

Suitability of different plastic materials for head or nose spaces short term storage

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Abstract. Three types of plastic material (Saran, Tedlar and Teflon) were examined for their influence on the profile of a model headspace containing 13 volatile compounds of different volatility and polarity. As far as the emission of contaminants from the bags to the headspace is considered, the most appropriate material is obviously Teflon. However, the drawback of this material is a rapid sorption and then a slow adsorption of most volatile compounds tested, in particular polar ones. The authors suggest that acceptable time for headspace storage is between 4 and 12 hours, but with possible loss of the most polar compounds present in trace quantities.

Keywords. Plastic materials – flavour compounds – short term storage – head space.

Introduction

One of the most promising techniques in flavour analysis is nosespace as described by Linforth [1]. This approach is based on the analysis of volatile compounds collected from the nose of human subjects breathing out during food mastication and ingestion. The main advantage of nosespace, comparing to headspace, is that it takes into account all events and parameters monitoring the release of volatile compounds in the mouth (temperature in the mouth, food fragmentation or dilution with saliva, pH, enzyme activities...).

Initially, authors trapped first the volatile compounds present in the nosespace on an adsorbent (Tenax), and analysed them afterwards with a gas chromatograph. For sensitivity reasons, the detection is often made by MS ion monitoring of specific ions of selected flavour active constituents as in tomatoes [2], strawberries [3, 4] and cheddar cheese [5].

When such flavour active compounds are not known, Priser [6] and Étievant [7] tried and then validated the direct use of nosespace extracts for GC-olfactometry analyses. When the analyst wants several subjects to sniff the nosespace extracts and to repeat the same analysis, large volumes of nosespace are required initially [7]. A possible issue to this problem, adopted in this experiment, was to collect the breath from several people into plastic bags, and then to sample this averaged breath on Tenax traps for GC-O.

In order to choose for this particular application between the different types of plastic bags most usually recommended in medicine and environmental analyses, we tested first the different materials for contaminants and then the most neutral one for its adsorption properties towards typical flavour active compounds.

Materials and methods

Bags

Three different types of bags were successively tested:

1. Laboratory made bags from Tedlar (Polyvinyl fluoride) films (Micel, Cachan, France). The Tedlar sheets were fitted with one Teflon connector for sampling, and then soldered together (80 °C) to form a leak proof bag (dimension 32 × 45 cm, approximately 10 L capacity).
2. Saran bags (Chrompack, Les Ulis, France), 28 × 28 cm, 4.8 L capacity, equipped with a silicone nozzle.
3. Teflon (Polytetrafluoroethylene) bags (Touzart et Matignon, Paris, France), 30 × 30 cm, 6 L, equipped with a Teflon connector.

All bags were flushed before use three times with nitrogen purified on activated charcoal.

Analytical reagents

A model solution containing a concentration known precisely and close to 0.5 g/l of 3-methyl-1-butanol, ethyl hexanoate, ethyl octanoate, 1-phenyl-2-ethanol, dimethyl-disulfide, 2-hexanone, 3-methyl-1-butanol, acetic acid, furfural, benzaldehyde, guaiacol and 4-ethylphenol in water: ethanol (1:1) was prepared and stored in a refrigerator.

All solutions were prepared using purified water (milli-Q system, Millipore SA, Saint-Quentin-Fallavier, France).

The saturated solution of ammonium sulphate (PRO-LABO, Fontenay-sous-Bois, France) was prepared at room temperature in purified water.

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Adsorbent

Tenax TA 60-80 mesh (Chrompack, Les Ulis, France) was used for headspace trapping. Before each use, each trap was submitted to 12 cleaning cycles identical to the injection cycle described in the Gas-Chromatography section below.

Desorption tests

The bags were filled with pure nitrogen and deflated three times. They were then filled once more with nitrogen, and 1.5 L samples were taken from the bag immediately after filling, and then after 24, 48 and 72 hours. The samples were trapped on Tenax using a Casella SP-15 pump (Bioblock, France) at a flow rate settled to 150 mL·min⁻¹. Humidity was then removed from the adsorbent under a stream of nitrogen (100 ml·min⁻¹ for 2 minutes). During all the experiment, the bags were kept in an air-conditioned room (19 ± 1 °C) until GC analysis.

The content of Teflon bags was submitted to GC-O after 48 hours of storage. Each experiment was repeated once.

Adsorption tests

Four litres of purified water were poured into a 10 L glass reactor with a glass cap equipped with two outlets and Teflon seals. One ml of the model solution was added in the reactor with a pipette, the reactor was closed, and the solution was stirred for 30 min with a magnetic Teflon rod. The solution was then kept still for 12 h in order to get the thermodynamic equilibrium between the aqueous and the gas phases. A glass vessel containing 4 litres of a saturated ammonium sulphate solution was connected to a glass tubing ending at the bottom of the reactor through one of the two outlets and the second outlet to an empty Teflon bag. This solution was then decanted in approximately 10 min into the reactor, avoiding mixing up with the flavour solution, and resulting in the transfer of 4 L of the equilibrated gas phase into the bag.

After 0, 4, 12, 36, 72 and 168 hours of storage, 1.5 l samples were taken from the bag and trapped as described above. This series of analysis was realised three times.

Gas Chromatography

The analyses were carried out using a Hewlett Packard 5890 II gas chromatograph, equipped with a thermal desorption cold trap injector (TCT, CP 4010, Chrompack, Les Ulis, France), a FID detector and a home made sniffing port. Conditions of injection were: a 5 min precool at -130 °C, a 20 min desorption at 240 °C by a 20 ml·min⁻¹ desorption flush flow, injection at 250 °C, a 20 min backflush at 30 ml·min⁻¹. The separation took place in a DB-Wax fused silica capillary column (J&W Inc., 30 m × 0.32 mm × 0.5 µm) programmed from 27 °C (5 min) to 220 °C (10 min) at 5 °C·min⁻¹. The carrier gas was hydrogen (50 cm·s⁻¹) and the temperature of detector was 250 °C.

After each analysis, the Tenax trap was cleaned by applying six times the same desorption cycle as above, but without precooling.

Gas chromatography-olfactometry

The same instrumental set-up was used for sniffing analyses. The sniffing panel consisted of four people, all volunteers, who were instructed not to smoke or eat at least 1 hour before sniffing, and to evaluate the intensity of the odours perceived as described previously [8]. The panellists sniffed the effluent corresponding to the Teflon bag twice. The same panellists also sniffed the effluent of a blank sample, consisting of a Tenax trap on which 1.5 L of air has been passed.

Statistics

One way analysis of variance (normal distribution) or Kruskal–Walis test (KW, non-normal distribution), and Student–Newman–Keuls pair comparisons were made using the SigmaStat 2.03 software (SPSS Inc.).

Results and discussion

Desorption tests

Prior to analysis of contaminants released by desorption from the plastic bags, the contaminants from the Tenax adsorbent were evaluated after the normal cleaning step. The whole process was repeated five times and a typical chromatogram obtained is shown in figure 1. A second chromatogram obtained after applying a cleaning step and a perfusion of 1.5 L of nitrogen is given in figure 2. They both show low levels for contaminants released from the Tenax adsorbent (peak area < 10000), except for two peaks eluted very early, which seems acceptable. Nevertheless, the sniffings released 12 odours observed more than two times in both the blank and the bag samples. These odours are concluded to have as origin the Tenax trap, and their contribution to olfactometric profile must be considered.

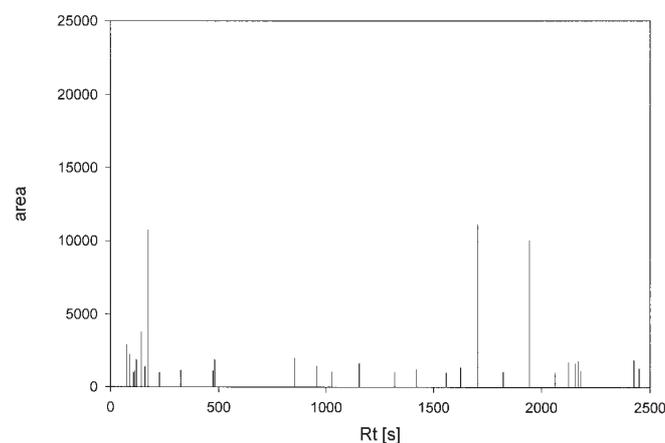


Figure 1. GC profile: desorption of a clean Tenax trap.

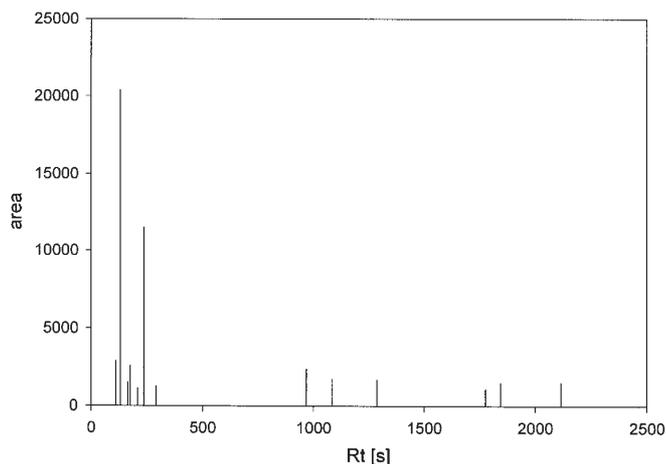


Figure 2. GC profile: desorption of a clean Tenax trap, flushed with purified nitrogen.

The desorption tests realised on the bags (Fig. 3 to 5) demonstrate an emission of contaminants higher for the Tedlar bags as estimated from the maximum peak areas. When comparing Saran and Teflon, the average peak areas corresponding to contaminants are found equivalent, but the number of these peaks is clearly lower for Teflon, which therefore appears to be a more suitable material.

In order to evaluate the risk taken when storing the bags before analysis, the variation of the amount of these contaminants with time was evaluated. Figures 6a and 6b show for the Tedlar bags a drastic increase of the level of the contaminants emitted after 24 hours which is typical also for the results obtained with Saran. Comparing to Tedlar (Fig. 3) and Saran (Fig. 4) bags, the pollutants from Teflon bag are less numerous (Fig. 5) and their amount does not increase significantly with time (not shown).

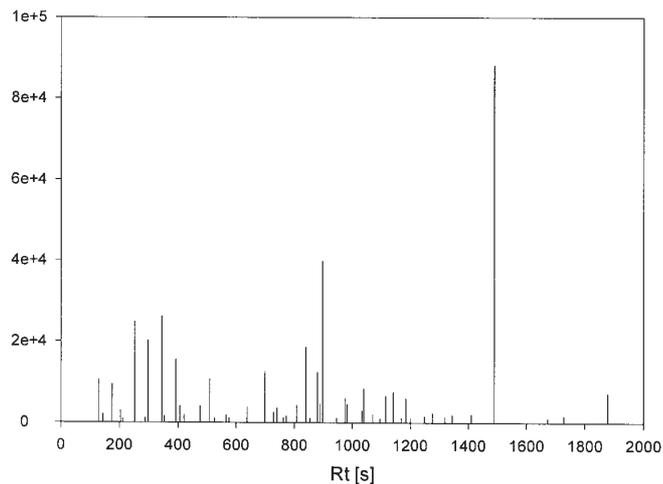


Figure 4. GC profile of the volatiles contained in 1,5 L nitrogen stored 24 h in a Saran bag.

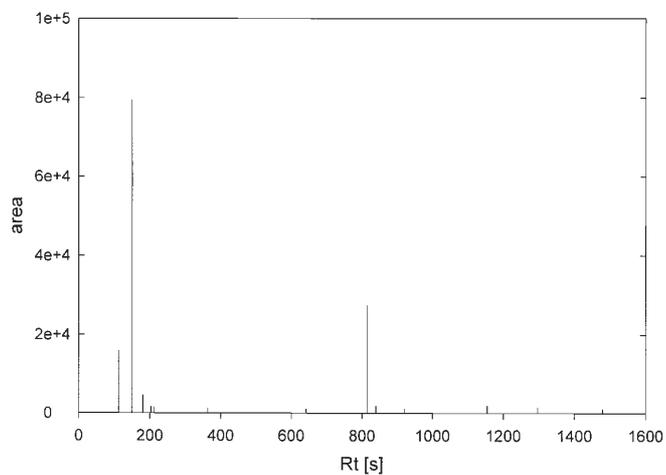


Figure 5. GC profile of the volatiles contained in 1,5 L nitrogen stored 24 h in a Teflon bag.

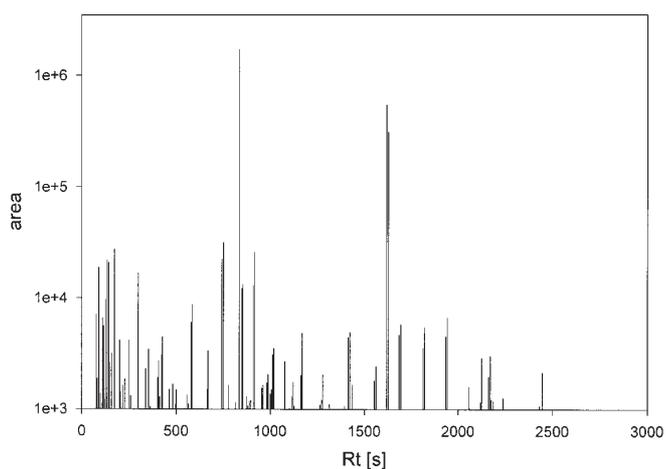


Figure 3. GC profile of the volatiles contained in 1,5 L nitrogen stored 24 h in a Tedlar bag.

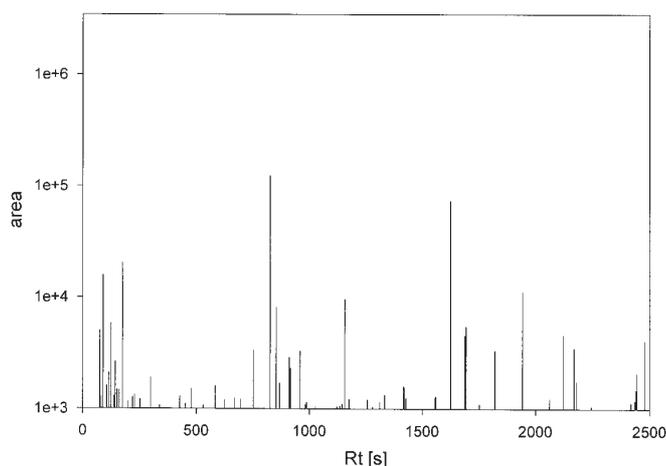


Figure 6a. GC profile of the volatiles contained in 1,5 L nitrogen stored 0 h in a Tedlar bag.

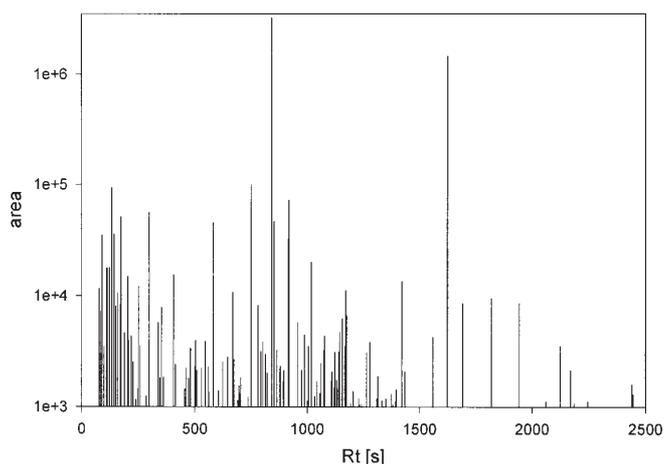


Figure 6b. GC profile of the volatiles contained in 1,5 L nitrogen stored 72 h in a Tedlar bag.

The number and the amount of undesirable compounds released when using Teflon bags are more compatible with head space or nose space analyses than when using Saran or Tedlar bags. If the number of substances detected in Teflon bags by a physical detector seems acceptable, it is however possible that this material might be not compatible with GC-olfactometry, if it releases traces of odour active contaminants.

A second problem must also be considered which is the possible adsorption of food flavour active compounds in the Teflon film during the headspace storage.

Test for odour active contaminants

Odours detected by GC-O were considered as confirmed only when found at least two times out of the twelve sniffings (4 sniffers \times [2 Teflon + 1 blank samples]). The result of these sniffings reveals that three odours only were

detected at the following retention indices: 1200 (lemon odour), 1264 (garlic, gas like odour) and 1784 (leather, burnt odour). The amounts of these compounds were too low for positive identification by GC-MS. This result therefore confirms the suitability of Teflon bags for GC-O analyses.

Test for adsorption

If the experimentation involves a panel of sniffers and repetitions, it may be necessary to load a large number of traps [7], which might take a long time depending on the back-pressure in the traps. Reliable quantitative results are therefore conditioned by the absence of interaction of the organic volatile molecules studied with the plastic film. Literature mentions for Teflon bags a good stability of the concentration of air constituents, when stored for less than 2 hours [9]. A model headspace containing 13 typical odour active compounds, chosen amongst polar and non-polar compounds, was thus specifically generated to study the influence of Teflon on headspace composition during a longer period of time. The evolution of the composition of this model headspace was followed by GC from its introduction into the bag until 168 hours of storage, in order to point out possible adsorption phenomenon. The raw peak areas measured for each substance in the three replicate chromatograms obtained at six different times of sampling were analysed by one way ANOVA to determine significant differences according to the duration of head-space storage.

No significant adsorption was observed for ethyl hexanoate, ethyl octanoate and 3-methyl-1-butanethiol. However, figure 7 and table I show for the three compounds a non-significant decreasing trend for concentrations, particularly after 12 or 36 hours storage.

The similar behaviour is observed for dimethyldisulphide and 2-hexanone, but the decrease is now significant after 72 hours (figure 7, table I).

For these five compounds, a phenomenon of low adsorption may explain this behaviour, allowing a storage of the

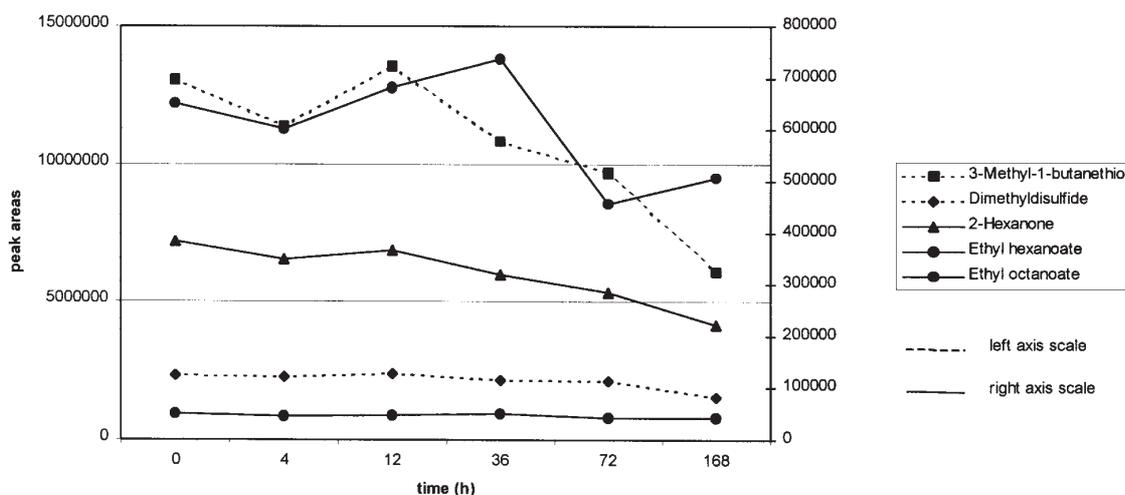


Figure 7. Compounds showing a slow concentration decrease with storage time.

Table I. Changes with time in the content of the compounds tested

| Compound | p (ANOVA) | Pair comparisons | 4 h | 12 h | 36 h | 72 h | 168 h |
|------------------------|-----------|------------------|-----|------|------|------|-------|
| ethyl hexanoate | 0,314 | - | | | | | |
| ethyl octanoate | 0,385 | - | | | | | |
| 3-methyl-1-butanethiol | 0,195 | - | | | | | |
| dimethyldisulphide | < 0,001 | 0 | - | - | - | - | + |
| | | 4 | | - | - | - | + |
| | | 12 | | | - | - | + |
| | | 36 | | | | - | + |
| | | 72 | | | | | + |
| 2-hexanone | < 0,001 | 0 | - | - | - | + | + |
| | | 4 | | - | - | - | + |
| | | 12 | | | - | + | + |
| | | 36 | | | | - | + |
| | | 72 | | | | | + |
| phenol* | 0,022 | 0 | - | - | - | - | + |
| acetic acid | < 0,001 | 0 | + | + | + | + | + |
| | | 4 | | - | - | - | + |
| | | 12 | | | - | + | + |
| benzaldehyde | < 0,001 | 0 | + | + | + | + | + |
| | | 4 | | - | + | + | + |
| | | 12 | | | + | + | + |
| | | 36 | | | | - | + |
| furfural* | < 0,001 | 0 | + | - | + | + | + |
| | | 4 | | - | - | + | + |
| | | 12 | | | + | + | + |
| | | 36 | | | | + | + |
| 3-methyl-1-butanol | < 0,001 | 0 | + | + | + | + | + |
| | | 4 | | - | - | + | + |
| | | 12 | | | - | + | + |
| | | 36 | | | | + | + |
| 1-phenyl-2-ethanol | 0,002 | 0 | + | + | + | + | + |
| guaiacol | < 0,001 | 0 | + | + | + | + | + |
| | | 4 | | + | + | + | + |
| 4-ethylphenol | <0,001 | 0 | + | + | — | — | — |
| | | 4 | | + | — | — | — |

+ significant difference between pairs tested

- no significant difference

— not observed

* increasing with time

headspace during 36 hours without noticeable bias in the analyses performed on the bag content. The evolution of phenol is more surprising since we observe an increase of its concentration, however not significant until 72 hours (Fig. 8, Tab. I). The explanation of a possible contamination from Teflon can be evoked similarly to Tedlar, which was shown to release large amounts of phenol in the head space (large peak at 1620 s in figure 3). For all other compounds, the phenomenon of decrease of the concentrations hardly observed above is more evident (Fig. 9), and starts immediately after the introduction of the headspace into the bag. This phenomenon of decrease which is fast just after the beginning of the contact with the plastic film, tends to slow down or to stop after a period of time which differs from one compound to another. Furfural and 3-methyl-1-butanol concentrations do not vary significantly between 4 to 36 hours, acetic acid between 4 to 72 hours and 1-phenyl-2-ethanol between 4 and 168 hours. Benzaldehyde shows a

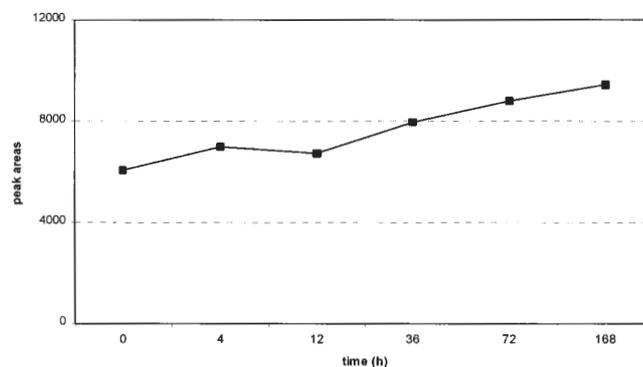


Figure 8. Phenol concentration increase with storage time.

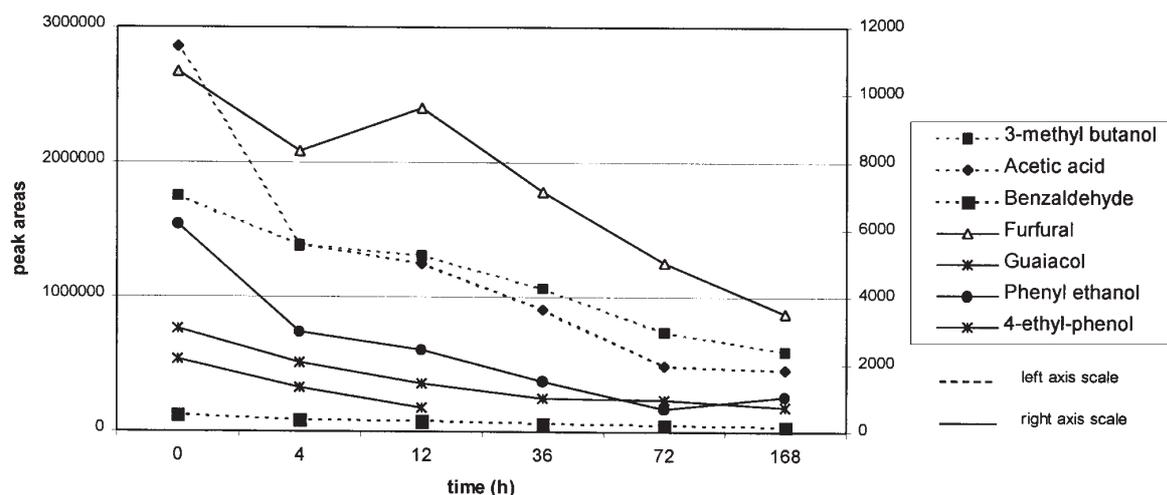


Figure 9. Compounds showing a drastic concentration decrease with storage time.

more complex behaviour with a significant decrease at the beginning, followed by a stable concentration between 4 and 12 hours, and then a final slower but significant decrease until 168 hours.

Finally, 4-ethylphenol and guaiacol concentrations are decreasing regularly, even leading to non-detection after 36 hours for the latter (Tab. I).

These results demonstrate that adsorption occurs on, or in, the plastic material chosen (Teflon), and that the kinetics of this phenomenon depends on the polarity of the substances in the headspace. Esters and thiols are little absorbed, and more polar compounds as phenols or benzylic alcohol are more extensively adsorbed. The results also suggest that two phenomena are involved in the decrease of their concentrations: a quick adsorption on the surface of the film that probably occurs in less than 4 hours, and then a slower diffusion into the film.

According to our results, the best time for sampling of volatile compounds in Teflon bags is higher than 4 hours and lower than 12 hours. During this period, no significant decrease of the concentration could be observed for most compounds tested, except guaiacol and 4-ethylphenol (Tab. I).

Conclusion

Amongst the different types of plastic material used to store head spaces for aroma analysis purpose, Tedlar and Saran were proven to be unsuitable because they release a large number of volatile contaminants in significant amounts, large enough or odorous enough to mask the constituents studied by gas chromatography or by gas-chromatography coupled to olfactometry. Teflon appears to be more suitable as releasing an amount of contaminants compatible with GC and GC-O analyses. However, a phenomenon of sorption

and/or adsorption occurs in these bags which limits the time of storage of the head space, in particular when quantitative determinations have to be realised. Concerning the more polar substances, the experimenter must be aware of their absorption after a time, the extent of which depends on their initial concentrations in the headspace.

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