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Suitability of ultrasound-assisted extraction for chromatographic determination of selected flame retardants used in styrenic polymers

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Abstract

The ultrasonic induced degradation behaviour of flame retardants in several organic solvents and in water was studied for sample preparation purposes. Comparative studies were performed using p-nitrophenol as a reference for ultrasonic degradation. An ultrasonic probe and an ultrasonic bath were applied. Degradation was only detected in the treatment of aqueous solutions of p-nitrophenol and tetrabromobisphenol A. In contrast, no degradation could be observed on treating such solutions in aliphatic solvents. Decomposition of the aromatic solvent toluene was only found on treatment with an ultrasonic probe. As a consequence, a rapid and reliable ultrasound-assisted sample preparation procedure for the chromatographic determination of flame retardants developed before could be confirmed.

Keywords:

Brominated flame retardants, ultrasonic extraction, RoHS, WEEE, PBDE and PBB

1. Introduction

Application of ultrasound (US) for scientific purposes is becoming more and more popular. US is applied for cleaning, degassing, solid-liquid dissolution, homogenisation and emulsification, US-assisted filtration, US-assisted reactions and reagent generation, extraction and digestion. Detailed descriptions of US applications for sample preparation have been reported [1 - 14]. In comparison to other sample preparation methods, e. g., Soxhlet extraction [8, 9, 13 - 15], supercritical fluid extraction [8, 16 – 18] or microwave-assisted extraction [8, 9, 13 - 15, 19, 20], US-assisted sample preparation provides the advantage of saving time and solvent. In addition, US-assisted sample preparation can also be applied to the extraction of thermo-labile analytes, provided the appropriate conditions are selected. Moreover, other sample preparation methods often require expensive equipment, e. g., an extraction apparatus or a microwave oven, which is not the case for US-assisted sample preparation [1 - 5].

Fast US-assisted methods for the determination of brominated and phosphate-based flame retardants (FRs) in polymers by HPLC/UV-Vis, GC/MS and GC/ECD were developed in our group [21, 22]. For HPLC/UV-Vis, an extraction time of 5 min in 2-propanol was sufficient for a rapid identification [21]. For GC/MS and GC/ECD measurements, the polymer was first completely dissolved in toluene for the extraction of the FRs. In a second step, the polymer was precipitated using another organic solvent, e. g. iso-octane or

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1-propanol [22]. Soxhlet extraction takes between 4 ½ and 8 h [21], or even longer [22, 23], when an extraction quality comparable to the US-assisted methods is to be achieved.

For the quantification of FRs, European legislation provides an important background. According to the European RoHS directive [24], polybrominated biphenyls (PBB) and polybrominated diphenyl ethers (PBDE) must not exceed 0.1 % (w/w) in homogeneous materials of electrical and electronic equipment (EEE) and their waste products (WEEE). In 2008, the International Electrotechnical Commission (IEC) published a test method for the determination of PBB and PBDE in polymers by GC/MS [25]. However, this Soxhlet-based method has only the status of an informative Annex and is currently under revision.

Although US has a great potential for saving time and cost, it can lead to the generation of radicals and destruction of molecules. The reason is the US-induced, so-called "cavitation". Available literature mainly deals with US degradation of substances in aqueous solution [26 - 30]. Reports that describe the sonolysis of pure organic solvents can also be found [31 - 33]. However, there is limited published data available dealing with US degradation of substances dissolved in these organic solvents.

In this study we will show in detail that no degradation occurred when the US-assisted extraction method mentioned above was applied to brominated and phosphate-based FRs in organic solvents, using an ultrasonic bath (USB).

2. Experimental

2.1. Instrumentation

A Bioblock Scientific Leo-80 Bath (2.0 L bath volume, 46 kHz US frequency, 80 W US power, Fisher Bioblock Scientific, Illkirch Cedex, France) and a Branson B12 ultrasonic probe (USP) (20 kHz US frequency, Branson Ultrasonics Corp., Danbury, USA), equipped with a titanium horn (1.3 cm in diameter), operated at the highest level (ca. 40 - 50 W), were used to treat the solutions with US.

A Varian Cary 1G UV-Vis spectrophotometer (Varian Inc., Palo Alto, USA) was used for spectrophotometric measurements. Data were collected with a computer system running the associated "WinUV Scan" and "WinUV Concentration" software (Varian).

HPLC/UV-Vis measurements were accomplished using a combination of SP8800 HPLC pump, SP8780 auto sampler (equipped with a 50 µL sample loop) and a Spectra FOCUS scanning UV-Vis detector (all devices from Spectra-Physics, Darmstadt, Germany). Data were collected on a computer running an OS/2 WARP operating system and the "PC1000" software package (Spectra-Physics).

2.2. Materials

All solvents and 1 mol L^{-1} HCl solution were of Rotisolv®, HPLC- or Pestilyse-grade, or of comparable purity (Roth GmbH, Karlsruhe, Germany). p-Nitrophenol (pNP) (98 % purity) was purchased from Acros Organics (Geel, Belgium). Potassium hydroxide (KOH) (p.a.) was supplied by Merck (Darmstadt, Germany). Triethylamine (≥ 99.5% purity) and acrylonitrile-butadiene-styrene-copolymer (ABS) were purchased from Sigma-Aldrich, Germany. The technical FRs tetrabromobisphenol A (TBBPA, containing approx. 98 % tetrabronmobisphenol A), 2,4,6-tribromophenol (TBP, 98 % purity), 1,2-bis(tribromophenoxy)ethane (TPBE, contains approx. 99 % 1,2-bis (trimbromophenoxy) ethane), pentabromodiphenyl ether (PENTA, contains approx. 52 % pentabormodiphenyl ether), octabromodiphenyl ether (OCTA, contains roughly 37 % octabromodiphenyl ether) and decabromodiphenyl ether (DECA, contains roughly 97 % decabromodiphenyl ether) were obtained from Great Lakes Europe (Frauenfeld, Switzerland). Octabromobiphenyl (OBB, contains roughly 51 % octabromobiphenyl) and deca-bromobiphenyl (DBB, contains approx. 98 % decabromobiphenyl) were supplied by Ultra Scientific Europe (Wesel, Germany). Resorcinol-bis(diphenylphosphate) (RDP, contains approx. 88 % resorcinol-bis(diphenyl-phosphate) and bisphenol-A-bis (diphenylphosphate) (BDP, contains approx. 99 % bispheno-A-bis(diphenylphosphate) were courtesy of the Fraunhofer Institute for Process Engineering and Packaging (Freising, Germany). Detailed information of the composition of the used, technical FRs can be found in [22]. Sample tubes were obtained from VWR International (Darmstadt, Germany).

2.3. Ultrasonic conditions

Different solutions of pNP, TBBPA, TBP, DECA and DBB were prepared for US treatment, subsequently followed by UV-Vis measurements (Table 1).

Table 1. Concentrations of the prepared solutions for US treatment in mg·L^{-1} (µmol·L^{-1}). In curly brackets: wavelength of the absorption peak in nm.

Solvent	pNP	TBBPA	TBP	DECA	DBB
Water	13.9 (100) {401}	Saturated[a] {247, 311}		-	-
Methanol	13.9 (100) {392}	54.4 (100) {313}	33.1 (100) {321}	-	-
1-Propanol	13.9 (100) {407}	54.4 (100) {315}	33.1 (100) {322}	48.0 (50); 48.0 (50[b]); 9.6 (10) {228, 232[b]}	51.9 (55) {228}
Toluene	13.9 (100) {317}	54.4 (100) {294, 311}		95.9 (100) {307}	-
Iso-octane	13.9 (100[b]) {304}				

a) approximately 2 mg·L^{-1}

b) Due to solubility reasons, a high concentrated stock solution of the substance in THF was diluted with the particular solvent. In case of DECA in 1-propanol a shift of the absorption maximum was observed.

The aqueous pNP solution was adjusted to a pH of 5 using 1 mol L^{-1} HCl. The pNP solutions in methanol and 1-propanol were treated with an adequate amount of hydrochloric acid to decolourise. TBBPA was dissolved in KOH solution of pH 10.

For USB treatment, 10.0 mL of each testing solution (Table 1) were transferred into a centrifuge tube and treated with US for a maximum of 40 min (pNP in water), 120 min (FR solutions) or 360 min (in the long-term experiment, pNP and TBBPA in water). To keep the temperature of the USB close to room temperature, it was partially exchanged using cold water or ice during US treatment, depending on the measured temperature.

For HPLC/UV-Vis measurements, solutions of TBBPA, TBP, TBPE, PENTA, OCTA, DECA, OBB, DBB, RDP and BDP were prepared in concentrations of 20 mg·L^{-1} in 1-propanol. 20.0 mL of each solution were transferred into a test tube and treated for a maximum of 40 min. After specific times, 1 mL of solution was taken from the test tube and analyzed using HPLC/UV-Vis.

For USP treatments, 25.0 mL of either aqueous or alcoholic solutions were transferred into 50 mL plastic sample tubes, whereas the solutions in toluene or iso-octane were transferred into glass sample tubes, respectively. The samples were treated for different times, for a maximum of 45 min. During treatment, the tubes were thermostatted using iced water.

2.4. UV-Vis measurements

For UV-Vis measurements, the phenol derivatives TBBPA, pNP and TBP were measured in alkaline solution. KOH and triethylamine were used as basic reagents, at final concentrations of 0.1 mol L^{-1} each in the studied solution. Water, methanol and 1-propanol were treated with KOH, whereas toluene and iso-octane were treated with triethylamine.

UV-Vis spectra of the selected compounds were recorded. Spectra of pNP and the FRs except DECA and DBB (in water and 1-propanol) were recorded from 220 to 500 nm (TBBPA) or 600 nm (pNP), respectively. Spectra in toluene and isooctane were recorded from 280 nm to the limits given above. Spectra of DECA and DBB in 1-propanol were recorded from 200 to 500 nm. The scan speed was set to 600 nm min^{-1}.

For concentration versus time measurements, each solution was measured in triplicate at the UV-Vis maximum of the corresponding substance. As shown in Table 1, the absorption peak of pNP in the polar solvents water, methanol and 1-propanol, shifted about 80 nm to higher wavelengths compared to the absorption peak in the nonpolar solvent toluene and isooctane.

2.5. HPLC/UV-Vis measurements

Conditions and parameters were identical to those described in [21], viz. a Luna 5 µm phenyl-hexyl column from Phenomenex (Aschaffenburg, Germany) with 4.6 mm I.D. and 150 mm length was used for separation. The isocratic mobile phase consisted of methanol containing 2.0 mL buffer per litre methanol. The buffer consisted of 5 mL 2-aminoethanol and 26.5 mL 1 M HCl. 10 µL of sample were injected at a flow rate of 2.5 $mL\cdot min^{-1}$, a column temperature of 50±2 °C and a total analysis time of 4.5 min. Each solution was injected three to six times. UV-spectra were recorded from 200 to 400 nm with a scan speed of 6.4 scans per seconds at a 5 nm interval.

3. Results and Discussion

The US behaviour of different brominated and phosphorous based FR was studied. TBBPA was investigated, which is the brominated FR showing the largest production volume worldwide (145000 t/a) [34]. PBB and PBDE are regulated as described above. TBPE is a very commonly used FR, sold under the trade name FF-680. In addition, it is used as substitute for PBDEs [35]. RDP and BDP are halogen free, phosphate based alternatives for the use of TBBPA and DECA in housings of electronic equipment [34]. TBP can be formed from TBPE and of some PBDE congeners.

As further reference for substance degradation under the influence of US, pNP was chosen. Due to its good UV-Vis absorbance it facilitates the observation of modifications. In addition, pNP was selected due to its well known degradation behaviour. Kotronarou et al. treated pNP in aqueous solution using USP and investigated the degradation mechanism, rates and products [26].

Although the studied FRs do not contain carbon bound nitro groups as found in pNP, the carbon-bromine bond of a brominated FR is also considered as target for sonolysis. Likewise, the phenolic structure of pNP is also found in many FRs.

3.1. Ultrasonic behaviour of TBBPA and TBP

At first, aqueous solutions of TBBPA were studied, and the obtained results were compared with reported experiments for pNP.

Kotronarou et al. [26] conducted their experiments at a temperature of 15 °C, applying a USP of 84 W power. This resulted in a rate constant of 3.7 x 10^{-4} s^{-1} for the US decomposition of pNP. In contrast to Kotronarou et al. [26], we performed US irradiation of an aqueous pNP solution at ca. 0 °C using an USP of 40 to 50 W power. As a result of the milder conditions, the determined first-order rate constant for decomposition was (9.2 ± 0.2) x 10^{-5} s^{-1}, which is only a quarter of the reported value [26]. As seen in Fig.1, the absorbance after 45 min of treatment was 78 % of that for the untreated solution.

For measurement of US decomposition of aqueous TBBPA solution, some parameters were changed. Due to moderate solubility of TBBPA in water, a saturated solution was used. To increase the solubility, TBBPA was dissolved in alkaline solution at pH 10 instead of an acidic solution. To increase the UV absorption in this case, the UV-VIS measurements were carried out in a 50 mm quartz cuvette, while all other UV-Vis measurements were carried out in 10 mm cuvettes.

Results of the USP treatment of aqueous solutions of TBBPA corresponded to the results of the pNP experiments, and degradation of TBBPA was observed (Fig.2). The initial increase in absorption can be explained in terms of the formation of an unknown degradation product of strong absorbance, e.g. some quinone, which was formed during the decomposition of TBBPA. This substance is then readily decomposed during the continued irradiation process, which results in a decrease in absorption on longer irradiation. Hence, a short USP treatment in aqueous solutions can already lead to degradation products.

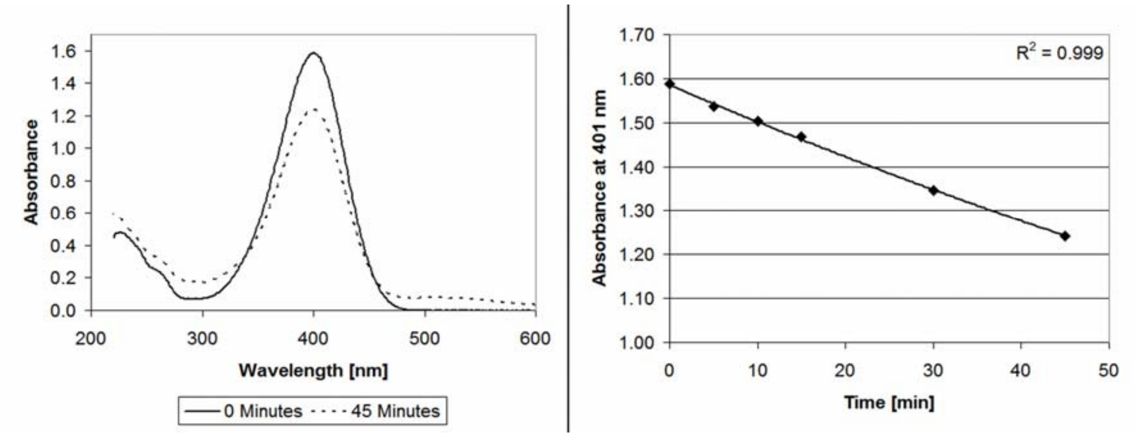

Fig. 1. Absorbance spectra of aqueous pNP solution vs. treatment time using the USP (on the left); Absorbance changes vs. time (on the right).

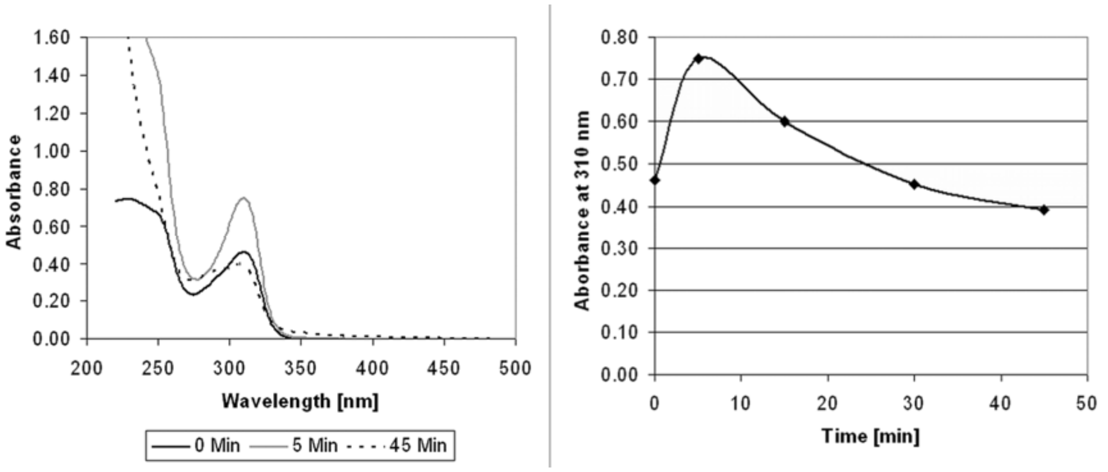

Fig. 2. Absorbance spectra of aqueous TBBPA solution vs. treatment time using the USP (on the left); Absorbance changes vs. time (on the right).

For the studies in our group, an USB instead of an USP was used to extract FRs from polymers during sample preparation. For this reason, the substances described above were also treated using an USB. Apart from using test tubes or centrifuge tubes, reaction parameters were identical to the treatment described above.

As the results clearly show, no significant degradation of pNP could be observed after treating pNP solutions in water using the USB for up to 40 min. In a long-term experiment, degradation of pNP was observed after a treatment of 6 h. This was, however, approximately 18 times longer than the exposure during the USB extraction procedure described above. The observed first-order rate constant of $(1.10 \pm 0.02) \times 10^{-5}\ s^{-1}$ for this experiment was ca. one order of magnitude smaller than observed using the USP. In numerical values, this means that the decrease in absorbance after 40 min of treatment was only 2.5 %, and the decrease after 6 h was 21 %, compared to the untreated solution.

However, even in a long-term experiment, no detectable degradation could be found for TBBPA after USB treatment (Fig. 3). Absorbance of untreated and solutions treated for 6 h showed the same values, with variations between 97.5 and 101.5 % of the absorbance value of the untreated solution and the standard deviation of 3 measurements was already 1.0 %.

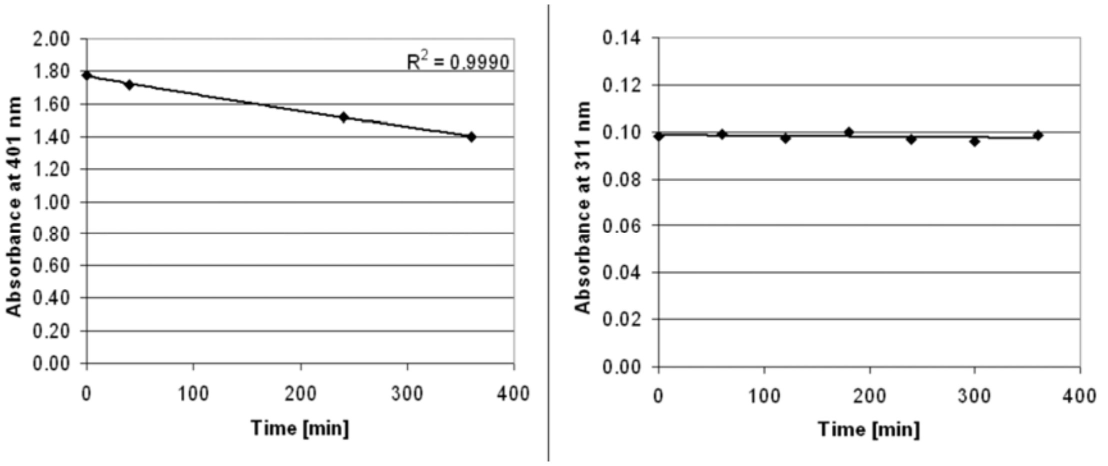

Fig. 3. Absorbance vs. time of an aqueous pNP solution treated with USB (on the left); Absorbance vs. time of an aqueous TBBPA solution treated with USB (on the right).

To approach sample preparation conditions, the degradation behaviour in organic solvents was examined next. As the results clearly show, no degradation occured, on treating pNP, TBBPA and TBP in methanol, 1-propanol or iso-octane using USB or USP.

Due to only marginal differences expected to be found in the spectra of the FRs and their possible degradation products, spectral interference of both could not be excluded. For this reason, recovery rates for TBBPA and TBP in 1-propanol were determined using HPLC/UV-Vis. However, the results clearly show that neither TBBPA nor TBP decomposed during US treatment for up to 120 min. Recovery rates for both substances vary from 95 to 103 % in the UV-Vis measurements, whereas HPLC/UV-Vis measurements show recovery rates between 95 and 108 %. The main difference between both measurement techniques is a seven times lower standard deviation (3 measurements) for the UV-Vis technique. The larger error in HPLC measurements is caused by applying a chromatographic method.

During USP treatment of solutions of pNP or TBBPA in toluene, the solutions were heated and the colour of previously colourless solutions turned to pale yellow. The absorbance spectra for pNP or TPPBA showed an increase in absorbance with decreasing wavelength.

Even pure toluene showed visible degradation when treated by USP. This behaviour corresponds to the US-induced sonolysis (described as “pyrolysis” by Cataldo [32]) of aromatic hydrocarbon, which was suggested to generate radicals.

Spectra of untreated solutions of pNP or TBBPA were recorded, as well as spectra of solutions treated for 45 min, and difference spectra were calculated. The difference spectra were very similar to the spectrum of the 45 min treated, pure toluene solution. Hence, it was proven that the increase in absorbance of pNP or TBBPA solutions was caused by degradation of toluene. Thus, the stability of pNP and TBBPA against the irradiation of the USP cannot be proven by performing only photometric measurements.

In contrast, application of USB showed none of the above results. Solutions of pNP or TBBPA in toluene, as well as pure toluene, were treated in the way described above. Spectrophotometric measurements showed no evidence of degradation. Thus, suitability of USB was proven for treating toluene and solutions thereof.

3.2. Ultrasonic behaviour of other flame retardants

Besides the already mentioned ones, the behaviour of other FRs (listed above) during US irradiation was examined. In particular, solutions of DECA in both 1-propanol and toluene, as well as solutions of DBB in 1-propanol were treated using USB. UV-Vis measurements did not reveal any degradation for treatments up to 120 min. DECA is especially known to be unstable in alcoholic solutions under the influence of light [21, 36]. Yet no evidence for US degradation could be found.

As mentioned above, spectral interference of possible degradation products and the original FRs could not be excluded. For this reason, treated solutions of TBPE, OBB, DBB, PENTA, OCTA, DECA, BDP and RDP in 1-propanol were analysed using HPLC/UV-Vis. Figure 4 shows the peak area evolution versus time of treatment for these FRs. These results reveal no evidence for degradation.

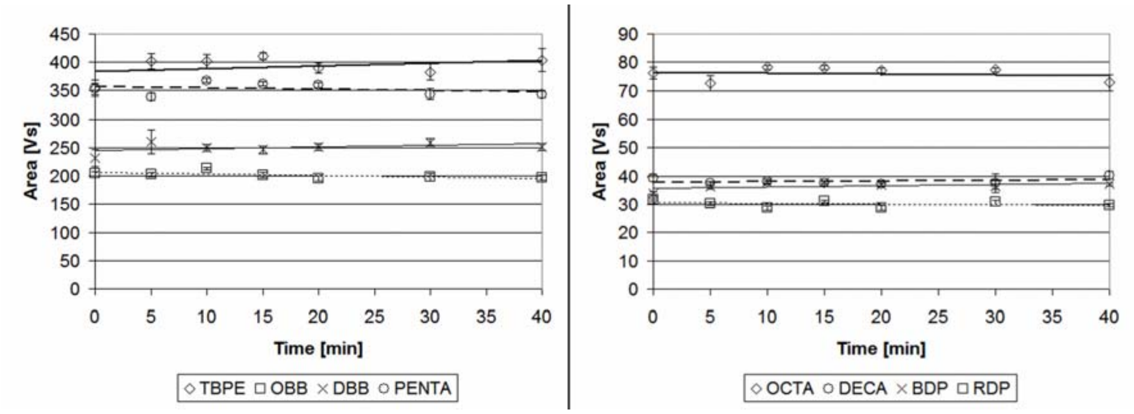

Fig. 4. Area vs. radiation time of eight FRs analysed by HPLC/UV-Vis. Error bars represent the standard deviation of 3 injections.

In Table 2, the area-% distribution of the eight major peaks contained in technical OCTA as a function of treatment time is given. A typical chromatogram of OCTA, from which the area-% distribution (Table 2) was calculated, is given in Figure 5. The increase in the area-% of the smaller peaks is a result of integration inaccuracy caused by the minor peak size. Chromatograms and given values clearly show that no changes in peak area-% occurred.

Table 2. Area-% distribution of eight peaks of OCTA vs. treatment time. Standard deviation was calculated from 6 injections. Peak numbers refer to the numbers given in Fig. 6.

	OCTA 1	OCTA 2	OCTA 3	OCTA 4	OCTA 5	OCTA 6	OCTA 7	OCTA 8
0 Min	0.38±0.02	5.51±0.06	37.73±0.06	1.47±0.02	9.1±0.2	28.4±1.6	1.58±0.05	15.8±0.1
15 Min	0.54±0.04	5.61±0.07	37.72±0.09	1.64±0.04	9.1±0.1	28.1±0.2	1.65±0.05	15.58±0.08
30 Min	0.54±0.03	5.57±0.07	37.7±0.1	1.68±0.07	9.2±0.2	28.1±0.1	1.75±0.06	15.6±0.1
40 Min	0.54±0.03	5.57±0.06	37.7±0.1	1.65±0.05	9.08±0.08	28.0±0.1	1.79±0.04	15.61±0.07

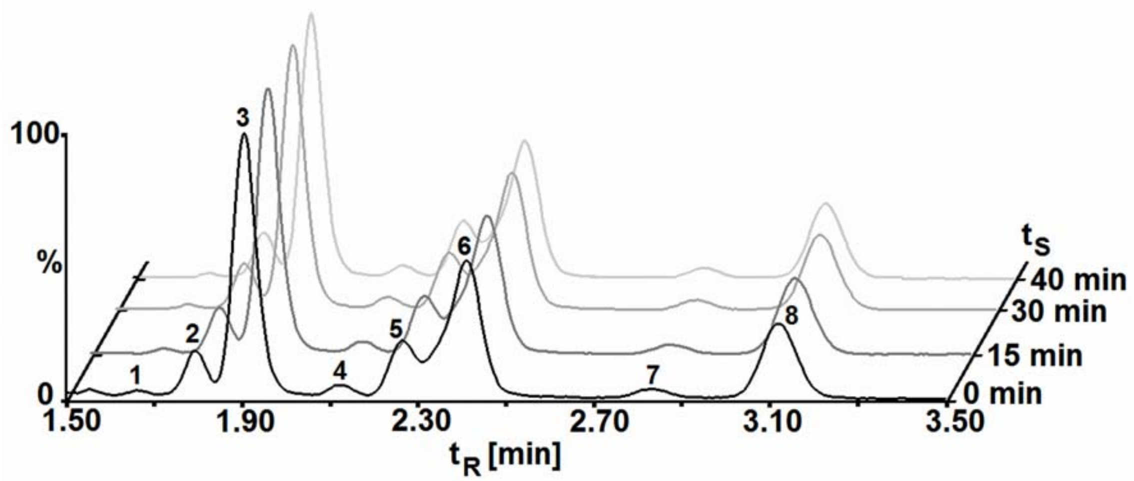

Fig. 5. Chromatograms of OCTA at 224 nm in 1-propanol treated with USB.

To exclude the influence of dissolved polymer on the degradation behaviour, a common polymer-FR-mixture [23] of TBPE and ABS was tested. For that purpose, pure ABS was suspended in 1-propanol, the suspension was spiked with TBPE, treated in the USB and analysed using HPLC/UV-Vis. No degradation was observed, which clearly showed that the polymer had no effect on the degradation behaviour of the FR.

This could also be demonstrated by investigations of the remaining FRs mentioned above. The results of HPLC/UV-Vis-measurements did not reveal any degradation after a treatment time of 40 min.

4. Conclusions

When the ultrasonic bath (USB) was used, degradation was exclusively observed in aqueous solutions, and only in combination with extended treatment times. In organic solvents, however, no degradation was detected.

When the ultrasonic probe (USP) was used, especially but not exclusively in combination with aqueous solutions, decompositions occurred after shorter treatment times. For this reason, aqueous extraction using USP is generally not recommended. This also applies when USP is used in combination with aromatic hydrocarbons as solvents, due to the observed sonolysis.

However, the results clearly show the stability of the selected FRs after treatment in the USB in combination with the applied organic solvents. The conditions applied for these investigations are exactly met by the conditions applied for the extractions performed in our group and described in refs. [21] and [22]. Furthermore, it was demonstrated that none of the investigated organic solvents enforced a degradation of analytes when treated in the USB for up to 120 min. Even DECA, which is known to be unstable in alcoholic solutions, was not decomposed in 1-propanol under the influence of the US.

Due to the proven stability of the analytes, it can be proposed that US assisted sample preparation is a suitable sample preparation method for the extraction of FR from polymers. As mentioned above, US assisted sample preparation provides the advantage of saving time and solvent. Furthermore, as mentioned in refs. [21] and [22], the extractions were performed in disposable test tubes and centrifugal tubes, respectively. Thus, no time and solvent consuming cleaning procedure is required, and the risk of contamination is minimized.

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