TDTS 23

Using the UNITY method development mode to analyse dried foodstuffs by direct desorption

Summary

This Application Note demonstrates how the automatic method development mode of the UNITY™ thermal desorber allows samples to be sequentially desorbed at progressively higher temperatures. This allows identification of the desorption conditions that produce a representative VOC profile without causing degradation of the sample.

Introduction

Thermal desorption is widely used as a high-sensitivity alternative to solvent extraction and static headspace for the determination of volatile organic compounds (VOCs) in solid matrices. Examples of successful applications include:

- Flavour and fragrance profiling of foodstuffs
- Off-odour and taint analysis in dried foodstuffs, soap powders and food packaging
- Residual solvent analysis in pharmaceuticals and food packaging
- Residual monomer measurements in polymers.

Direct desorption

Direct desorption of dry or homogeneous materials, such as ointments and resins, is straightforward and cost-effective means of extraction of VOCs from small samples. Sample preparation is kept to a minimum – the only requirement being that the sample mass is known.

The main criterion for direct thermal desorption of solid materials is that the extraction takes place at a temperature below the decomposition point of materials in the sample matrix. Typically, samples are desorbed at least twice, at a low temperature to start with. The desorption temperature is then gradually increased and the analysis repeated until the required chromatographic profile is obtained or until all components of interest have been extracted. Complete extraction is shown to have occurred when repeat analysis at the same or a slightly higher temperature generates a blank chromatogram. The unique method development mode of Markes' UNITY thermal desorber allows automation of this process, with substantial time savings.

Method development

The objective was to generate a representative odour profile of a common food additive (used to enhance flavour and colour in a number of dried foodstuffs), which could be used to assess the quality of the material.

Preparation of material for direct desorption

Considerations when preparing materials for direct desorption include:

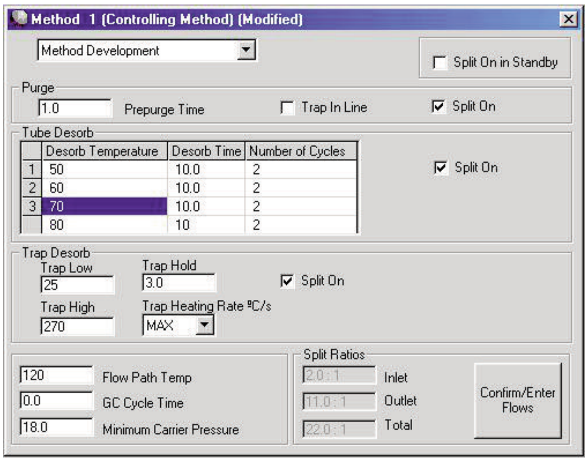
- The sample size (typically approximately 100 mg) must be representative of the sample as a whole.
- The surface area of solid materials should be as high as possible. Bulk solid samples such as tablets should be ground to fine granules (<1 mm^3) using a coolant such as solid CO_2 to prevent premature volatile release.
- Gas must be allowed to pass through the sample unrestricted. This is a particular concern when handling resinous samples, or if a plastic sample is allowed to melt. In such cases keep sample masses low (~20 mg) to prevent blockage.
- Samples must be placed inside the sample tube so that they are well within the central 60 mm heated zone of the thermal desorption oven. Samples less than 15 mm from the ends of the tube will not reach the required temperature.

In this case, the additive was weighed into a PTFE tube liner[1] between two plugs of clean, unsilanised glass wool (Figure 1). This prevents contamination of the inner surface of the tube and eliminates the risk of metal tube surfaces causing sample degradation.

Figure 1: Schematic of sample loaded into a PTFE liner ready for insertion into an empty stainless steel tube.

Thermal desorption

Based on experience, it was decided to start method development at a desorption temperature of 50°C for 10 minutes. The analysis was carried out twice at 50°C, 60°C, 70°C and 80°C. An additional single desorption was programmed to be carried out at 90°C, which was known to be near the maximum safe temperature of the material.



Method Development

☐ Split On in Standby

Purge

Prepurge Time: 1.0

☐ Trap In Line

☑ Split On

Tube Desorb

	Desorb Temperature	Desorb Time	Number of Cycles
1	50	10.0	2
2	60	10.0	2
3	70	10.0	2
	80	10	2

☑ Split On

Trap Desorb

Trap Low: 25

Trap Hold: 3.0

☑ Split On

Trap High: 270

Trap Heating Rate ºC/s: MAX

Flow Path Temp: 120

GC Cycle Time: 0.0

Minimum Carrier Pressure: 18.0

Split Ratios

Inlet: 2.0 : 1

Outlet: 11.0 : 1

Total: 22.0 : 1

Figure 2: Screenshot showing method development table from UNITY software.

Using the method development mode of the UNITY software, a method table was constructed to do this automatically. No user intervention was required after the sample was loaded and the first run initialised (Figure 2).

Using the GC cycle time facility on UNITY, the instrument can be programmed to start the next desorption before completion of the previous GC run, so that at the end of the desorption period, the GC is ready to accept the next injection as soon as the trap heats. After the first run, this reduces the overall cycle times to that of the GC. For an entire method development sequence, the overall time saving can be very significant.

The complete TD–GC method was as follows:

TD:

Desorb temp.:	50/60/70/80/90°C
Flow path temp.:	120°C
Desorb time:	10 min
Carrier pressure:	18 psi
Focusing trap sorbent:	Tenax® TA
Desorb flow:	20 mL/min
Focusing trap low:	25°C
Split flow:	20 mL/min
Focusing trap high:	270°C
Total split ratio:	22:1
Focusing trap hold:	3 min

GC:

Column:	30 m × 0.32 mm × 0.5 µm, methyl silicone (non-polar)
Temp.:	50°C (5 min), then 10°C/min to 230°C (5 min)

Results

Chromatograms for each desorption run are shown in Figures 3–7.

Desorptions at 50°C (Figure 3)

The first desorption at 50°C shows quite large quantities of the more volatile components. Components eluting at 4.5, 6.2 and 12.7 min are the most significant at this temperature. After the peak at 15 min (column temperature 150°C) there are very few significant peaks.

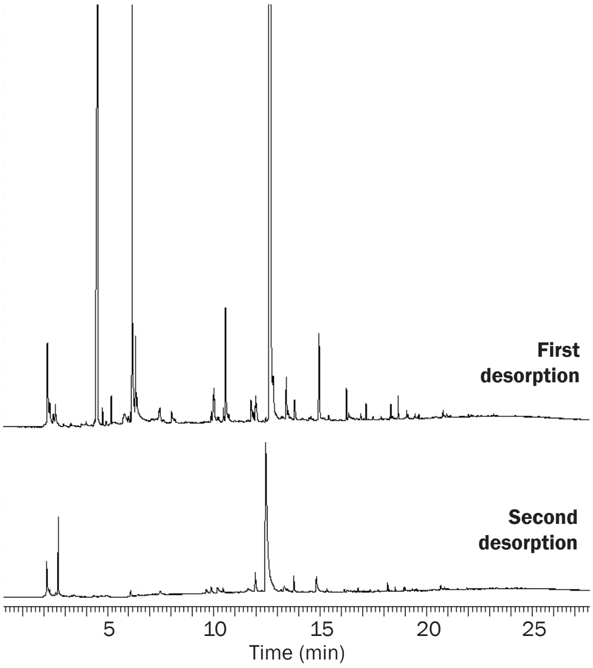


Figure 3: First and second desorptions at 50°C.

A second desorption of the sample at 50°C shows that most of the volatile components were completely desorbed from the tube during the first desorption. However, there is still a significant amount of the component at 12.7 min.

There are very few volatile peaks in these two chromatograms. The components at 4.5 and 6.2 min have been completely extracted during previous desorptions at 50°C. The component at 12.7 min is still eluting in significant quantities, and the peak at 15 min is also present at a similar concentration to the previous desorptions.

Desorptions at 60°C (Figure 4)

The second desorption at 60°C produced a very similar chromatogram to the first desorption, and is still releasing the component at 12.7 min.

The chromatogram shows almost no volatile peaks, and it is clear that they have all been desorbed in previous runs. Less volatile components are now starting to be released from the sample, with the component at 15 minutes starting to increase in size and another component eluting at 16.3 min.

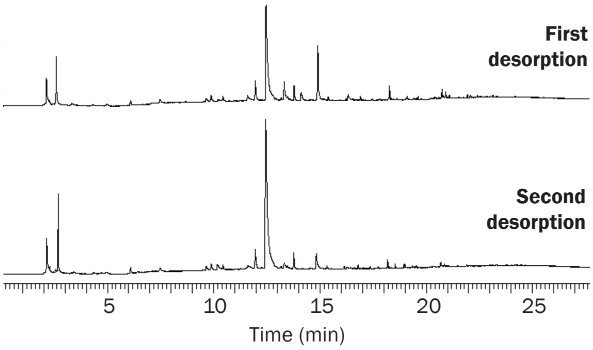


Figure 4: First and second desorptions at 60°C.

Desorptions at 70 °C (Figure 5)

No new components appear during the first desorption at 70 °C, but less volatile components are now being extracted from the sample in significant amounts, especially components at 15, 16.3 and 19 min.

The second desorption produces an almost identical chromatogram. This is a good indication that 10 min at 80 °C is likely to produce a stable and representative chromatographic profile.

Desorptions at 80 °C (Figure 6)

A significant amount of the component eluting at 19 min can be observed in this run, but there are no significant new components.

Desorption at 90 °C (Figure 7)

As 90 °C was known to be near the maximum for this material, only one desorption was carried out at this temperature. After analysis, the sample showed signs of degradation – it had darkened in colour and was starting to solidify. No further desorptions were carried out.

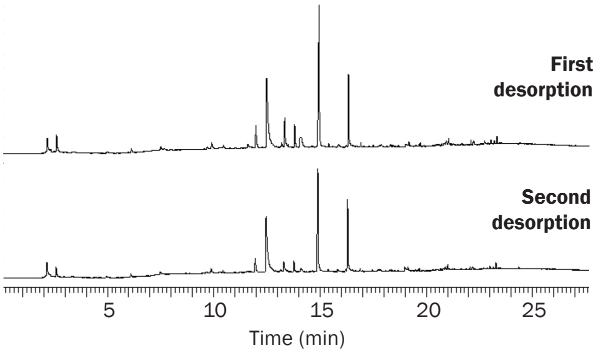


Figure 5: First and second desorptions at 70 °C.

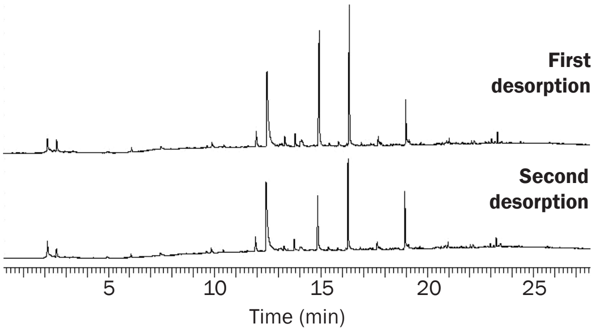


Figure 6: First and second desorptions at 80 °C.

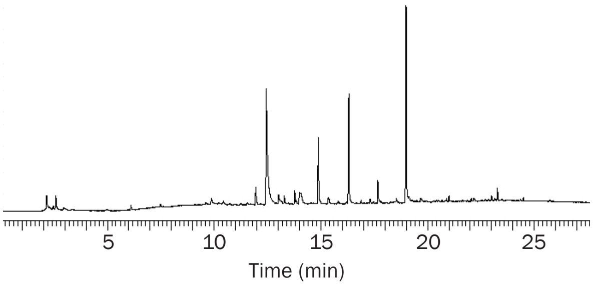


Figure 7: Desorption at 90 °C.

Figure 8 compares the first desorption at 50 °C with that at 90 °C, and clearly shows that additional components are eluted from the sample at the higher temperature.

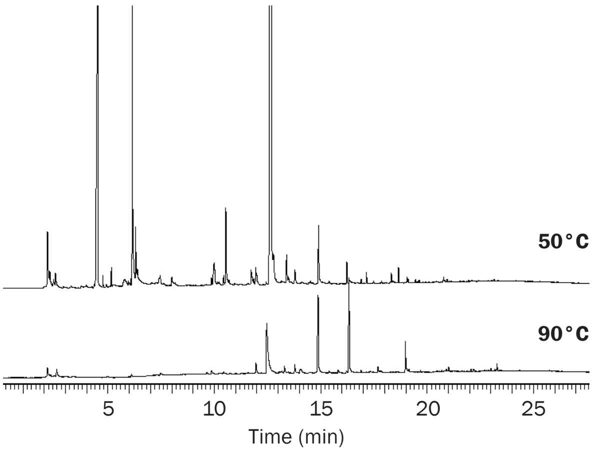


Figure 8: Comparison of first desorption at 50 °C (top) with that at 90 °C (bottom).

Conclusions

The automatic method development mode of UNITY instruments enabled this sample to be sequentially desorbed at progressively higher temperatures, allowing optimum desorption conditions to be identified. Use of the GC cycle time parameter also reduced the total time taken for this work.

In this case, it is clear that a desorption temperature of 80 °C would produce a profile representative of the complete range of volatiles present in the sample, without causing noticeable degradation of the sample.

Trademarks

UNITY™ is a trademark of Markes International Ltd, UK.

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