

Short Communication

Influence of dissolved gases in the dynamic headspace analysis of styrene and other volatile organic compounds and improvement of their determination

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Abstract

The on-line purge and trap dynamic headspace technique (PTI) was optimized for styrene. High-boiling volatiles such as styrene were efficiently desorbed from oil and from oil–water matrices. The effects governing the desorption were identified by comparison with an off-line procedure. The recovery of styrene depends dramatically on the amount of fat and on the desorption temperature. For oil–water systems, the aqueous phase had to be saturated with both sodium chloride and carbon dioxide; with PTI, no desorption occurs if the sample is initially degassed; regassing improved desorption, carbon dioxide giving the best results.

1. Introduction

Volatile organic compounds (VOCs) are usually determined by gas chromatography (GC). The main difficulty in their determination is their isolation from various matrices, especially for the higher boiling compounds. Styrene (b.p. 145°C) is a ubiquitous contaminant, which will be considered here as a model of these higher boiling VOCs. The isolation of styrene from solid, fatty or aqueous matrices has been carried out by azeotropic [1] and vacuum [2] distillation, and also by static [3] and dynamic headspace [4–8] methods. The latter can be either on-line or off-line. We report here a net improvement of the on-line method usually known as purge–

trap–inject (PTI), mainly by paying attention to the influence of dissolved gases.

In off-line GC, styrene is swept from the matrix by a purge gas such as helium or nitrogen and trapped in a solvent [4] or on an adsorbent such as Tenax, from which it is then eluted [5]. In on-line GC, the preconcentration can be carried out on an adsorbent [6,9] or on a cryogenic trap. This is achieved on the head of the chromatographic column at room temperature [10,11] or, in the PTI method, on a coated capillary cooled well below room temperature, and connected to the column [12]. The cold trap usually contains a small amount of adsorbent [12]. The main advantage of the cold trap method is that if other volatiles are present, the efficiency of the trapping is not affected by their chemical structure [5] as with an adsorbent. The main difficulty associated with the PTI cold trap method is that when aqueous matrices are used,

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the swept water must be selectively condensed before reaching the cryogenic trap, which would otherwise be blocked [12].

With the PTI technique, the recovery is governed by several processes, such as the removal of hydrocarbons from the liquid matrix, their discrimination from the condensed water or their condensation along the glass tubing of the device. In order to monitor separately the influence of these processes, we repeated the experiments with an alternative off-line purge and trap method, using Carbotrap, an adsorbent not sensitive to the presence of water vapour. This method consists of a purge sequence towards an adsorbent trap, followed by elution of the volatiles with hexane and finally a manual injection into the gas chromatograph. This procedure will be named here the [PAT,E,I] method.

2. Experimental

2.1. Chemicals

Hexane (RP grade, Prolabo, Paris) was distilled before use; styrene (Aldrich, Strasbourg, France) and ethylbenzene (Aldrich) were used without further purification. Peanut oil (Lesieur) was purchased in a retail store. The trap was Orbo 100 Carbotrap (Supelco, Bellefonte, PA, USA) containing two layers of 350 and 175 mg of graphitized carbon as adsorbent. NaCl and $(\text{NH}_4)_2\text{SO}_4$ were of analytical-reagent grade. Ultrapure water was obtained from a Milli-Q system (Millipore, Bedford, MA, USA).

2.2. Solutions of aromatic hydrocarbons

For the dissolution of the aromatic hydrocarbons, we used peanut oil rather than the official fatty food simulants (olive and sunflower oils), which naturally contain many volatile compounds.

2.3. Gas chromatography

In the [PAT,E,I] method, a Girdel 300 Delsi chromatograph equipped with a Jennings injec-

tor was used. The column was DBWax ($0.5\ \mu\text{m}$) ($30\ \text{m} \times 0.32\ \text{mm}$ I.D.) (J&W Scientific, Folsom, CA, USA). Flame ionization detection (FID) was applied. An Enica 10 Delsi integrator was used.

For PTI, a Packard Model 427 gas chromatograph was equipped with a Chrompack purge and trap injector. The column was DBSil 5 ($1\ \mu\text{m}$) ($30\ \text{m} \times 0.32\ \text{mm}$ I.D.) (J&W Scientific). FID was applied. A Spectra-Physics Model 4290 integrator was used.

2.4. Description of the [PAT,E,I] system (Fig. 1)

The purge gas flow was regulated with a valve and bubbled through a flask containing water to prevent clogging of the needle when using a saturated salt solution in the purge cell. This flask was connected to the purge cell via a stainless-steel Luer connection (Aldrich Z10,246-6) and a needle (Aldrich Z10,271-7), through a teflonized septum. We made the purge cell ourselves. It consists in a tube ($15\ \text{mm}$ I.D.) with a conical bottom, equipped with a lateral inlet (neck and septum adapted from a Varian 2-ml vial, ref. 03-906195-90) and an SVL No. 15 screw-stopper (Bibby Science), making adaptation of the Carbotrap tubes through an 8-mm SVL ring possible. Two different purge cell lengths were used: 5 cm for small samples (only oily solutions) and 11 cm when large volumes of saturated NaCl solution was added to the oily styrene solution.

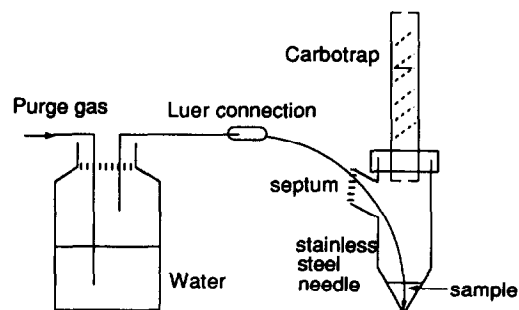


Fig. 1. The [PAT,E,I] procedure.

2.5. Analytical procedure with the [PAT,E,I] system

A solution of the VOCs in peanut oil was weighed into the purge cell and saturated NaCl solution (1 ml) was added in some experiments. The purge gas was admitted into the cell with a 150 ml min^{-1} flow. At the end of a purge period, the adsorbent tube was quickly replaced by a new one. The next purge period was started immediately. All the traps were analysed separately. The trapped volatiles were desorbed with hexane (5.0 ml). The elution time was adjusted between 2 and 5 min with the help of pressure at the top of the Carbotrap. A second elution with 1 ml of hexane was made in order to check that all the volatiles had been removed from the trap. A separate analysis was then carried out. Cumene ($5.48 \mu\text{g ml}^{-1}$ in the eluent) was then added as an internal standard for the GC determination.

The method as used here had a sensitivity of 500 ng for styrene, with a signal-to-noise ratio of 5.

2.6. Analytical conditions for the PTI system (Fig. 2)

The Chrompack purge and trap injector was used as recommended by the manufacturer [12] under the following conditions: purge gas, hydrogen; purge gas flow-rate, 15 ml min^{-1} ; purge gas time, 20 min; and clean-up flow-rate, 6 ml min^{-1} . The cryogenic trap was a fused-silica tube ($30 \text{ cm} \times 0.53 \text{ mm I.D.}$) coated with Cp-Sil8CB ($5 \mu\text{m}$) (Chrompack).

As direct injection was not possible, the recovery yield could not be determined, and our results were expressed by the ratio:

$$\text{area ng}^{-1} = \frac{\text{area of the GC signal}}{\text{ng styrene introduced into the cell}}$$

A control of purge efficiency could be made with a second purge by checking whether there was still styrene which could be swept from the matrix. Each experiment was repeated 2–5 times. The variability was 20%.

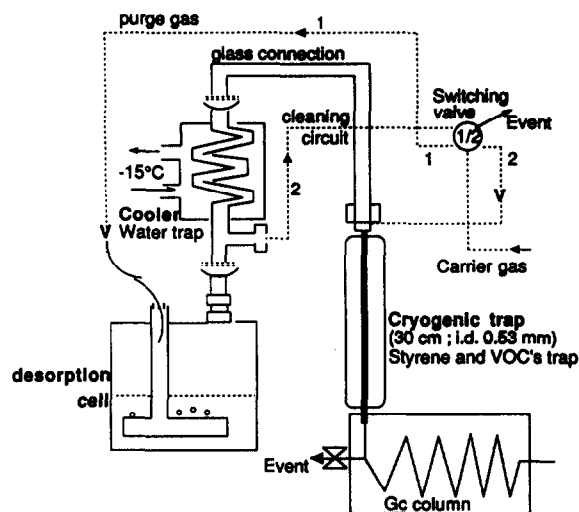


Fig. 2. The PTI system.

The method as used here had a sensitivity of 1 ng for styrene, with a signal-to-noise ratio of 5.

3. Results

3.1. Influence of the amount of oil for a given amount of styrene

Results with the PTI technique

With a constant amount of hydrocarbon (35 ng of styrene) introduced into the cell, and using a constant purge time, the area ng^{-1} values were measured for different amounts of oil in the cell, ranging from 1.1 to 91.3 mg. The results are reported in Fig. 3. Surprisingly, for very small amounts of oil, the area ng^{-1} value passes through a maximum at ca. 2.2 mg of oil. This was probably the result of a change in the evaporation mechanism [13], interface effects playing an important role for very small amounts.

Results with the [PAT,E,I] procedure

The results obtained using about 550 μg of styrene in the cell are presented in Fig. 4. Within a 30-min purge with nitrogen, 93% of the styrene

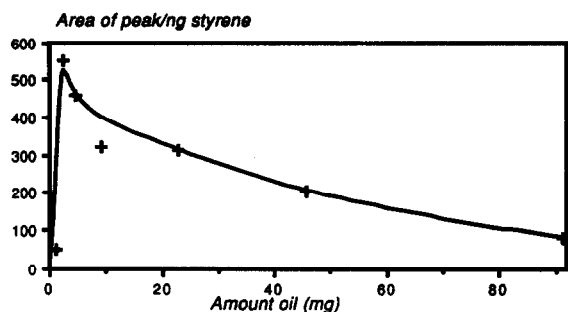


Fig. 3. Influence of the amount of peanut oil on the area ng^{-1} value for styrene (with 5 ml of water).

was desorbed from 26 mg of oil, but only 14% from 2185 mg of oil.

3.2. Influence of the temperature of the [PAT,E,I] cell

To decrease as much as possible the purge time required for a quantitative purge, whatever the concentration of styrene and the amount of oil, one approach consists in raising the temperature of the desorption cell. With *ca.* 500 μg of styrene in *ca.* 2000 mg of oil, the recovery in a 30-min purge increased with increasing temperature up to 80°C. Temperatures as high as 150°C, which corresponds more to distillation of styrene, have been reported in similar procedures [14], but they do not seem to be strictly necessary in view of our results. This result could certainly be extended to the PTI method.

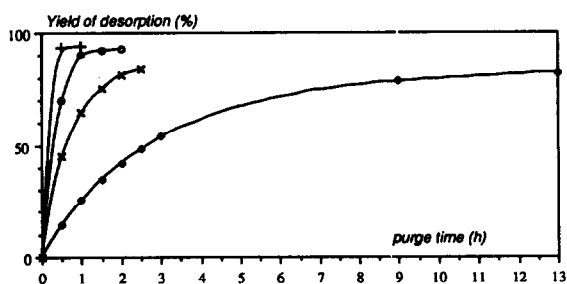


Fig. 4. Influence of the amount of oil (*ca.* 550 μg of styrene) in the cell in the [PAT,E,I] method. + = 26 mg of oil, 506 μg of styrene; \circ = 189 mg of oil, 647 μg of styrene; \times = 353 mg of oil, 682 μg of styrene; \diamond = 2185 mg of oil, 510 μg of styrene.

3.3. Influence of the addition of aqueous solutions and of dissolved gas

Results with the PTI technique

It has been reported that adding water to the oil improved the GC determination of styrene by static headspace methods through the formation of a mixed vapour of water with the aromatic hydrocarbon [15]. We therefore added water to the analytical cell. With the PTI technique, this also permitted the immersion of the sintered glass (Fig. 2), thus allowing the purge gas to bubble through the solution. However, as shown in entries 1 (oil only) and 2 (oil + stock distilled water) in Table 1, this did not improve the area ng^{-1} value. This suggests that the effect of water in headspace methods might be more complex.

As this result could be due to the slight solubility of styrene in water (0.032% at 25°C) [16], the water was saturated with $(\text{NH}_4)_2\text{SO}_4$ or NaCl. When such solutions were freshly prepared, their use markedly enhanced the removal of styrene from the oil solution, as can be seen by comparing entries 2 (oil + water), 3 [oil + $(\text{NH}_4)_2\text{SO}_4$ saturated solution] and 7 (oil + NaCl saturated solution) in Table 1.

However, when the freshly prepared saturated salt solutions were reused the next day, the purge efficiency of styrene was disastrous (entries 4 and 8, Table 1). This difference in the behaviour of freshly prepared and "old" stock solutions could be linked to the decrease in solubility of the gases on going from pure water to the saturated solution, a hypothesis which was confirmed by the following experiments. A freshly prepared $(\text{NH}_4)_2\text{SO}_4$ saturated solution was thoroughly degassed by sonication for 10 min, then added to the PTI cell containing styrene in oil, then purged with hydrogen: no styrene was desorbed (entry 5, Table 1). When the same saturated salt solution was first sonicated, then regassed for 15 s by bubbling carbon dioxide immediately before use, the recovery of the hydrocarbons was excellent (entry 6, Table 1). A similar efficiency was obtained when a 1-day-old stock solution was regassed with CO_2 immediately before use (entry 9, Table 1). Bubbling nitrogen through the aqueous solution before

Table 1
Determination of ethylbenzene (40 ng) and styrene (35 ng) in oil (8 mg) by the PTI technique, using hydrogen as purge gas

Entry	Volume of aqueous solution added (ml)	Preparation and type of aqueous solution	Ethylbenzene (area ng ⁻¹)	Styrene (area ng ⁻¹)
1	None	–	393	453
2	5	Stock distilled water		190
3	5	Sat. (NH ₄) ₂ SO ₄ prepared just before use	327	334
4	5	Sat. (NH ₄) ₂ SO ₄ stock	– ^a	51
5	5	(1) Sat. (NH ₄) ₂ SO ₄ prepared just before use (2) Degassed by sonication	– ^a	– ^a
6	5	(1) Sat. (NH ₄) ₂ SO ₄ prepared just before use (2) Degassed by sonication (3) Regassed with CO ₂ ^b	394	408
7	5	Sat. NaCl prepared just before use	217	233
8	5	Sat. NaCl 1-day-old solution	80	135
9	5	(1) Old sat. NaCl solution (2) Regassed with CO ₂ ^b	550	485
10	5	(1) Old sat. NaCl solution (2) Regassed with N ₂ ^b		214
11	5	(1) Distilled water (2) Regassed with N ₂ ^b	241	284

^a Only trace levels of the hydrocarbon were detected by GC.

^b 100 ml min⁻¹, 15 s, just before use.

introduction of the hydrocarbons also increased the efficiency of the styrene purge, although the effect was less pronounced (entries 10 and 11, Table 1).

Dissolved gases seem to play a critical role in the efficiency of the added aqueous solutions. The poor efficiency of "old" stock solutions was the result of a slow release of the dissolved gases from the saturated solution after their preparation. Regassing the solution with carbon dioxide just before starting the purge turned out to enhance the purge efficiency of the hydrocarbons; in order to prevent the carbon dioxide from freezing in the cold trap, the temperature of the latter was raised from –150°C (recommended by the manufacturer) to –70°C.

Results with the [PAT,E,I] procedure

The use of aqueous solutions led to similar effects to those described above with the PTI procedure, but to a much lesser extent. The influence of the dissolved gases was far less than with the PTI technique: using the same purge gas, hydrogen, the sonication of the aqueous

solution had only a slight effect on the desorption yield (entries 1 and 2, Table 2). With nitrogen as the purge gas, the desorption from solutions diluted in peanut oil was only slightly decreased by the use of an old stock saturated NaCl solution (Table 2, entries 4 and 5). Regassing this solution with carbon dioxide just before use gave an excellent recovery of styrene (Table 2, entries 5 and 6).

Considering the enhancement of the desorption of hydrocarbons by carbon dioxide with the PTI technique, this gas was adopted as the purge gas in the [PAT,E,I] method; however, the recovery of styrene decreased on replacing nitrogen with carbon dioxide. This was shown to be the result of an interaction of carbon dioxide with the Carbotrap, through the following experiment: styrene (150 µg) in solution in hexane (50 µl) was added directly on the top of two carbotrap columns; one of the columns was swept with nitrogen (150 ml min⁻¹ for 1 h and the other was swept with carbon dioxide (150 ml min⁻¹) for the same time. The hydrocarbons still present on the adsorbent were then eluted with

Table 2

Influence of the purge gas on the recovery of styrene (500 μg) from peanut oil (30 mg) using a 30-min purge with the [PAT,E,I] procedure

Entry	Purge gas	Special features	Recovery (%) after 30-min purge		
			Styrene	Ethylbenzene	Propylbenzene
1	H ₂	Old sat. NaCl solution ^a	85 ^c	87	86
2	H ₂	(1) Old sat. NaCl solution ^a (2) Sonicated before use	80 ^c	87	79
3	H ₂	Distilled water ^a	84 ^c	94	84
4	N ₂	No aqueous solution added	94 ^c		
5	N ₂	Old sat. NaCl solution ^a	79		
			89 after 1-h purge		
6	N ₂	(1) Old sat. NaCl solution ^a (2) Regassed with CO ₂ ^b	93 ^c		
7	CO ₂	Old sat. NaCl solution ^a	72 ^c		
8	CO ₂	Old sat. NaCl solution ^a (4 purges 7.5 min)	86		

^a 1 ml.

^b 100 ml min⁻¹, 15 s, just before use.

^c No improvement in the recovery after a second purge period of 30 min.

hexane and analysed as usual. The recoveries thus determined were 100% for the tube swept with nitrogen and only 84% for the tube swept with carbon dioxide. It thus appeared that whereas carbon dioxide accelerates the purge of styrene from the matrix, it also induces the desorption of styrene from the Carbotrap. It should also be noted that ethylbenzene and styrene did not behave similarly. The behaviour of styrene was more similar to that of propylbenzene, which should be used as an internal standard for quantitative analyses when needed.

According to this result, high recoveries (88%) could be obtained using carbon dioxide as the purge gas in the [PAT,E,I] procedure with frequent replacement of the trap (every 7.5 min during 90 min).

4. Discussion and conclusion

4.1. Determination of volatile aromatic hydrocarbons by dynamic headspace analysis

In all our experiments, efficient purges were

achieved with solutions of hydrocarbons in peanut oil, as long as the samples were small (less than *ca.* 50 mg). High-boiling volatile hydrocarbons such as styrene and propylbenzene can be determined efficiently by these dynamic headspace techniques [17]. Peanut oil appears to be a very convenient solvent for handling volatile compounds with dynamic headspace methods.

4.2. Determination of styrene in two-phase systems

The use of saturated salt solutions reduces the solubilities of the hydrocarbons in water and displaces the equilibrium towards the gas phase. The recoveries are thus higher than in the experiments where only distilled water is added; if the determination has to be achieved in aqueous media or in emulsions, it seems adequate to saturate the aqueous phases. In all instances, the preliminary bubbling of a gas through the aqueous solution enhances the recoveries.

Influence of the nature of the purge gas

The results with the PTI technique show that a

preliminary treatment of the matrix with carbon dioxide or, to a lesser extent, nitrogen enhances the purge efficiency. This might suggest that the nature of the purge gas could increase the sweeping efficiency of styrene, with the order $\text{CO}_2 > \text{N}_2 > \text{H}_2$, which seems to correlate with the solubilities of these gases in water at 20°C [18]: $1750 > 23 > 19 \text{ ml l}^{-1}$. In fact, the experiments carried out with the [PAT,E,I] procedure showed that the nature of the purge gas has little effect on purge efficiency: nitrogen, carbon dioxide (with frequent replacement of the trap) and hydrogen gave similar recoveries (Table 2, entries 5, 8 and 1). It is therefore not the nature of the purge gas that accounts for the dramatic effects observed in PTI method. This is most likely the result of the preliminary saturation.

The results presented here could be explained consistently if one assumes that the volatile hydrocarbons can only be swept when the matrix is saturated by the purge gas. The time required to reach this saturation could then be a crucial parameter. The difference between the two techniques appears strikingly for the experiments using sonicated aqueous salt-saturated solutions (entry 5, Table 1 and entry 2, Table 2). In the PTI experiments, where both the purge flow and purge time are low (as recommended by the manufacturer), starting with a sonicated matrix and using hydrogen as the purge gas, this saturation would not be reached within the purge period (entry 5, Table 1). In the [PAT,E,I] experiments, the amount of matrix is five times smaller and the flow-rate ten times higher, resulting in the time required for saturation by the purge gas being 50 times lower than in PTI experiments. It could then in fact be reached within the purge period. This explains why the [PAT,E,I] experiment with sonication (entry 2, Table 2) showed little difference from those in which the matrix was not initially degassed.

The hypothesis that with the PTI method the system does not have the time to reach the required gas saturation, unless a preliminary purge is used, could also explain the poor reproducibility of the results usually reported with dynamic headspace techniques [19]. This could also explain why, in the volumetric dilution

procedure, the use of a pipette (creating a depression above the liquid surface) is less suitable than the use of a burette [19], a fact which has been reported, but never coherently explained.

The best conditions for the desorption of the volatile aromatic hydrocarbons involve a short preliminary bubbling of carbon dioxide into a saturated NaCl solution, which is then added to the sample just before starting the purge (Table 1, entry 9; Table 2, entry 6). This procedure should be recommended for all dynamic headspace methods where rapid desorption of high-boiling organic volatiles is needed. The great efficiency of carbon dioxide could be linked to its high solubility in water, and probably also to its dissolution kinetics.

Among the factors governing the recovery, we found that the removal of hydrocarbons from the liquid matrix is essential, and greatly enhanced by the dissolved gases.

5. References

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