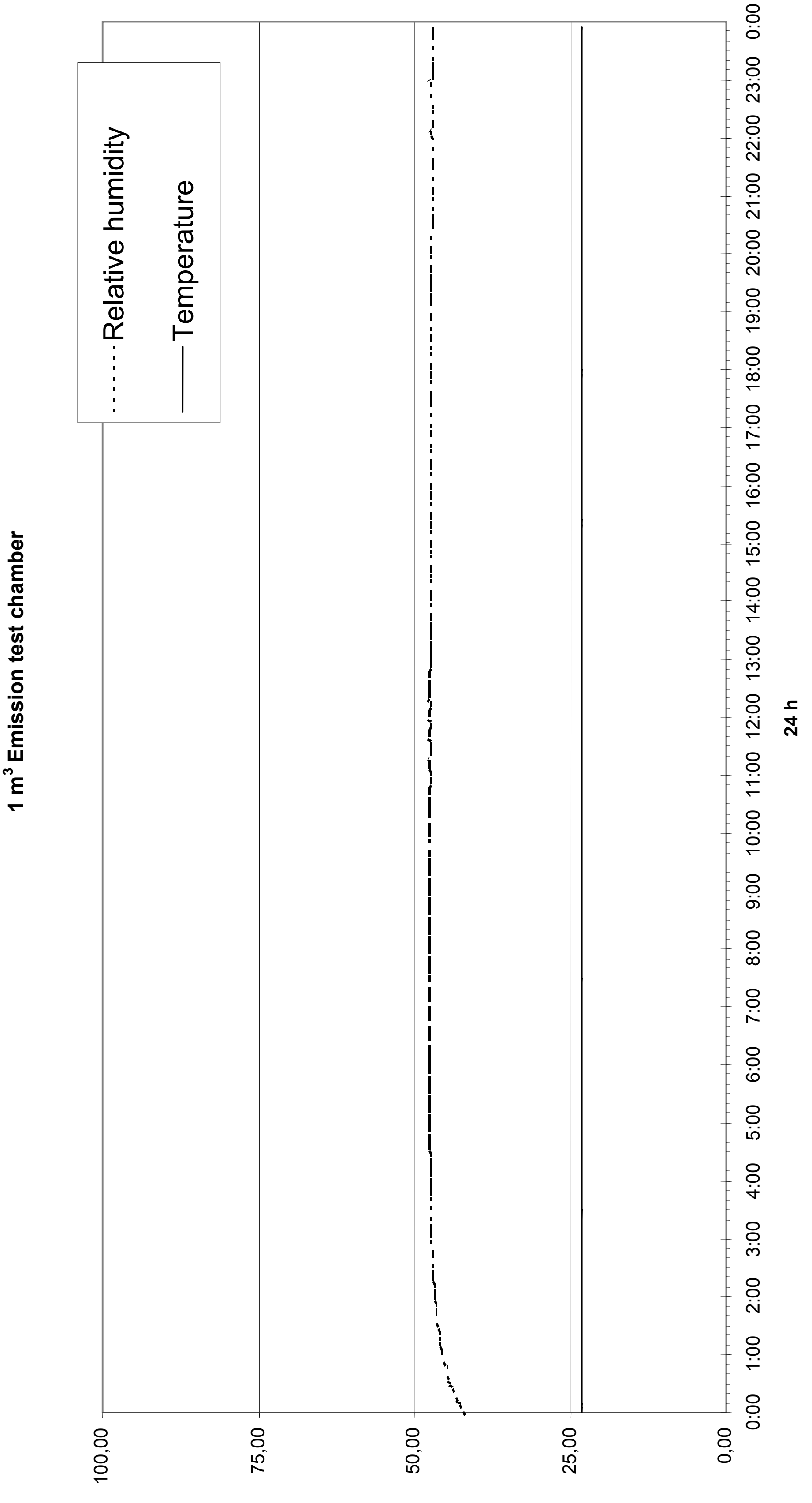
50
40
30
20
°C
30
25
20
15
10
5
0
20.08.2002
03.09.2002
17.09.2002
01.10.2002
15.10.2002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