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Quantification of 3,5-di-tert-butyl-4-hydroxystyrene migrating from organic materials in contact with drinking water: True occurrence or analytical artefact?

Cynthia Kalweit *, Sabrina Berger, Thomas Rapp

Umweltbundesamt (Federal Environment Agency), Heinrich-Heine-Str. 12, 08645 Bad Elster, Germany

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ABSTRACT

The occurrence of 3,5-di-tert-butyl-4-hydroxystyrene (S.I) diffusing from cross-linked polyethylene (PE-X) pipes has been a topic of debate among industries, regulatory authorities, and scientists due to inconsistent findings. This study aimed to clarify the origin of S.I in migration waters and provide analytical recommendations for the certification process of pipe materials.

First, it was demonstrated that analysing migration waters by liquid–liquid extraction (LLE) followed by gas chromatography–mass spectrometry (GC/MS), according to EN 15,768 with an injector temperature of 250 °C, significantly biases the measured S.I concentrations, which are due to thermal degradation of 7,9-di-tert-butyl-1-oxaspiro[4,5]deca-6,9-diene-2,8-dione (S.II). Under these conditions, artificially high concentrations of S.I are obtained. Reducing the injector temperature to 150 °C improves S.I. accuracy, however, a reliable solid-phase microextraction (SPME) method was developed to quantify S.I. independently of S.II.

Second, four types of PE-X pipes were evaluated using LLE with injector temperatures of 250 °C and 150 °C, as well as SPME. LLE significantly increases the likelihood of detecting S.I concentrations in the migration waters well above the 0.1 μg/L limit stipulated by the European Commission Implementing Decision. Although the fraction of S.I formed from S.II is small (0.7–2% with LLE), the concentration of S.II itself can reach up to 100 μg/L (legal limit), leading to substantially biased S.I values that exceed 0.1 μg/L. Consequently, materials could fail European certification despite being compliant, which would have significant commercial implications.

Therefore, the use of SPME is recommended as an alternative method for analysing S.I in this context.

1. Introduction

For decades, research has focused on materials used in contact with drinking water, significantly improving its quality. Thanks to scientific and technological advances, numerous solutions have been developed to ensure the sanitary safety of drinking water. Among the various pipe materials used for drinking water distribution, polyethylene (PE) is one of the most common. For internal plumbing systems PE is often cross-linked (PE-X) to enhance its thermal resistance for use with warm and hot water.

To achieve a highly stable material, antioxidants and other stabilizers are added to the polymers. These additives protect the material against oxidative degradation during manufacturing, processing, final use, and recycling [1]. The aim of stabilizers is to prevent polymer chain scissions in the material. To achieve this, the stabilizers undergo a chemical transformation, which is often not clearly defined, leading to the migration of unexpected substances into drinking water. This may impair water quality and even pose health risks to consumers. Consequently, it has become essential to identify the relevant degradation products.

A large number of contaminants have already been reported in the literature [2–4]. In 2002, Brocca et al. [5] identified ten substances migrating from PE pipes that show similarities to the antioxidants used during pipe manufacturing. They have been widely reported in the literature, with migration levels from PE pipes into drinking water typically in the low μg/L range [2–8]. Among them, 3,5-di-tert-butyl-4-hydroxystyrene (referred to here as S.I – see Fig. 1) has been the subject of debate among industries, regulatory authorities, and scientists due to discrepancies in its reported occurrence. While some studies suggest that S.I migrates from PE pipes into drinking water [5,9–11],

* Corresponding author.
E-mail address: cynthia.kalweit@uba.de (C. Kalweit).

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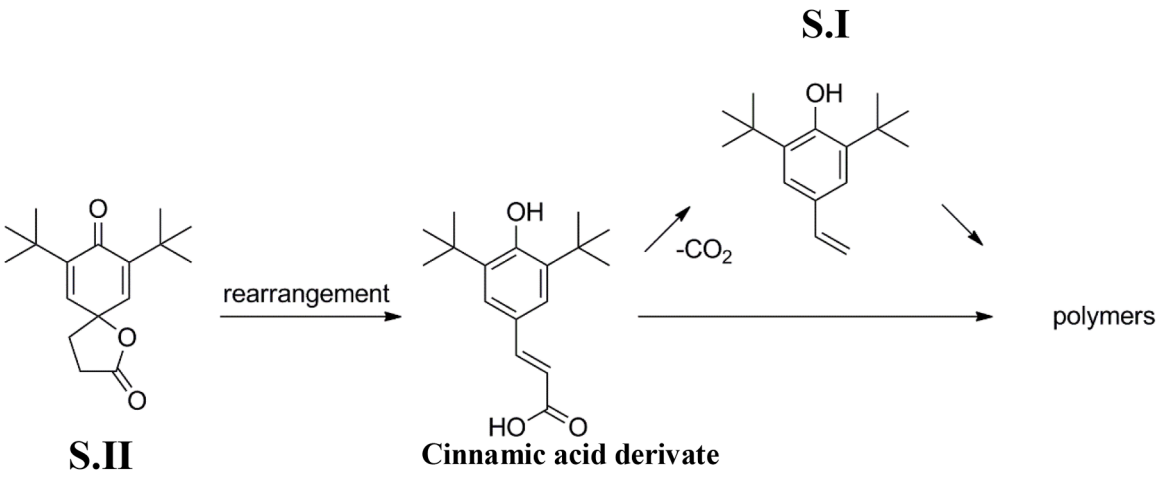

Fig. 1. Degradation pathway of S.II to S.I [12].

Table 1
Material sample description.

Pipes	Year of purchase	Designation	Barrier layer	Outer diameter (mm)	Wall thickness (mm)	S/V (dm^{-1})
PE-Xa	**2011**	PE-Xa	EVOH	20	2.8	27.8
PE-Xb	**2002**	PE-Xb (1)	Aluminium	16	2.0	33.3
PE-Xb	**2023**	PE-Xb (2)	Aluminium	20	2.0	25.0
PE-Xc	**2007**	PE-Xc (1)	Aluminium	20	2.0	25.0
PE-Xc	**2023**	PE-Xc (2)	Aluminium	20	2.8	27.8
PE-Xc	**2025**	PE-Xc (3)	Aluminium	17	2.8	34.8
PE-RT	**2010**	PE-RT (1)	Aluminium	20	2.0	25.0
PE-RT	**2025**	PE-RT (2)	Aluminium	16	2.0	33.3

Depending on dimensions of the tested pipes four to ten pipes segments of the same length (2 m) were necessary to prepare the required water volume (600 mL) for the LLE and SPME analysis.

there is evidence indicating that it might instead be an analytical artefact originating from 7,9-di-tert-butyl-1-oxaspiro[4,5] deca-6, 9-diene-2,8-dione (referred to here as S.II) [12,13]. Kalweit et al. [12] observed that S.I, resulting from decarbonization of S.II, is consistently detected by gas chromatography coupled with mass spectrometry (GC/MS) when S.II standards are injected into the gas chromatograph set-up with an injection port temperature of 250 °C. It is believed that S. II undergoes rearrangement to a cinnamic derivative, which is itself prone to polymerisation, potentially forming S.I during the process (Fig. 1).

While toxicological assessments have been conducted for most of the degradation products identified so far [13], no such studies are available for S.I. In the Commission Implementing Decision (EU) 2024/367 [14] maximum tolerable concentrations at the tap (MTC_{tap}) are set for the ten substances identified by Brocca et al. [5]. As no further toxicological studies are available for S.I, the MTC_{tap} is 0.1 µg/L. The migration testing procedure for the final materials is defined in the Commission Implementing Decision (EU) No. 2024/368 [15], stipulating that the identification and semi-quantitative analysis of unexpected substances must be carried out using a GC/MS screening, in accordance with the standard EN 15768 [16]. Hence, critical questions arise regarding whether

(1) the analytical method allows quantification of S.I within the range of the MTC_{tap} (0.1 µg/L),
(2) S.I migrates directly from the material or results from the degradation of S.II during analytical procedures.

To address these questions an alternative method for determining S.I was established using solid-phase microextraction (SPME) combined with GC/MS. The aims of establishing an alternative method were to detect S.I independently of the occurrence of S.II and to improve the quantification of S.I. Additionally, the quantitative analysis of S.I and S. II following the extraction procedure in accordance with EN 15768 [16] was validated. Both quantitative methods were then applied to compare the concentrations of S.I and S.II leaching from different PE pipes in migration waters.

2. Materials and methods

2.1. Materials and chemicals

Eight domestic plumbing pipes made from four PE-based materials were purchased on the local German market (Table 1). The different PE types are: PE-Xa (cross-linked by peroxides), PE-Xb (cross-linked by silanes), PE-Xc (cross-linked by electron beam processing) and PE-RT (raised temperature resistance). The dates of purchase are given in Table 1. The pipes received before 2023 were stored at room temperature, with the ends covered with aluminum foil until testing. All of them were certified for drinking water applications by national certifying bodies. While the two PE-Xb pipes are products of the same manufacturer, all PE-Xc pipes and PE-RT were purchased from different manufacturers. All pipes are multilayers products. PE-Xa has an EVOH (ethylene-vinyl alcohol copolymer) oxygen barrier layer and the other materials have an aluminum layer in-between an outer and an inner plastic layers. This aluminum layer can be regarded as a total barrier so that the outer layers do not affect the water in contact with the inner layers. The dimension of the different pipes and their corresponding ratio between surface area and water volume (S/V) for the migration tests are also given in Table 1.

With each of these product samples a migration test was performed followed by (1) liquid-liquid extraction (LLE) & GC/MS analysis as well as (2) SPME in a liquid-phase & GC/MS analysis.

The ultra-pure water used was from an UF / UV system (SG Hamburg-Barsbüttel, Germany). Reference standard S.I (purity of 95%)

Table 2
Preparation of the migration water (cold and warm test) following the European Standard EN 12,873–1 [17].

COLD WATER (23°C)					WARM WATER (60°C)	
		Migration	Overall contact time (d)	Migration		
Pre-treatment	24 h Stagnation	0	1	0	24 h Stagnation	Pre-treatment
	72 h Stagnation	1	2	1	24 h Stagnation	
			3	2	24 h Stagnation	
			4	3	24 h Stagnation	
	72 h Stagnation	2	5	4	72 h Stagnation	
			6			
			7			
	72 h Stagnation	3	8	5	24 h Stagnation	
			9	6	24 h Stagnation	
			10	7	24 h Stagnation	

Grey boxes: the samples were dismissed and not analysed. Although the standard stipulates to dismiss the pre-treatment waters, it was here analysed.

was obtained from BLD Pharmatech (Germany) and S.II was available from Paragos (Germany). For the extraction, dichloromethane from Rathburn (United Kingdom), HPLC grade and stabilized with 0.1% methanol was used.

2.2. Preparation of the migration waters

The migration waters were prepared according to EN 12,873–1 [17] following the sequence presented in Table 2. This procedure is used for the certification of products in contact with drinking water in the EU. After a pre-treatment procedure of flushing, the migration procedure is carried out as follows: test pieces were filled with freshly prepared ultrapure test water: the pipes segments were filled and left in the temperature-controlled laboratory at 23 °C (cold water test) for 72 h. For the pipes intended for testing with warm water, filled pipe segments were placed in an oven at 60 °C for 24 h. At the end of each migration period the migration waters obtained were directly transferred into cleaned glass bottles and vials for LLE-GC/MS and SPME-GC/MS, respectively. For each next migration period, test pieces were refilled and followed the same procedures. Blanks were similarly prepared to check for any eventual external contamination.

2.3. Analytical methods

2.3.1. Liquid-liquid extraction followed by gas chromatography / mass spectrometry (LLE-GC/MS)

For the quantification of S.I and S.II using LLE, the extraction of the calibration standards prepared in ultra-pure water and of the migration water samples was performed according to EN 15768 [16]: An isotopically labelled internal standard mix containing d_{21}–2,6-Di-tert-butyl-4-methylphenol (d_{21}-BHT) (Neochema, Germany) was added to 500 mL of the migration water samples or to the calibration standards, respectively, resulting in a final d_{21}-BHT concentration of 8 µg/L. Then the migration water samples and the calibration standards were extracted twice with 50 mL dichloromethane at pH 2 and also twice at pH 10. The four extracts were combined and dried over sodium sulphate. The extract was reduced to a final volume of approximately 500 µL by evaporation using a Kurdena Danish apparatus. The samples were finally transferred to an auto-sampler vial and analysed with an Agilent 6890 GC coupled to an Agilent 5973 MS (Agilent Technologies, Germany): a volume of 1 µL was injected splitless at 150 °C (LLE_{150}) and 250 °C (LLE_{250}). The separation was carried out by a DB-5 MS column (60 m x 0.25 mm x 0.25 µm) with a helium carrier gas at a flow rate of 1.0 mL/min. The initial oven temperature was 35 °C, held for 4 min followed by an 8 °C per minute temperature ramp to 300 °C and held for 20 min. The MS ionization was operated in selected ion monitoring (SIM) mode. The quantification ion was *m/z* 217 for S.I and 205 for S.II. The control ions were *m/z* 232, 218 and 57 for S.I and *m/z* 217, 189 and 175 for S.II.

2.3.2. Liquid-phase – solid-phase microextraction (SPME) – GC/MS

As an alternative method, the migration waters were analysed using SPME. To perform this, 20 µL of the internal standard d_{21}-BHT, resulting in a final d_{21}-BHT concentration of 8 µg/L, was injected into a final volume of 100 mL of the migration waters. Then, 18 mL of the migration water with internal standard was extracted from the aqueous phase using a polyacrylate fiber (85 µm – fused silica, Merck, Germany) – previously conditioned in the inlet of the GC for a given period of time and temperature as required by the manufacturer – via stirring at 250 rpm (revolutions per minute) for 15 min with a Robotic Pro auto-sampler (Gerstel, Germany), while maintaining a temperature of 40 °C. The analytes were desorbed from the fibre at 220 °C for 1 min in the GC's inlet using splitless mode. These parameter settings were aligned with those used by a collaborating partner and were chosen to ensure comparability with prior data. As the original method is not publicly available, the selected parameters, such as extraction/desorption time and temperature, were subsequently examined and experimentally verified within this study. The polyacrylate fibre was used for approximately 350 injections, with a maximum of about 400 injections under the applied conditions. Fiber performance was monitored through regular analysis of quality control (QC) samples and evaluation of calibration curves. A decline in performance was indicated by deviations in QC results or when calibration criteria were no longer fulfilled, at which point the fibre was replaced.

Separation and oven conditions were identical to those mentioned in the previous section.

2.4. Conversion of test results to estimate the concentration at the tap

The ratio of the surface-area of the material to the volume of the water (S/V) for the testing is defined by the geometry of the pipe. The stagnation periods (contact time) specified in EN 12873–1 [17] do not reflect the real use of the end products. Therefore, the concentrations determined in the migration tests are converted to estimate the maximal

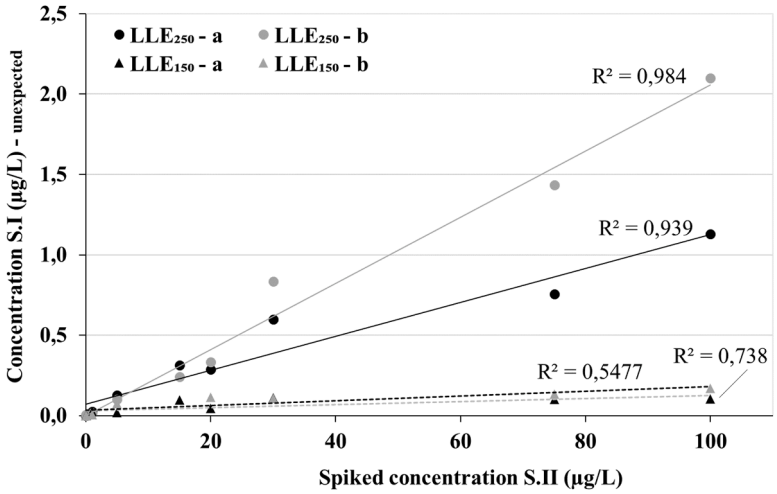

Fig. 2. Concentration of S.I (unexpected) determined in the spiked solution of S.II. Injector temperature set at 150 °C (LLE_{150}) and 250 °C (LLE_{250}).

concentration at the consumer's tap (C_{tap}):

$$C_{tap} = (F_c \times C_{measured}) / ((S / V) \times t) \quad (1)$$

where

F_c is the conversion factor for pipes, here $F_c = 20$ d/dm for pipes with ID < 80 mm (internal plumbing system)

$C_{measured}$ is the concentration measured in the migration waters according to EN 12873–1 [17],

S/V is the surface area-to-volume ratio in the test setup, and t is the duration of the migration period in days.

The conversion factors and procedure are defined in the Commission Implementing Decision (EU) 2024/368 [15]. The concentration as C_{tap} is compared with MTC_{tap} to assess the acceptance of the product.

3. Results and discussion

3.1. Unexpected level of S.I with LLE

When S.II standards were analysed using LLE, an additional peak was consistently detected by GC/MS, which did correspond to S.I, indicating either contamination of the S.II standard or degradation of S.II to S.I during analysis. The transformation observed during analysis could occur either during the extraction procedure (performed at different pH values) or within the GC device due to the high temperature. Since the additional peak was also detected when standards of S.II were prepared directly in dichloromethane, it was hypothesised that high temperatures may promote the transformation of S.II to S.I, as the GC injection port was set at 250 °C. Reducing the injection port temperature to 150 °C clearly resulted in reduced S.I formation for a given S.II concentration as

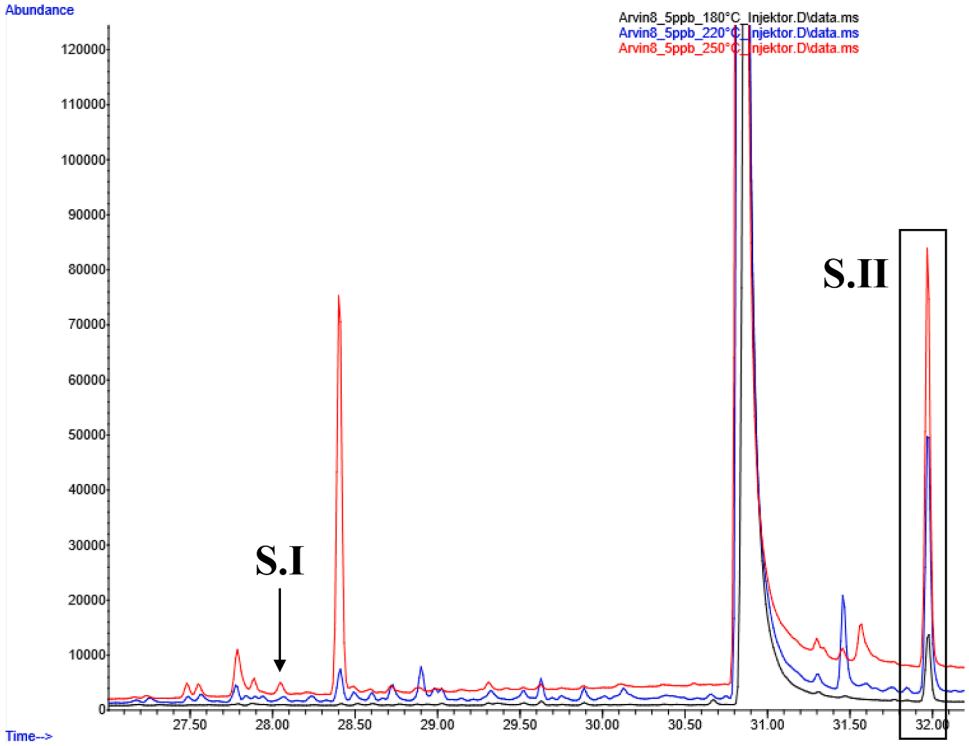

Fig. 3. SPME Chromatogram of S.II standard spiked at 5 µg/L at three desorption temperatures (180 °C, 220 °C and 250 °C).

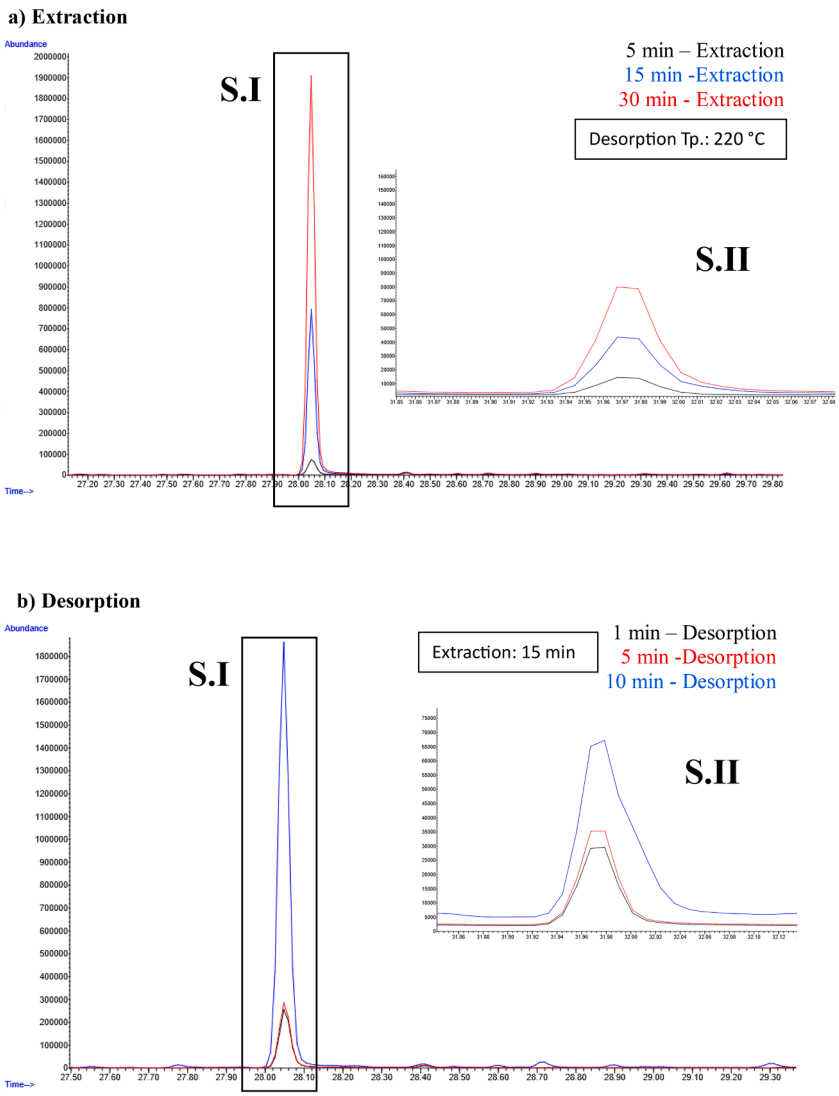

Fig. 4. Abundance for the peaks of S.I and S.II for different extraction and desorption times (desorption temperature: 220 °C) of standard solutions of S.I and S.II at 5 µg/L respectively (extraction: 15 min).

shown in Fig. 2. Even when a transformation from S.II to S.I occurred, it was still possible to independently calibrate both S.I (0.1 to 10 µg/L) and S.II (0.1 to 500 µg/L) at both injection port temperatures. To investigate the potential formation of S.I from S.II, eight S.II standards at different concentration levels (1, 5, 15, 20, 30, 75, and 100 µg/L) were analysed in duplicate on different days at 250 °C (LLE_{250}) and at 150 °C (LLE_{150}). In Fig. 2, the determined concentrations of S.I. are plotted against the spiked concentration of S.II. for the individual S.II standards. Although a variation in the conversion of S.II to S.I was observed when S.II concentrations were above 60 µg/L, it can be concluded that a better correlation can be observed when the injection port temperature was set at 250 °C. At 150 °C, all the S.I concentrations were below the MRL (minimum reporting level) (0.38 µg/L), making it difficult to establish a correlation. Nonetheless, it is evident that the partial conversion of S.II to S.I is mainly caused by the injection port temperature. The fraction of S.I formed from S.II was approximately 2% at 250 °C and less than 1% at 150 °C. This degradation is negligible for the quantification of S.II. However, since the MTC_{tap} for S.I is 0.1 µg/L compared with 100 µg/L for S.II, even a small conversion of S.II to S.I during the analysis (0.7 – 2%) could result in a non-compliance with S.I limits, even if S.I is actually not present in the migration waters. For example, up to 2 µg/L S. I could be detected (Fig. 2), although the substance was not present in the standard solutions. This indicates clearly that the occurrence of S.I. in the migration waters is questionable, even when determined by applying the described procedure. It remains difficult to distinguish whether the detected S.I. is entirely formed during the analytical procedure or if it was already present at low concentrations in the migration water. To address this, an alternative method was developed, a method that ensures the measured concentrations are not affected by the presence of S.II.

3.2. *SPME method development*

Several parameters were tested: (1) head-space (HS)-SPME vs. liquid-phase (LP)-SPME, (2) fiber type: divinybenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) vs. polyacrylate, (3) solvent of S.I standard dilution: methanol vs. acetonitrile, (4) with or without addition of sodium chloride (NaCl) and (5) shaking vs. stirring. The method was optimized for the quantification of S.I independently of the presence of S.II and to achieve a low detection limit for S.I. The best response and peak shape were obtained by applying the polyacrylate fibre in the liquid phase, which differs from the study of Lützhøft et al. [18], which reported antioxidants degradation products migrating to drinking water from PE materials and PEX pipes applying PDMS/DVB fibre in HS. Although, the reported substances [18] have structure similarities with S.I and S.II, both substances were not part of the study and this can

Table 3
Method performance SPME-GC/MS vs. LLE-GC/MS.

Method	Substance	Stability RSD (%)[a]	Detection limit LOD[b] (µg/L)	MRL (µg/L)[c]
SPME-GC/MS	**S.I**	3	0.02	0.05 – 0.06
SPME-GC/MS	**S.II**	17	0.30 – 0.33	0.90 – 0.99
LLE-GC/MS	**S.I**	13	0.13	0.38
LLE-GC/MS	**S.II**	11	0.65	1.95

[a] The stability RSD (relative standard deviation) was assessed for SPME with a 0.5 µg/l solution of S.I and a 15 µg/L solution of S.II both analysed over three days for six replicates. For LLE, the RSD was assessed with a 0.25 µg/L solution of S.I and a 10 µg/L solution of S.II extracted and analysed over three days for six replicates.

[b] Six replicates of a standard solution at 0.1 µg/L of S.I (SPME), at 0.5 µg/L of S.II (SPME), at 0.25 µg/L of S.I (LLE) and 0.5 µg/L of S.II (LE) were extracted and analysed over a period of three days for determining the LOD. LOD was calculated using the equation: $LOD = St_{(n-1,\ 1-\alpha=0.99)}$, where $t_{(n-1,\ 1-\alpha=0.99)}$ = Students t value for the 99% confidence level with n-1 degrees of freedom (3.365 for 6 replicates), n = number of replicates and S = standard deviation of the replicate analyses.

[c] Corresponds to the minimum reporting level (MRL) and is the threshold expected for accurate quantification in an unknown sample. It has to be at least three times the limit of detection.

explain, why the fibre selection and the phase differs. Desorption temperature of 180 °C, 220 °C and 250 °C were first tested with a standard solution of 5 µg/L of S.II, to make sure that no S.I was detected as it is the case with the LLE. Fig. 3 shows that at 250 °C a small peak could be seen when the desorption temperature was set at 250 °C. Although the response is small (less than 600 counts) and could be neglected, the method was validated with 220 °C, which also enables better response of S.II than with a desorption temperature of 180 °C. Fig. 4. shows the effect of the extraction (a) and the desorption (b) times on the abundance of the respective peaks for S.I and S.II. The response increase with the extraction time (Fig. 4a). It is assumed that no equilibrium was reached within the tested time, as it was also reported by Lützhøft et al. [18]. However, the extraction time was chosen to be 15 min, which resulted in sufficient signal and precision for the quantification of S.I and S.II. The choice of 1 min for desorption (Fig. 4b) was based on discussion with a collaborating partner. There was no difference observed between 1- and 5-minute desorption. A time of 10 min would result in a higher response. However, for comparison reason and because 1 min was still enough to give a sufficient signal, this specific time of desorption was maintained.

The method performance is presented in Table 3. The validation occurred with quality controls prior the quantification of analyte. The stability given as the relative standard deviation (RSD) of six replicates of a 0.5 µg/L and a 15 µg/L solution for S.I and S.II, respectively and extracted and injected over three days is low and demonstrates the good reproducibility of the method, but also that the substances were stable over the time. The lowest standard was 0.1 µg/L for both substances and for the three analytical methods, the highest was 10 µg/L for S.I and 500 µg/L for S.II. In total ten calibration points were plotted for each of them, dividing the range between a lower and a higher one. This enabled a more precise quantification in the low range, especially for S.I. The limit of detection was in the low µg/L range. The different criteria reported here assure a reliable quantification of S.I and S.II with SPME. The SPME method, in which the sample is extracted by adsorption onto a solid phase at a lower temperature (40 °C in this case), helps preserve the chemical integrity of the compounds. Although the GC/MS injector is set at 220 °C, the method is considered gentler than direct injection, as the analytes on the fibre are not directly exposed to high temperatures as when injected in a liquid sample. This reduces the risk of thermal degradation.

It can be here concluded that with this SPME method, a sound distinction between the two substances is possible, and hence, when pipe samples are analysed, the concentrations obtained for S.I correspond to a more accurate value rather than an artefact caused by the presence of S.II.

3.3. Migration of S.I and S.II from PE-X materials

The second objective of this study is to compare the concentrations of S.I and S.II migrating from PE pipes determined by applying (1) SPME, (2) LLE_{250} and (3) LLE_{150}.

For this, 8 pipes were selected, four of them were older than ten years old and four were newly bought between 2023 and 2025 (see detailed information in Table 1).

The Commission Implementing Decision (EU) 2024/368 [15] stipulates the compliance with the pass/fail criteria at the 10th day of testing. For this reason Figs. 5 and 6 present the concentrations of S.I and S.II, respectively, determined at the 10^{th} day of overall contact time for the cold (a) and warm (b) water tests using the three analytical methods. The red line (in Fig. 5a) corresponds to the maximum tolerable concentration of S.I at the tap (MTC_{tap}), which is fixed at 0.1 µg/L in the Commission Implementing Decision (EU) 2024/367 [14]. The observed concentrations of S.I. determined under cold and warm conditions differ considerably within the same sample across the three quantification methods. It is also evident that the LLE_{250} yields the highest detected concentrations of S.I. in the samples. The concentrations of S.I, expressed as C_{tap}, detected at 23 °C using LLE_{250} range from below the MRL of 0.05 µg/L up to 0.67 µg/L. In contrast, the concentrations detected in samples extracted using the other two methods remain below the MRL. The difference becomes even more pronounced in the migration waters from the warm water test, where concentrations detected using LLE_{250} range from below the MRL to as high as 26 µg/L, while the levels measured with LLE_{150} and SPME reached at the maximum 0.34 µg/L and 0.60 µg/L, respectively. This is one of the key findings of this investigation: the method used for quantification has a major impact on the resulting value, potentially biasing it and leading to significantly false results.

When comparing with the values found for S.II, presented in Fig. 6(a) and (b), it can be seen that the extraction method has little to no effect on the results. Although some differences can be observed at higher concentrations between SPME and LLE, the quantification using LLE_{150} and LLE_{250} yielded very similar results, indicating that the injector temperature has here no significant impact.

In four materials – PE-Xa, PE-$Xb_{(1)}$, PE-$Xc_{(1)}$ and PE-$RT_{(1)}$, the reported values of S.II (Fig. 6b) measured in the migration water from the warm water tests were either in the range or well above the fixed MTC_{tap} of 100 µg/L. However, these pipes were purchased at least 14 years ago, and it is known that during long-term storage – when only exposed to air – the amount of stabiliser decreases [19]. As a result, higher amounts of S.II or its direct precursors, such as 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propanoic acid or cyclohexa-1,4-dien-1,5-bis(tert-butyl)-6-one-4-(2-carboxy-ethylidene), proposed by Löschner et al. [2] as degradation products of antioxidants like Irganox 1010, are accumulated in the pipes. This leads to increased concentrations of S.II in the migration waters as shown by Kalweit et al. [12].

Section 3.1 clearly demonstrates a relationship between S.I and S.II when the injector of the GC/MS is set at 250 °C. The more S.II is present in the water the more S.I is detected. Consequently, this explains the high concentrations of S.I, presented in Fig. 5(a) and (b) determined by applying LLE_{250} for the pipes stored for a longer period. However, it can be concluded that the high values of S.I detected in the migration waters under cold and warm condition are an artefact of the analytical method and does not represent the actual concentrations of the samples.

The concentrations determined using the LLE_{150} method provide a reasonable approximation and are likely closer to the actual levels of S.I

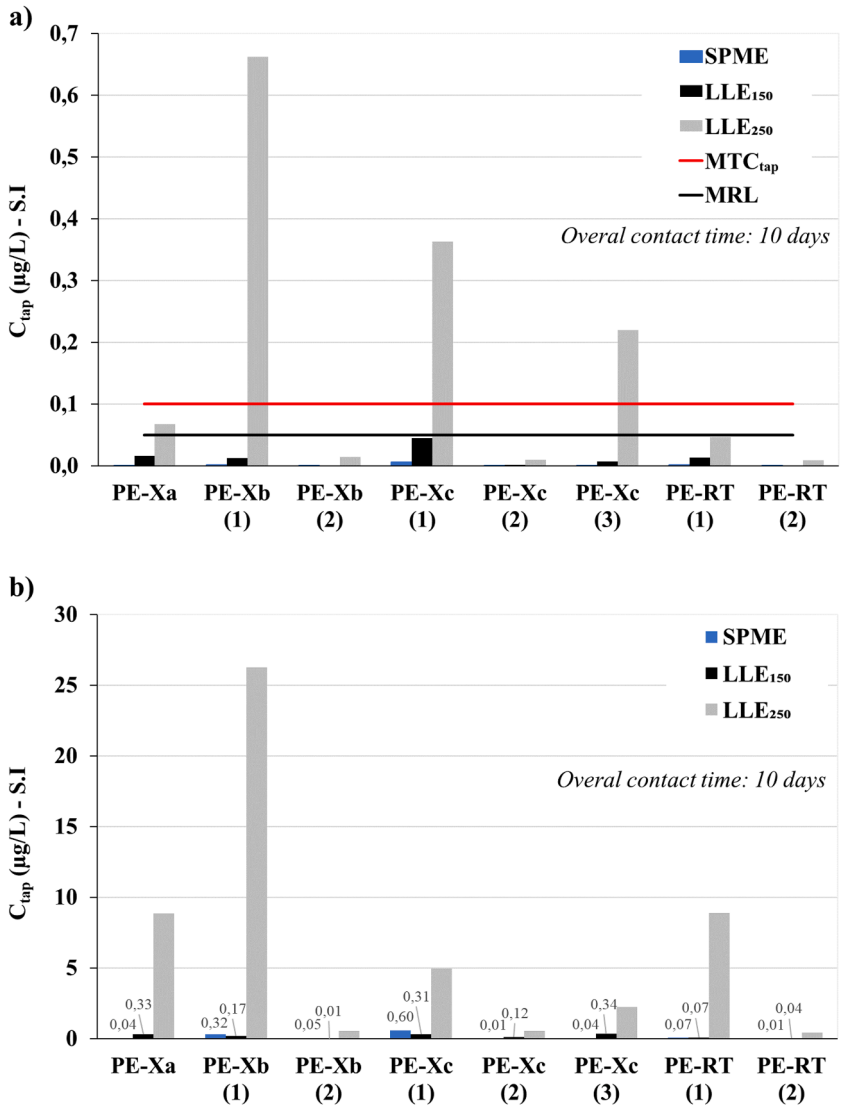

Fig. 5. Detection of S.I from PE material under cold (23 °C) (a) und warm (60 °C) (b) conditions – Concentrations determined at the 10th migration day. MTC_{tap}: Maximum Tolerable Concentration at the tap (0.1 µg/L). MRL: minimum reporting level (0.05 µg/L – see Table 3).

in the migration waters. For the determination of more accurate concentrations of S.I in the migration waters the SPME method remains the most suitable and reliable analytical approach. If we trust these results, then S.I might indeed be present in concentrations exceeding 0.1 µg/l as C_{tap} in the migration waters. This means that the transformation of S.II to S.I also occurs either in the pipe material or in the migration waters but due to the lower temperatures (23 °C and 60 °C) compared with the temperatures in the injection port of the GC at a much lower rate.

3.4. Migration of S.I in relation to S.II

In accordance with the Commission Implementing Decision (EU) 2024/368 [15], an additional pass/fail criterion for relevant substances is that C_{tap} shall not increase over time. For this, the concentrations of S.I and S.II were determined in the migration samples of the 1st, 2nd and 3rd migration period of the cold water test according to EN 12873–1 [17]. In the migration tests carried out with warm water the migration waters of the 6th and the 7th migration period were analysed additionally (see Table 2). Only the results obtained by applying SPME are considered in the following, as this method has been shown to be the most representative. The results (not presented here) indicate a slight decreasing trend observed after the fourth day of overall contact time. Thereafter, most concentrations remained stable.

All data generated during the migration test performed at 60 °C and analysed by applying SPME were then plotted to determine whether a relationship exists between the measured concentrations of S.I and S.II. The results are presented in Fig. 7. Most values for S.I were below the MRL of 0.05 µg/L and are therefore considered unreliable. Among the remaining data, no clear correlation can be identified. For instance, S.I concentrations ranging between 0.10 and 0.15 µg/L were observed for PE-Xa, $PE\text{-}Xb_{(2)}$, and $PE\text{-}RT_{(1)}$. However, the corresponding S.II concentrations in the same migration waters varied significantly: while PE-Xa and $PE\text{-}RT_{(1)}$ showed high S.II levels (above 250 µg/L), $PE\text{-}Xb_{(2)}$ exhibited much lower concentrations (below 11 µg/L). In the $PE\text{-}Xc_{(3)}$ material, detected concentrations of S.I were 0.17 µg/L and 0.22 µg/L, while S.II levels were 61 µg/L and 51 µg/L, respectively. However, the reported concentrations of S.I are close to the MRL making it difficult to establish a clear correlation. Due to complex chemical reactions occurring within the pipe material and the migration water, and because S.I and S.II are prone to further reactions [12], no clear correlation could be established. However, since S.I is present at very low concentrations, the weak correlation observed may also be attributed to limited analytical precision at these low concentration levels. Nevertheless, it is reasonable to assume that if S.II complies with its MTC_{tap} of 100 µg/l, the MTC_{tap} of

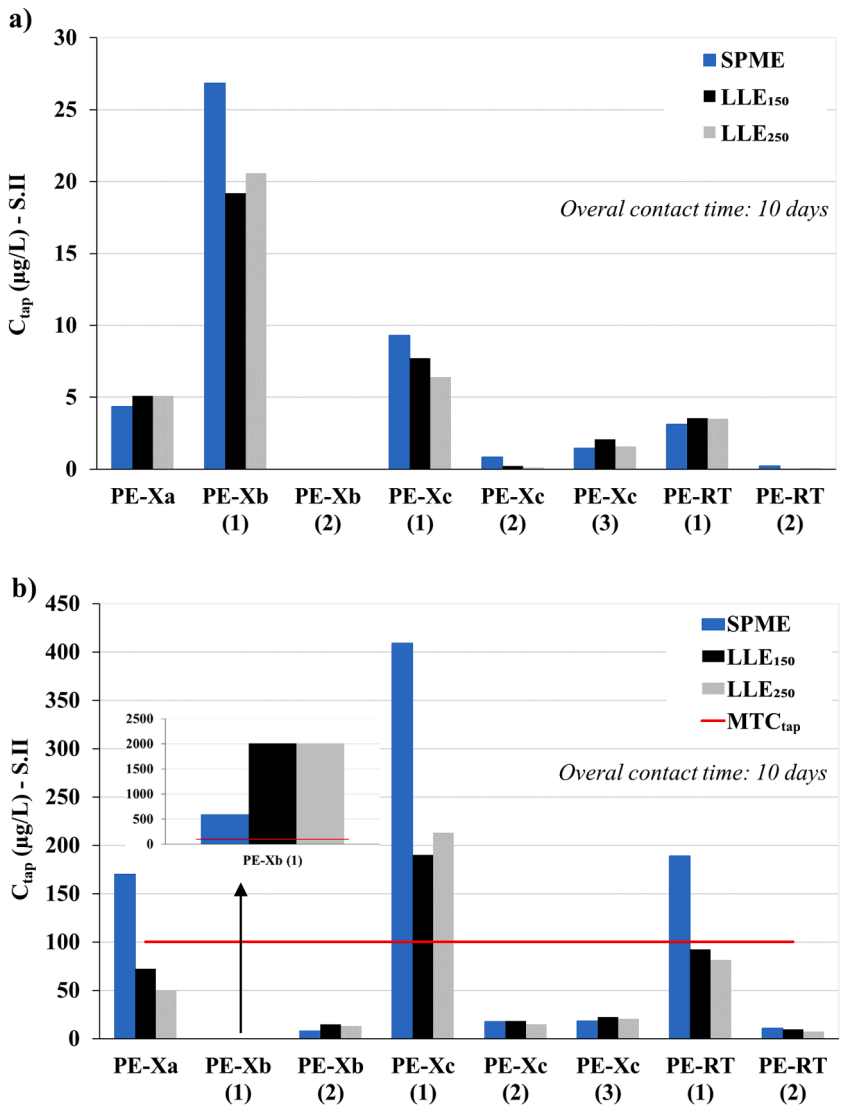

Fig. 6. Migration of S.II from PE material under cold (23 °C) (a) und warm (60 °C) (b) conditions – Concentrations determined at the 10th migration day. MTC_{tap}: Maximum Tolerable Concentration at the tap (100 µg/L).

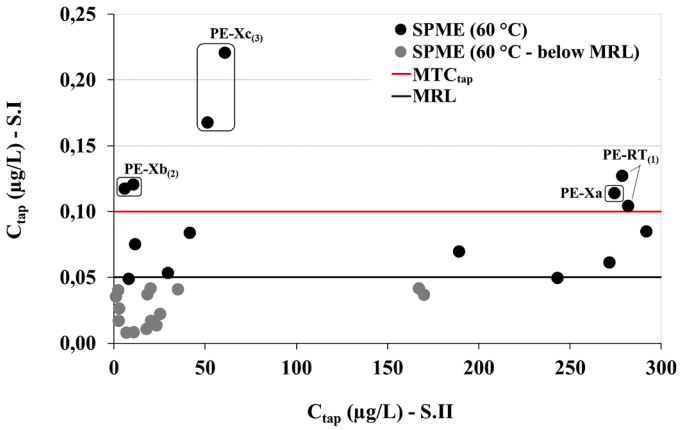

Fig. 7. Correlation between S.I and S.II.

0.1 µg/l for S.I will also likely be met.

4. Conclusions

The screening method applying a LLE according to EN 15768 [16] is a reliable method for the identification of leachable substances from materials in contact with drinking water using GC/MS with an injector temperature set at 250 °C [2]. The procedure described in this standard can also be used for the quantification of the identified substances, provided that standards for these substances are available. However, this method leads to biased results for the concentration of S.I, which stems from the thermal degradation of S.II in the injector. As a consequence, the measured levels of S.I are significantly higher than the actual amounts migrating from the material into drinking water.

To ensure safety and regulatory compliance, the Commission Implementing Decision (EU) 2024/367 [14] sets an MTC_{tap} = 0.1 µg/L for S.I, which is a very low value compared with the MTC_{tap} = 100 µg/L for S.II. By performing LLE, S.II partially decomposes to S.I, even with an injector temperature set at 150 °C, resulting in an inaccurate quantification of S.I, with measured levels higher than 0.1 µg/L. Processing the migration water with LLE_{250} greatly increases the likelihood of detecting concentrations of S.I well above the MTC_{tap}, which could prevent the tested material from meeting the criteria for European certification and have significant commercial consequences. Hence, despite the legal

documents cited above, the use of SPME, as an alternative method for the analysis of S.I is recommended in the present context.

The different value reported here also indicated that the fixed value of 0.1 μg/L rise the question of the applicability. Though, this study has demonstrated that the substance could be detected with SPME down to 0.05 μg/L, the reproducibility requires good laboratory practices. The quality check is essential. Most of the value found here with SPME at the 10^{th} day of overall contact time were below the MRL and 0.1 μg/L, which indicates that only marginal concentrations of S.I can be expected in the drinking water, if at all. However, because of the difficulty of analysis, and the risk of detecting biased concentration well above 0.1 μg/L, certain products could result in non-compliance. A comprehensive toxicological assessment for S.I might derive a higher MTC_{tap} and would reduce the risk for a non-compliance for certain pipes.

Declaration of generative AI and AI-assisted technologies in the manuscript preparation process

During the preparation of this work, the author(s) used ChatGTP to enhance language and readability. After using this tool/service, the author(s) reviewed and edited the content as needed and take(s) full responsibility for the content of the publication.

CRediT authorship contribution statement

Cynthia Kalweit: Writing – review & editing, Writing – original draft, Visualization, Validation, Formal analysis, Data curation, Conceptualization. **Sabrina Berger:** Writing – original draft, Visualization, Validation, Conceptualization. **Thomas Rapp:** Writing – review & editing, Writing – original draft, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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