Application
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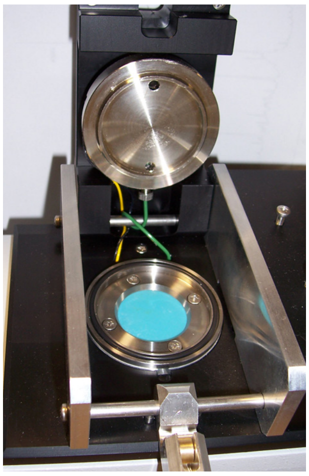
Application Note 121

A simple and reliable approach to assessing permeation of volatiles through materials

Summary

This Application Note describes the operation of the permeation accessory for Markes' Micro-Chamber/Thermal Extractor, and shows how it can be used for investigations into the permeation of volatile chemicals through thin membranes.



Introduction

Understanding the migration of volatile organic compounds (VOCs) through materials is an important field of study, with key applications including:

- Studies of the permeation of chemicals into (and out of) food packaging. This has an impact on the shelf-life and safety of pre-prepared and food products – especially ready-to-eat fresh fruit.
- Investigations into the efficacy of protective equipment, such as the nitrile gloves commonly used in laboratories. How safe they are to use is largely determined by their ability to prevent migration of hazardous chemicals.

The diffusion of gases and volatile chemicals through thin films of material is well-understood theoretically, and governed by long-established physical laws. However, these basic processes are complicated by various factors, such as variation in polymer micro-structure, chemical interactions between the volatiles and the polymer, the presence of polymer additives, whether or not a source of volatiles is in direct contact with the material, and environmental variables such as humidity and temperature.

Such factors make all but the simplest of systems very difficult to model, and means that comprehensive experimental data is needed for reliable characterisation. For the analyst, the need for a straightforward approach to obtaining such data is made more urgent by the recent development of advanced coatings and packaging materials – including laminates, polymer blends, bio-based materials and nanocomposites.

In this Application Note, we describe the background to the operation of a specialist permeation accessory for the Micro-Chamber/Thermal Extractor, and how, in conjunction with thermal desorption–gas chromatography–mass spectrometry (TD–GC–MS) it can be used to generate reliable data on the permeation of VOCs through three types of polymer films.

Background

Micro-Chamber/Thermal Extractor

Markes' Micro-Chamber/Thermal Extractor™ (μ-CTE™) (Figure 1) is a compact unit with four or six small cylindrical chambers, suitable for sampling chemical emissions into sorbent tubes, both from finished products and from raw materials. In conjunction with TD–GC–MS analysis, it has become very popular for the fast, inexpensive screening of materials as part of the monitoring of compliance with industry regulations.

Figure 1: The Micro-Chamber/Thermal Extractor, showing samples being placed in the instrument ready for sampling.

With the material in place in the chamber(s), the lids are closed, and a flow of pure air or nitrogen is applied. The chambers are held at a set temperature – from ambient up to 120°C (6-chamber model) or 250°C (4-chamber model). After a period of equilibration, a sorbent tube is attached to the outlet of each chamber to trap vapours released from the material, and these are then analysed off-line using TD–GC–MS. Alternatively, to monitor formaldehyde, a DNPH cartridge can be attached, which is then analysed by high-performance liquid chromatography (HPLC).

Bulk materials can be sampled with the µ-CTE by directly placing the material in the microchamber pot, while emissions from flat surfaces can be investigated by using spacers to raise the material up. A third mode of operation allows investigation of VOC permeation through a membrane, and this is the focus of the current study.

Permeation accessory

Permeation accessories are available to fit each model of the µ-CTE (Figure 2). These devices fit securely inside the heated cavities of the µ-CTE, in place of the usual sampling pots, and allow a section of test material ('membrane') to be secured in place, leaving a consistent 6 cm^2 area exposed to the source of VOCs in the well below.

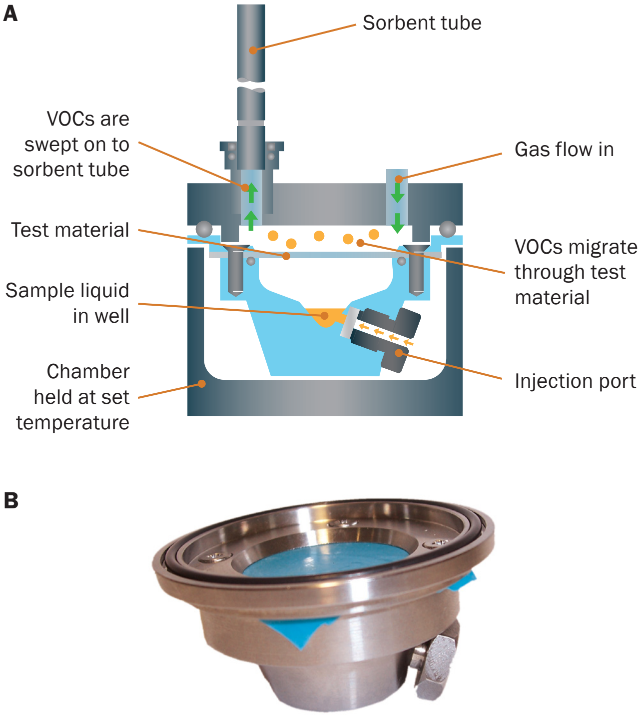
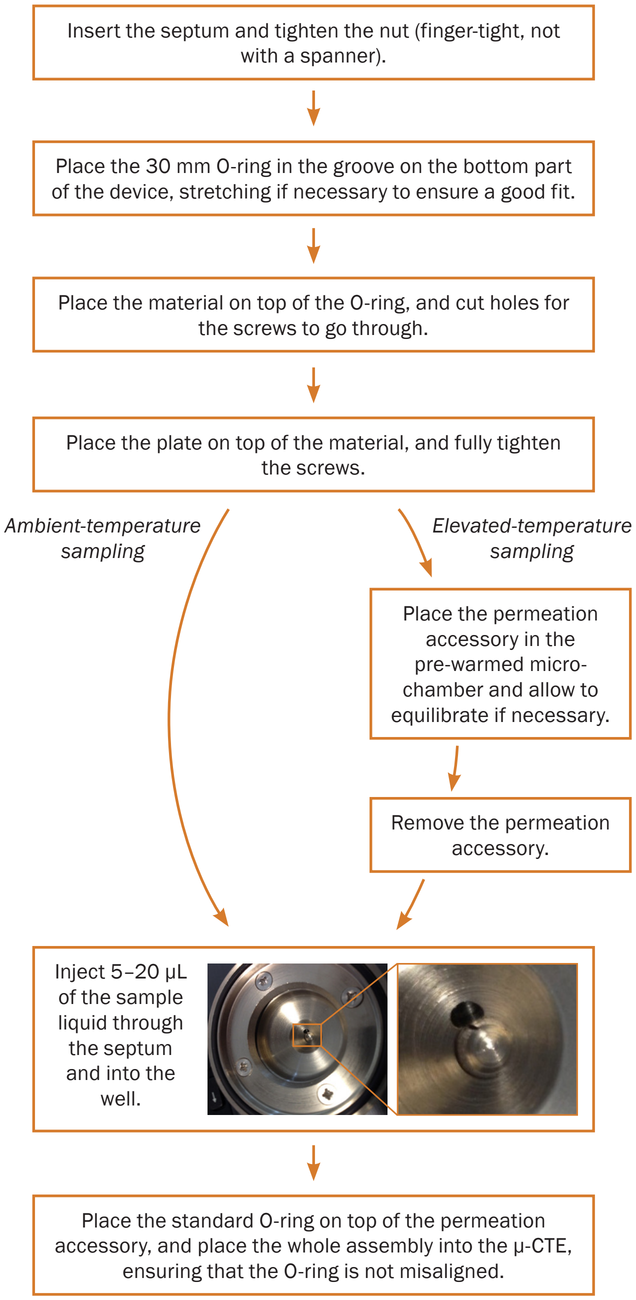


Figure 2: (**A**) Cutaway schematic, showing the permeation accessory insert (blue shading) within a single µ-CTE chamber (grey shading). (**B**) A permeation accessory insert, showing polymer material secured in place; the inlet for injecting the liquid sample is at bottom right.

Each permeation accessory comprises three main parts: a membrane pan, a membrane retainer, and a septum seal and needle guide. It is also supplied with two O-rings – a 30 mm ring for the membrane pan (part number M-PRO30-120), and a standard O-ring to seal the chamber lid (part number M-MCHOR for the 6-chamber model, and M-MCHOR250 for the 4-chamber model. Figure 3 describes how to set up the permeation accessory and load it with sample liquid and material ready for testing.



Insert the septum and tighten the nut (finger-tight, not with a spanner).

Place the 30 mm O-ring in the groove on the bottom part of the device, stretching if necessary to ensure a good fit.

Place the material on top of the O-ring, and cut holes for the screws to go through.

Place the plate on top of the material, and fully tighten the screws.

Ambient-temperature sampling

Elevated-temperature sampling

Place the permeation accessory in the pre-warmed micro-chamber and allow to equilibrate if necessary.

Remove the permeation accessory.

Inject 5–20 µL of the sample liquid through the septum and into the well.

Place the standard O-ring on top of the permeation accessory, and place the whole assembly into the µ-CTE, ensuring that the O-ring is not misaligned.

Figure 3: Flowchart showing the process for loading samples into the permation accessory at ambient and elevated temperature. Note that when injecting the sample liquid, care should be taken to ensure that it does not come into contact with the test material. Ideally, the mass injected should be representative of what might be present in a real-life situation, but it must also be enough that the well does not dry up while the experiment is running.

With the permeation accessory in place, sampling then proceeds as for surface emissions from a flat material, using a flow of warmed air or nitrogen over the material to sweep the escaping volatiles onto a sorbent tube. Tubes are easily replaced with clean tubes, in order to profile the rise or decay of emissions as the experiment proceeds – in this study the sampling period was 10 minutes.

It is good practice to run blanks with the material in place (to check for emissions from the material itself) and without the material in place (to check that the chamber background does not contain any of the test compounds). The permeation accessory can also be used with standard materials and test liquids, to assess between-chamber reproducibility.

Experimental

Materials:
Three polymeric materials were investigated:
(A) Polypropylene (PP) – 70 µm thickness.
(B) Polyethylene terephthalate (PET) – 23 µm thickness.
(C) Laminate comprising PET (23 µm), silicon oxide-coated PET (12 µm) and PP (70 µm).

Permeation sampling:

Instrument:	Six-chamber Micro-Chamber/Thermal Extractor (Markes International), fitted with a permeation accessory (part number M-PRMINSS-120)
Sample volume:	10 µL each of limonene and n-dodecane, injected separately into the well of the permeation accessory
Flow rate:	50 mL/min dry nitrogen
Chamber temp.:	30°C
Sampling tubes:	Stainless steel, packed with Tenax® TA (Markes International part number C1-AAXX-5003), changed every 10 min

TD:

Instrument:	TD100-xr™ (Markes International)
Flow path temp.	180°C
Focusing trap:	General-purpose hydrophobic (Markes International part number U-T2GPH-2S)
Pre-purge to split:	30 mL/min (1 min)
Primary (tube) desorb:	280°C for 10 min; trap flow: 30 mL/min; inlet split: 30 mL/min
Pre-trap-fire purge:	1 min at 30 mL/min
Secondary (trap) desorb:	Trap low: 10°C; trap high: 350°C; heating rate: max; hold time: 3 min; outlet split: 30 mL/min
TD split:	42:1

GC:

Column:	DB-5ms™, 30 m × 0.25 mm × 0.25 µm
Flow:	Constant-flow, 1.5 mL/min
Temp. programme:	50°C (3 min), then 15°C/min to 300°C (5 min)
Total run time:	24.67 min

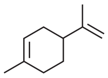
Quadrupole MS:

Ion source:	350°C
Transfer line:	310°C
Quadrupole:	150°C
Mass range:	m/z 35–450

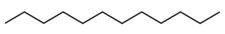
Results and discussion

Among the various chemicals potentially of interest, this study focused on two:

- Limonene (b.p. 176°C), to represent food/fragrance volatiles that might be released from a food sample wrapped in packaging.



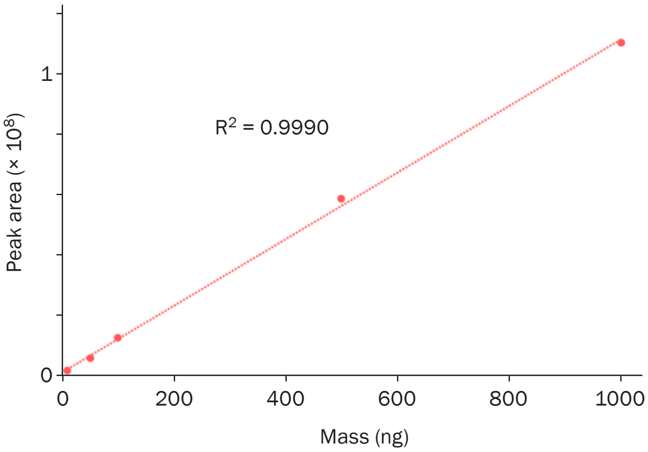
- n-Dodecane (b.p. 216°C), to represent hazardous chemicals that might migrate through the packaging into a food sample – for example, from a printed label.



Linearity

In order to be able to relate chromatographic peak areas to compound masses, calibration curves were constructed from 10–1000 ng – excellent linearity was obtained for both chemicals (Figure 4).

A – Limonene



B – n-Dodecane

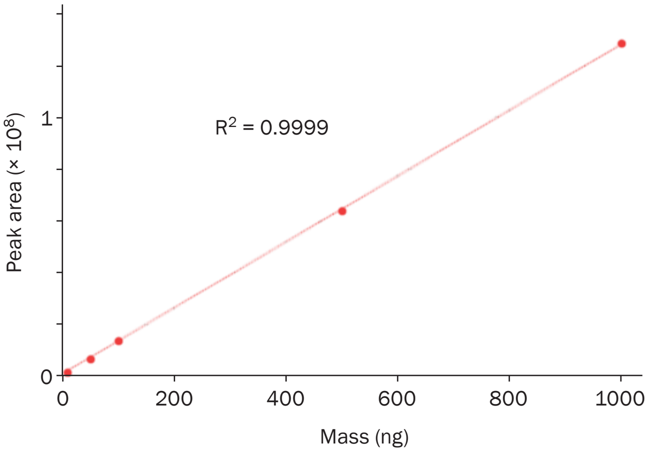


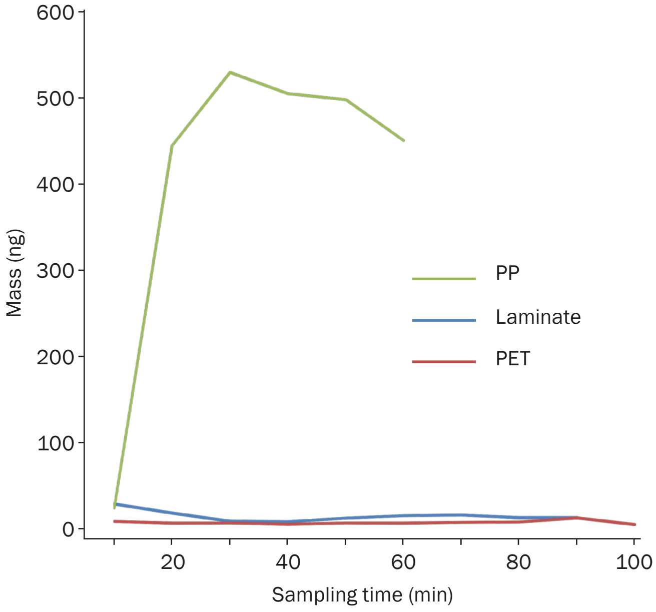
Figure 4: Calibration curves for (**A**) limonene and (**B**) n-dodecane from 10–1000 ng.

Polymer permeation tests

For the tests of polymer permeation, limonene and n-dodecane were injected into the well of the permeation accessory as a mixture, so that chemical-specific effects on the polymer's physical structure affected both data-sets equally.

The results (Figure 5) show that for both chemicals, PP is far more permeable than PET and laminate, and that the differences between the two sample chemicals are relatively slight.

A – Limonene



B – n-Dodecane

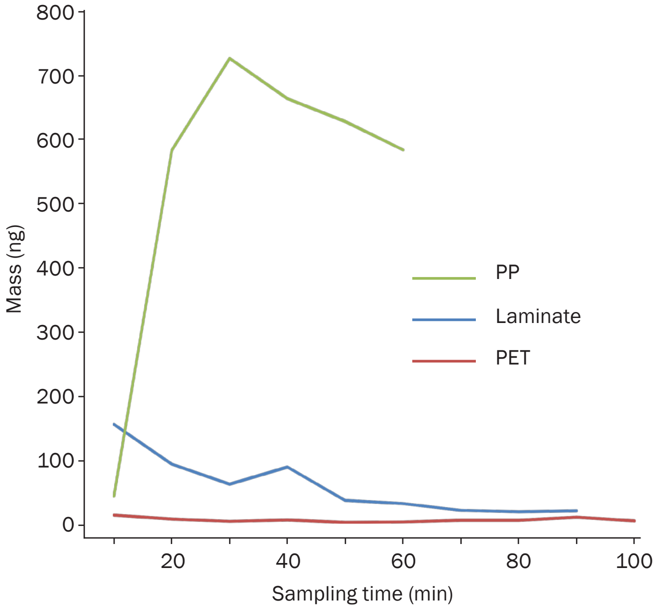
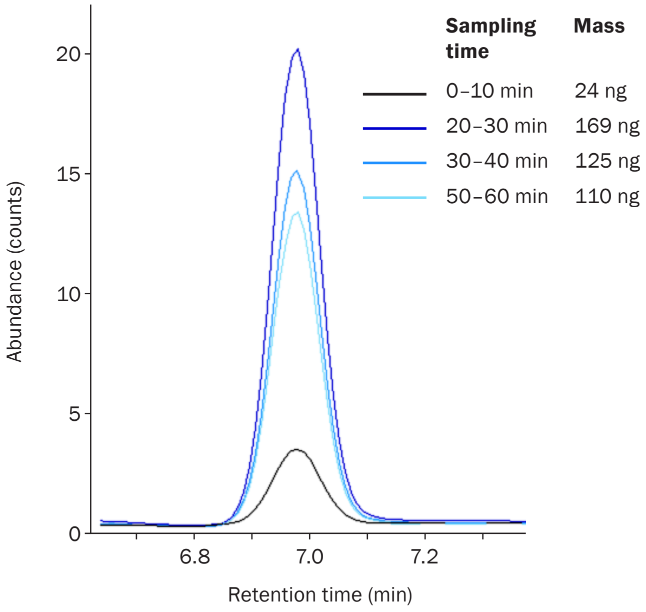


Figure 5: Comparison of the mean permeability profiles (n = 3) for each of the three polymers, for (**A**) limonene and (**B**) n-dodecane (the x-axis values are the times since the start of the experiment; the masses obtained are those collected over the previous 10 minutes).

Considering the PP experiment, it can be seen that the amount of limonene and n-dodecane migrating increases sharply over the first 30 minutes, as the integrity of the polymer reduces. After this point, the masses migrating through diminish, because of the reduction in the vapour concentration as the amount of the two compounds in the well approaches zero. Figure 6 illustrates this progression by two sets of overlaid chromatograms.

A – Limonene



B – n-Dodecane

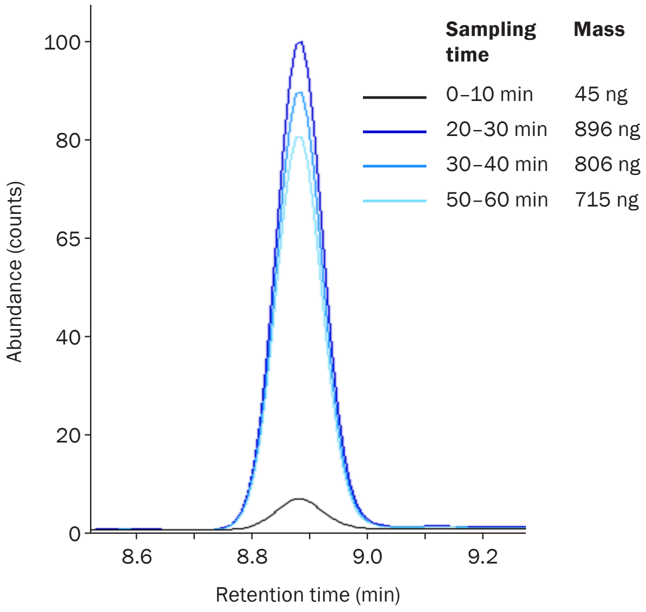


Figure 6: Examples of chromatographic peaks for (**A**) limonene and (**B**) n-dodecane, showing the response from each chemical permeating through PP film at four points over the course of the 60-minute experiment.

PET, on the other hand, shows a comparatively low permeability to both chemicals, and based on this initial assessment would appear to be the most desirable material for reducing chemical permeation.

Finally, the laminate sample, which as a composite material might be expected to have a low permeability, actually lets through a considerable quantity of limonene, at a rate that diminishes over the course of the first hour. (To confirm that this was indeed the result of permeation, blank tests showed that the laminate itself did not emit limonene or n-dodecane – see Figure 7). This rather surprising result is an example of the complex properties that can be exhibited by polymeric materials, and this clearly warrants further investigation.

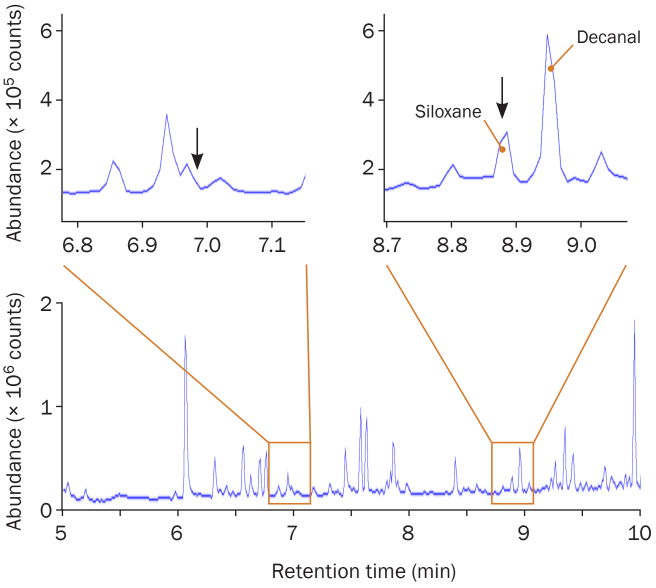


Figure 7: Analysis of a sample of laminate showing the absence of limonene (RT 6.98 min, arrow) and n-dodecane (RT 8.88 min, arrow). Mass spectra confirm the peak at 8.88 min belongs to a siloxane rather than n-dodecane.

Conclusion

In this Application Note, we have shown that the permeation accessory expands the application range of the µ-CTE, by providing a simple and reliable way of investigating the migration of chemicals through membranes – for example, the thin films used to protect food, or the materials used in personal protective equipment. It can also be used to validate the performance of the µ-CTE, by comparing results obtained by using standard materials and liquids in each of the chambers.

Used in conjunction with TD–GC–MS, the permeation accessory is able to provide data on the rates of migration of chemicals through a material, overcoming the difficulty in predicting how a given material will respond to a particular chemical (or indeed a mixture of chemicals).

It is expected that the empirical data generated by this approach will prove particularly valuable because of the rising use of polymer composites and other advanced materials that are very challenging to model theoretically.

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