TDTS 52

The use of TD–GC(MS) in flavour and fragrance profiling

Summary

This Application Note provides an overview of methods for the analysis of the flavour and fragrance profiles of natural materials and consumer products using thermal desorption (TD) in conjunction with GC(MS).

Introduction

The human nose is one of the most sensitive detection systems known, playing a pivotal role in our senses of smell and taste. It is therefore understandable that a great deal of research is concerned with ensuring that foodstuffs and products destined for human use are both safe and pleasing to our senses. An understanding of the flavour or fragrance profile of natural materials also allows certain flavours and scents to be artificially recreated by flavourists and perfumers.

Thermal desorption (TD) may be used to obtain representative profiles of volatile organic compounds (VOCs) contributing to the characteristic taste or smell of a substance. It provides a versatile and high-sensitivity alternative to other traditional sample preparation methods such as solvent extraction or static headspace, and involves minimal manual sample handling, thus reducing costs.

Thermal desorption is a versatile solution for materials testing, offering a variety of approaches to sample introduction. Key options include:

1. **Off-line collection** of organics by either pumping or purging headspace vapours onto sorbent tubes. These tubes are then placed into the thermal desorber for subsequent desorption and analysis.
2. **Direct desorption** of the material weighed into an empty sample tube or PTFE liner. Using this method organic compounds are extracted directly into the carrier gas stream and selectively focused, allowing them to be analysed without matrix or solvent interference.
3. Using the **Direct Inlet Accessory**, headspace vapours can also be pumped or purged on-line directly into the focusing trap of the UNITY™ thermal desorber, allowing continuous monitoring of changes in the vapour profile over time.
4. Use of **quantitative re-collection and analysis** (SecureTD-Q™ technology), to overcome the 'one-shot' limitation of thermal desorption.

1. Off-line sampling onto tubes

Representative fragrance or flavour profiles are readily obtained by purging headspace vapours onto a thermal desorption tube packed with sorbent (Figure 1). This 'purge-and-trap' technique involves connection of the sorbent tube to the outlet port of a vessel containing the sample of interest. Products suited to this method of sampling include drinks, toiletries (Figures 2–5), growing plants, natural oils, and fresh and prepared foodstuffs. This approach is also used to compare flavour profiles in the development of GM foods. After purging, the tube is removed from the sample flow path and analysed using two-stage thermal desorption.

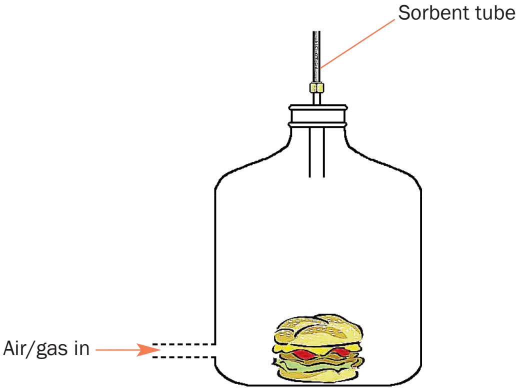

Figure 1: Example apparatus for purging headspace vapours onto sorbent tubes. Applications include off-odour and shelf-life testing.

In common with general air monitoring applications, sorbent selection is one of the most important considerations. Application Notes TDTS 5 and 20 give further information on sorbent selection and safe sampling volumes for a range of VOCs on different sorbents. Note that it is often possible to select a sorbent or series of sorbents that quantitatively retain the compounds of interest while allowing unwanted volatiles (*e.g.* water or ethanol) to pass through unretained. This enhances characterisation of flavour/fragrance profiles by reducing interference.

Another consideration, particularly during investigation of off-odours, is whether the components are likely to undergo thermal decomposition or react with non-inert sorbents/tubes. Stainless steel tubes that have been coated with a special inert coating, or glass tubes, can be used in combination with inert sorbents to preserve thermally labile compounds, which may otherwise decompose during analysis.

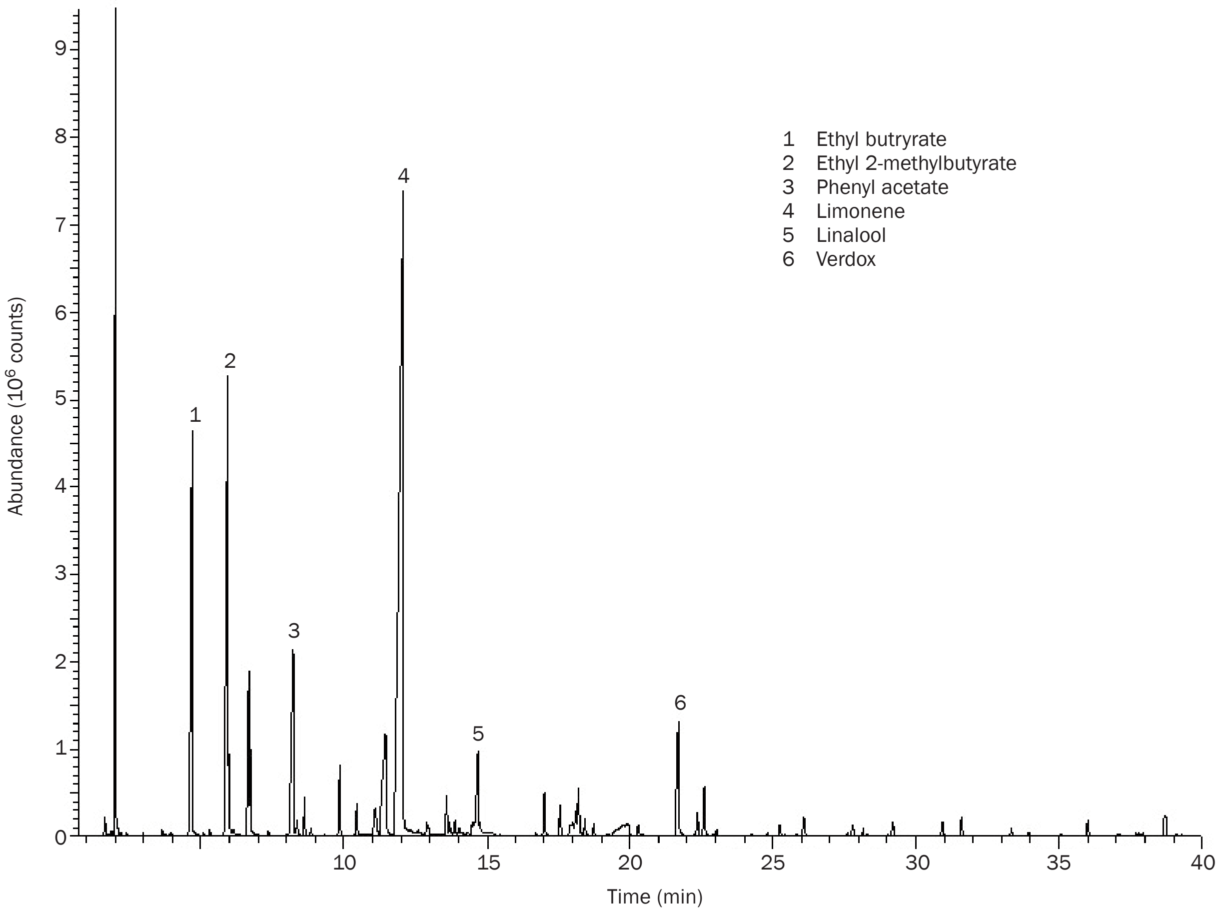

Figure 2: Profile of shampoo headspace, sampled off-line into sorbent tubes packed with Tenax® TA.

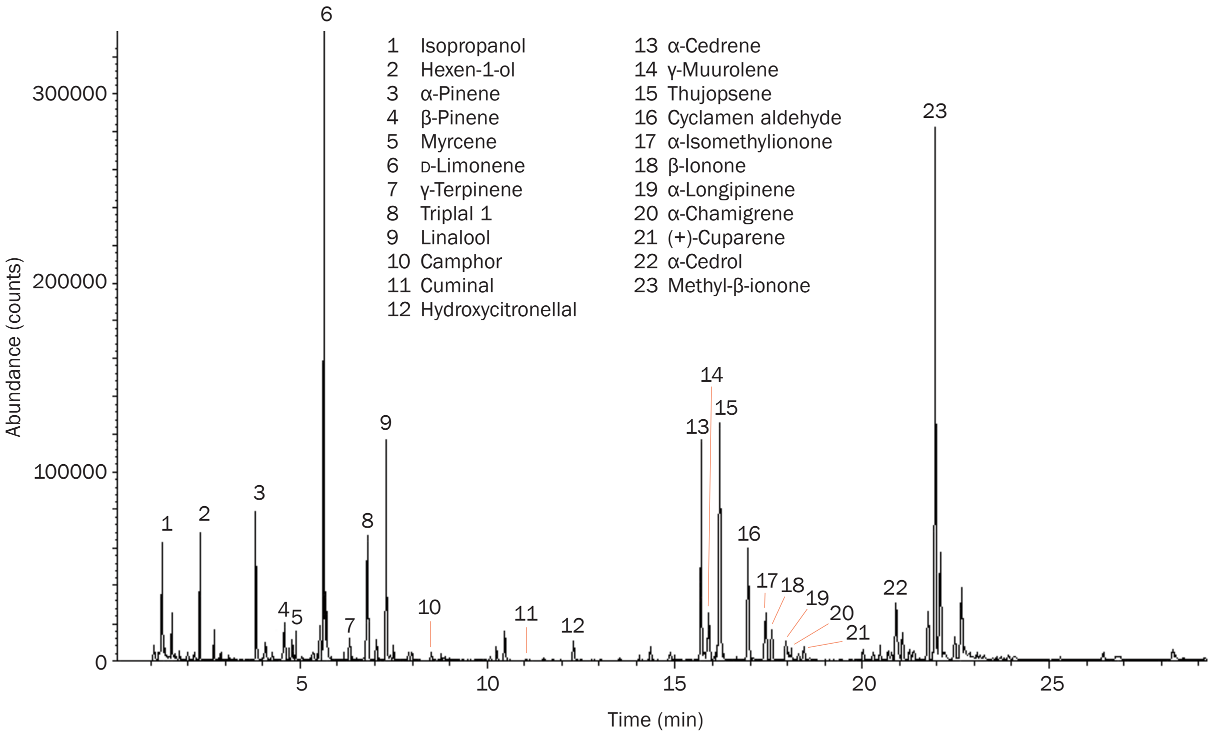

Figure 3: Profile of fabric conditioner headspace, sampled onto sorbent tubes packed with Tenax TA and UniCarb™.

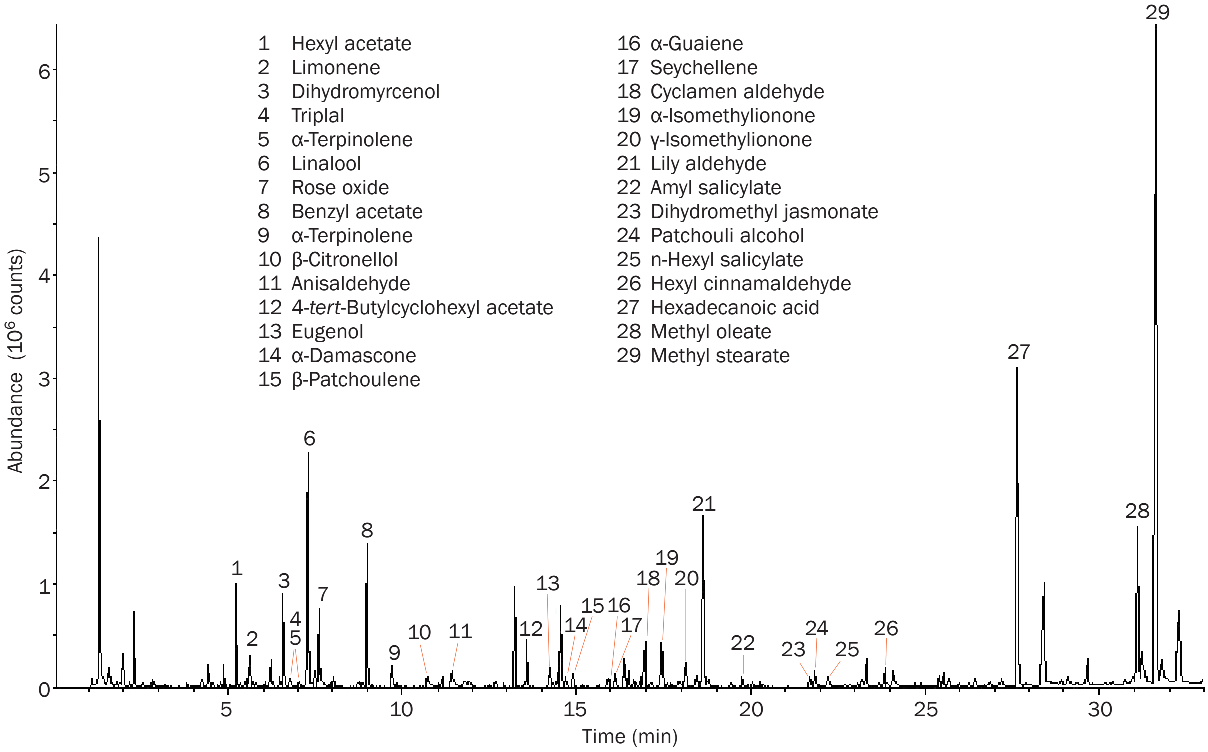

Figure 4: Profile of soap flake headspace, sampled onto sorbent tubes packed with Tenax TA and UniCarb.

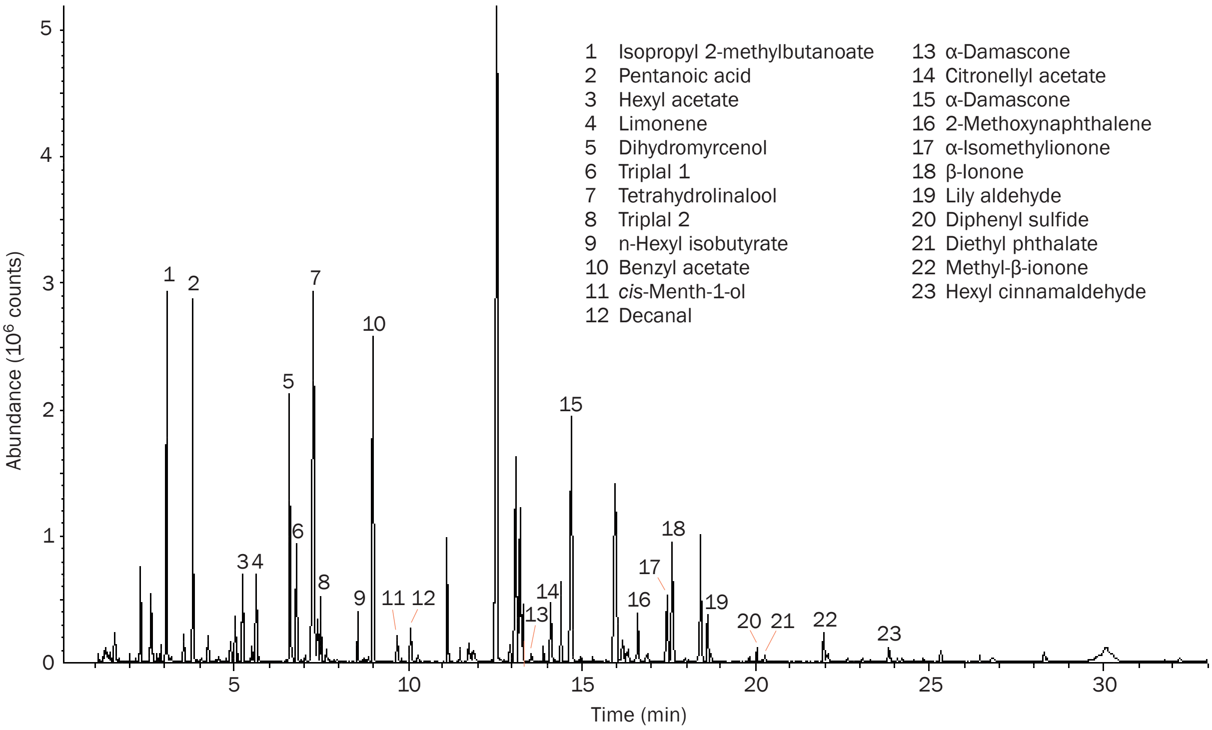

Figure 5: Profile of washing powder headspace, sampled onto sorbent tubes packed with Tenax TA and UniCarb. The powder was mixed with water in order to simulate the headspace generated under normal use.

2. Direct desorption

Direct desorption is particularly suited to homogeneous samples, where a small amount of sample taken is representative of the bulk material. Suitable samples include dried ground spices, ground coffee, packaging materials, fats, syrups and pastes.

Solid materials are typically weighed into a PTFE liner, which is then inserted into an empty metal thermal desorption tube for analysis (Figure 6a). Some dry and non-reactive sample substrates, like printed packaging film, can be weighed directly into empty glass or metal tubes (Figures 7 and 8). The mass of sample should be sufficient to be representative, but should not normally exceed 50 mg of powder.

Resinous samples (toothpastes, cosmetic creams or medical ointments) should be weighed into custom-made glass boats or smeared on the inside of a PTFE liner (Figure 6b). Masses are typically kept below 20 mg to prevent tube blockage.

If the material is a liquid (such as shampoo), approximately 5 µL can be deposited onto a plug of glass wool inside a PTFE liner using, for example, a Pasteur pipette (Figure 6c).

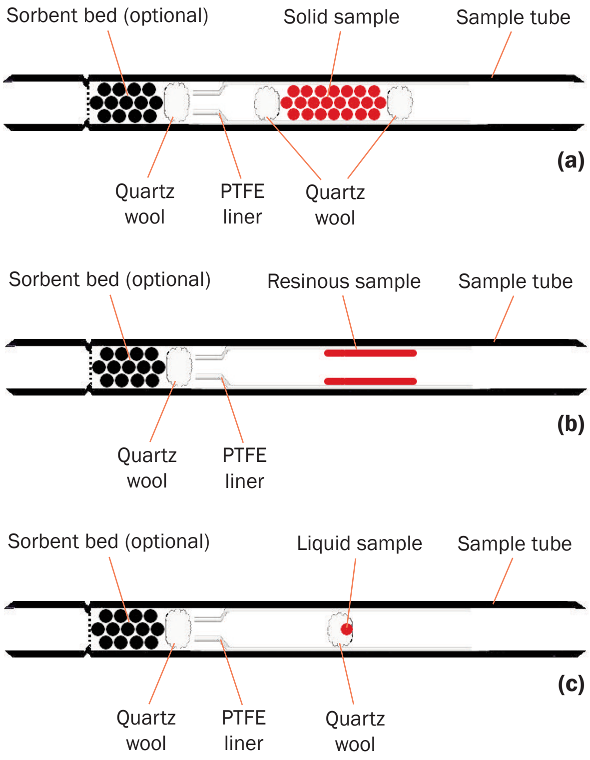

Figure 6: Preparation of sample tube for direct desorption of (a) solid, (b) resinous, (c) liquid samples.

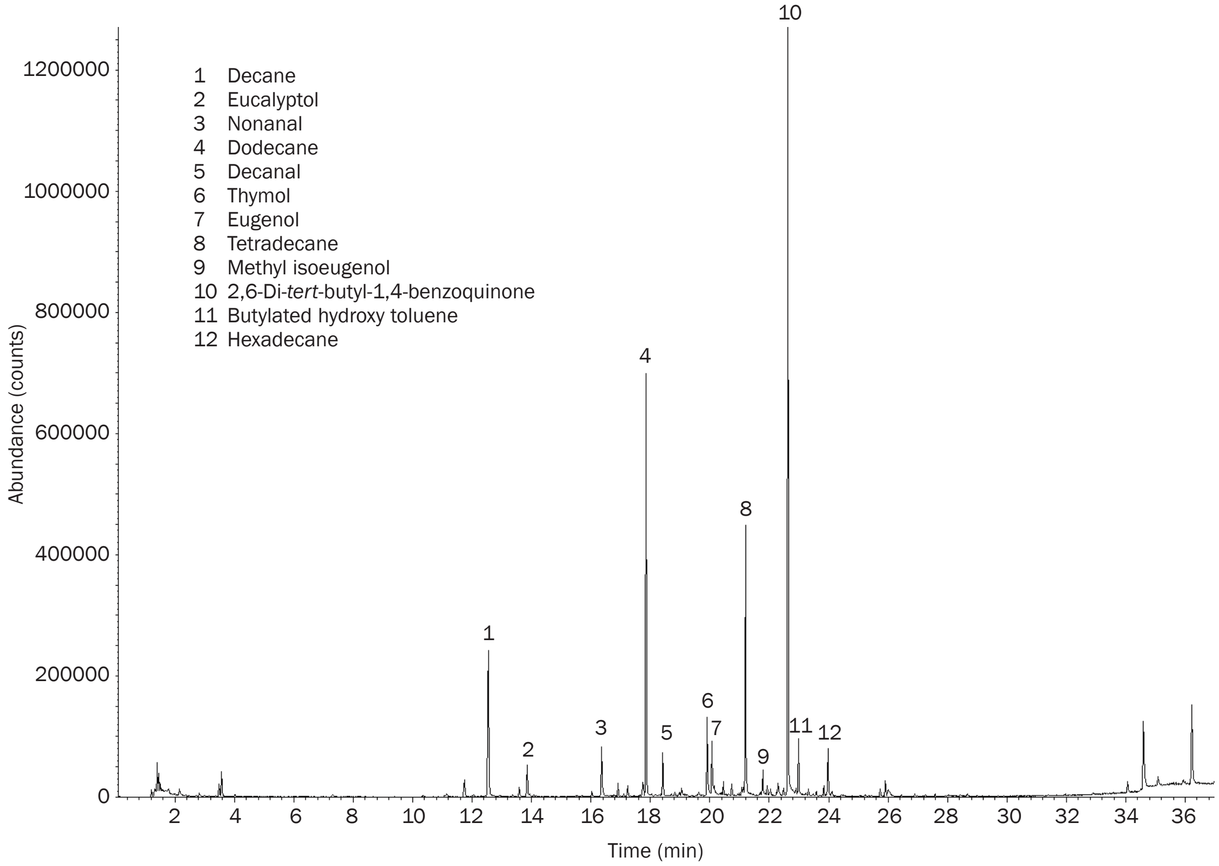

Figure 7: Direct desorption of animal foodstuff pellets. The sample was ground up and weighed into an empty glass TD tube before desorption at 80 °C.

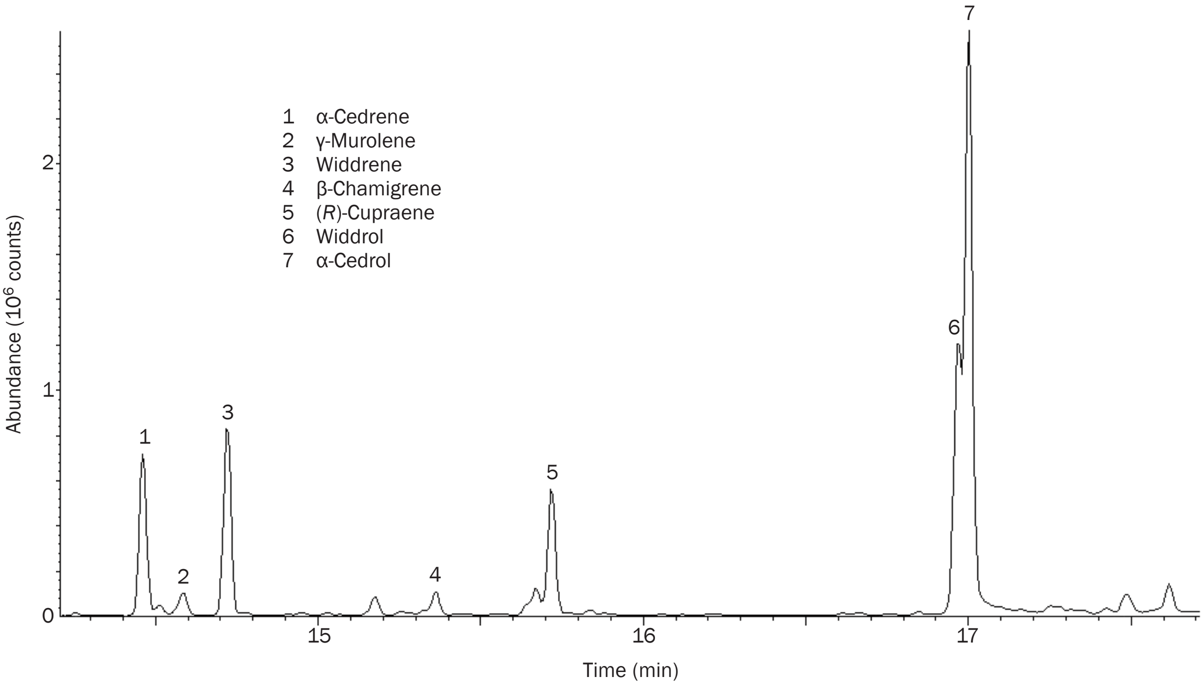

Figure 8: Direct desorption of cedar wood. The sample was inserted into an empty glass TD tube and secured with clean quartz wool before desorption at 120 °C.

In order to carry out successful direct desorption, it is important to follow a few guidelines:

- Do not block the thermal desorption tube with sample. The whole extraction process is reliant on gas flow through the tube to assist the desorption, so any restriction in the flow inhibits the dynamic process
- Ensure that the sample is located within the heated zone of the thermal desorption tube
- Flavour and fragrance applications normally require only modest desorption temperatures, so that no matrix or component decomposition occurs, and the profiles obtained are representative of real-world experience.

It may be necessary to pack a short (1 or 2 cm) bed of conditioned sorbent into the front of the metal sample tube to act as a ‘pre-column’ and prevent high-boiling components or sample matrix (*e.g.* fats) entering the flow path of the thermal desorber. In these cases the PTFE liner containing the weighed sample is then inserted into the sample tube behind the sorbent bed (Figure 6).

A major advantage of this approach is that the matrix material remains in the sample tube and cannot interfere with the analysis or contaminate the system. In many cases, careful selection of the focusing trap sorbents and temperature also means that unwanted volatiles such as water and/or ethanol can be purged to vent during the primary (sample) desorption phase. When the focusing trap is heated to desorb the focused analytes and trigger the GC run, a clean chromatogram is then obtained, free from both matrix and solvent interference.

This approach is particularly well-suited to ointments, pastes or pharmaceutical/cosmetic creams, which can cause serious system contamination issues if conventional solvent extraction methods are used.

3. Use of the Direct Inlet Accessory to transfer vapours directly to the focusing trap

Bulk or heterogeneous samples are incompatible with direct thermal desorption. In these cases on- or off-line sampling of headspace vapours is required. The Direct Inlet Accessory from Markes allows headspace vapours to be purged or pumped directly into the focusing trap of the UNITY thermal desorber. The accessory is heated and is compatible with a range of sample vessels, including headspace vials, Tedlar bags and bell jars (Figure 9).

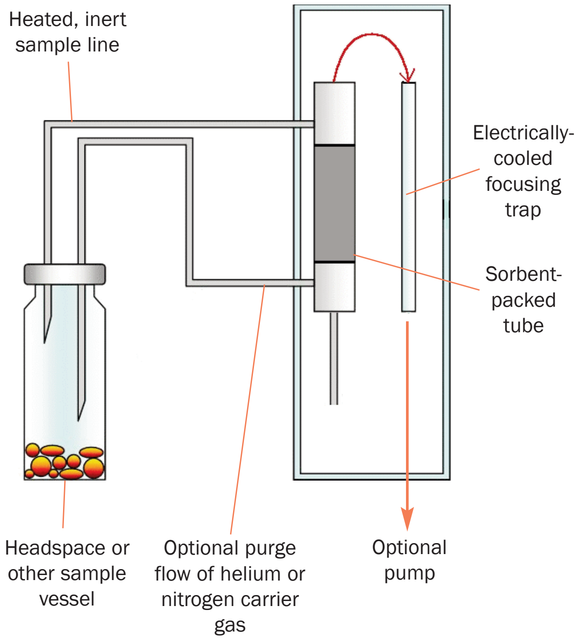

Figure 9: Using the Direct Inlet Accessory to purge/pump headspace vapours directly into the focusing trap of the UNITY thermal desorber.

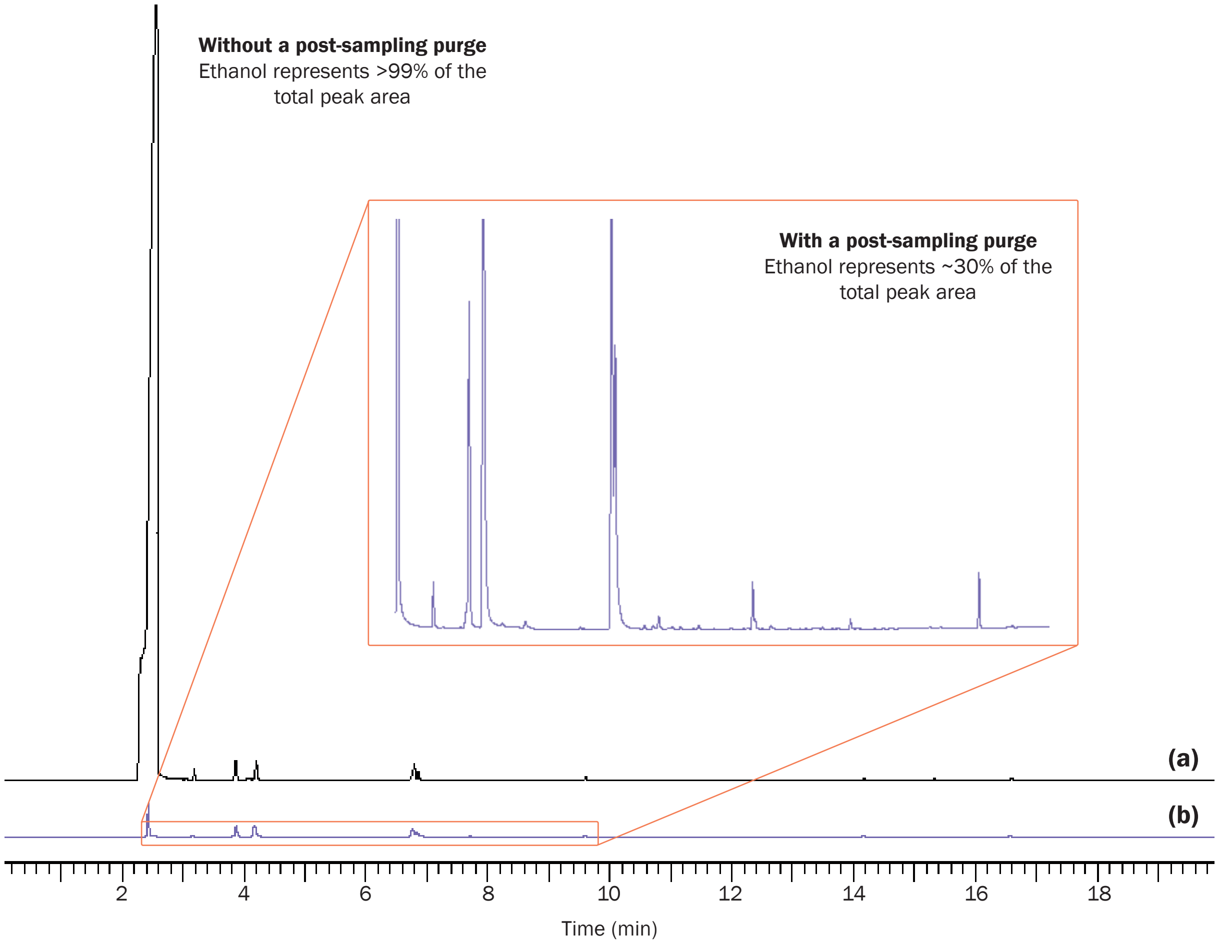

Figure 10: Analysis of whisky, (a) without solvent purging, (b) with solvent purging. Reduction of the large ethanol peak enhances interpretation of characteristic flavour components.

This method of sampling is particularly suitable when monitoring changes in odour profile over time, for example where the subjects are living organisms (*e.g.* insects, bacteria, plants) or prepared foods (*e.g.* pizza, ice cream). The sample vessel can be incubated as required.

The Direct Inlet Accessory can deliver sample to the focusing trap by a number of methods, including:

- Using carrier gas to purge headspace vapours directly onto the focusing trap
- Pumping air/vapours from collapsible or open vessels such as Tedlar bags or bell jars
- Pressurising sealed sample containers such as headspace vials using carrier gas and then allowing the gas to flow onto the focusing trap under its own pressure.

The extraction process can be repeated multiple times (to exhaustion if necessary) before the focusing trap is desorbed, thus maximising the sensitivity of the technique. In contrast to conventional equilibrium headspace (HS), dynamic sampling of HS vapours does not require an equilibrium to be established, thus saving time. It also prevents selective concentration of volatiles, so that the vapour profiles obtained include both volatile and less volatile components and are representative of those under real-world conditions. The transfer line between the sample vessel and the TD is heated to prevent condensation.

As with off-line tube sampling, it is possible to selectively remove certain components from the sample by careful selection of focusing trap sorbents and trapping conditions. For instance, a profile of whisky would normally contain large concentrations of water and ethanol, whilst the key olfactory components (ketones and esters) have very low relative concentrations. By carrying out a post-sampling purge of the water and ethanol from the focusing trap, whilst retaining the high-boiling flavour components, it is possible to enhance the odour profile and improve discrimination between samples (Figure 10).

The UNITY thermal desorber with the Direct Inlet Accessory can also be interfaced to certain commercial headspace analysers to provide sampling automation, in combination with the concentrating power of the thermal desorber (Figure 11). This is particularly useful in situations where the compounds are detectable by the human nose at very low levels.

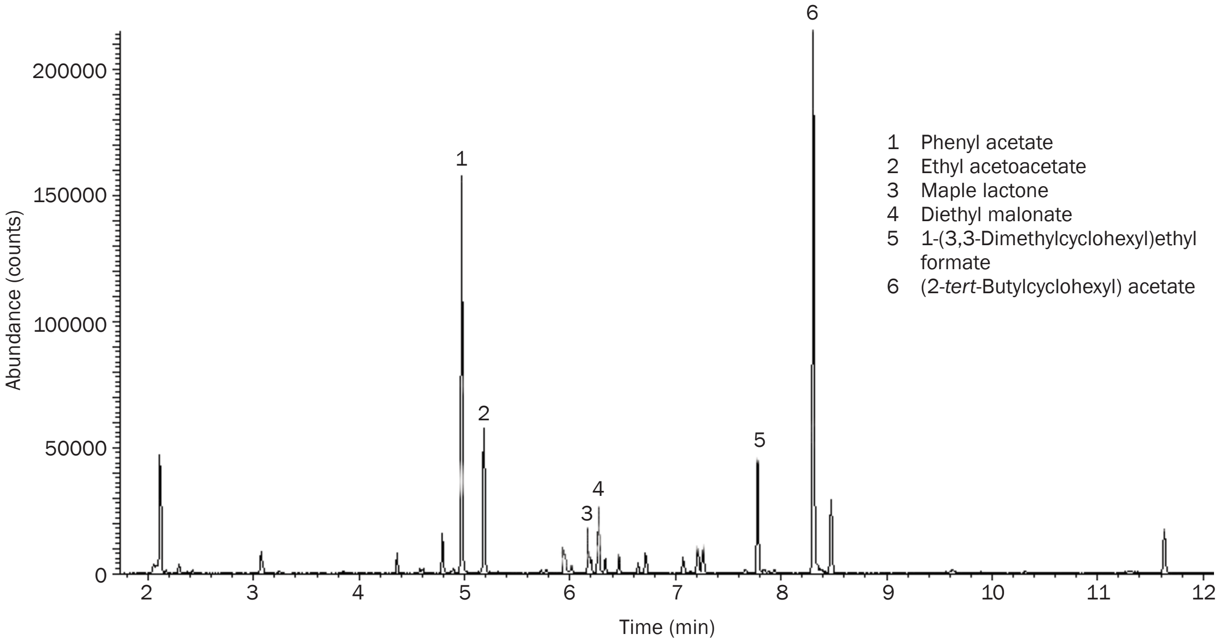

Figure 11: Headspace profile of candlewax, acquired using an Agilent 7694 headspace autosampler, and a Direct Inlet Accessory to transfer the vapours directly into the focusing trap of the UNITY thermal desorber.

4. SecureTD-Q as a tool in flavour & fragrance analysis

Markes' range of thermal desorption systems allow quantitative re-collection of the split flow as standard. This SecureTD-Q technology overcomes the historical 'one-shot' limitation of thermal desorption, with significant benefits for method development and validation (Figure 13).

SecureTD-Q offers significant advantages for flavour and fragrance analysis. For instance, vapours generated by direct desorption of a material or by using the Direct Inlet Accessory can be re-collected onto a sorbent tube for storage or repeat analysis by alternative technologies. It also facilitates re-analysis of samples that are not easy to obtain in duplicate (*e.g.* sampling of scent profiles from rare plants/flowers).

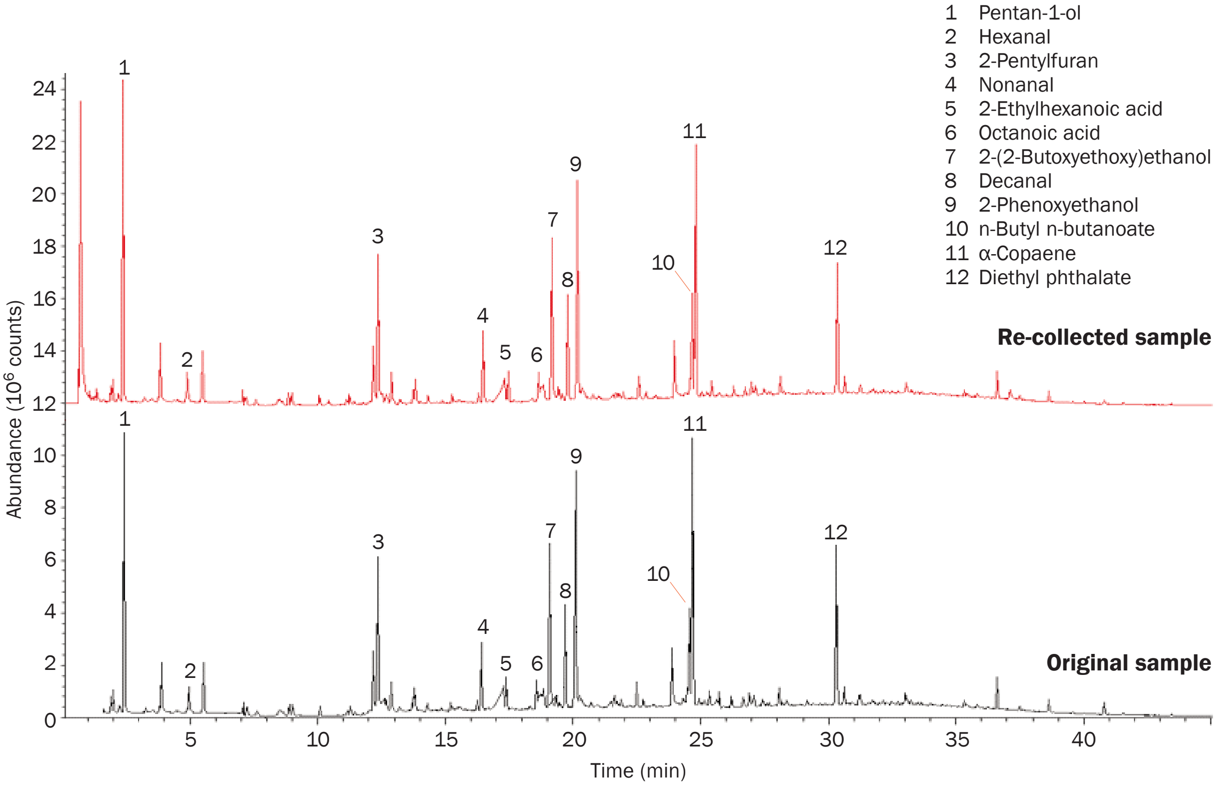

Figure 12: Primary and repeat analysis of the odour profile from boiling potato peel, obtained using quantitative re-collection of split flow (SecureTD-Q). The profile obtained from the re-collected sample exactly matches that from the original analysis.

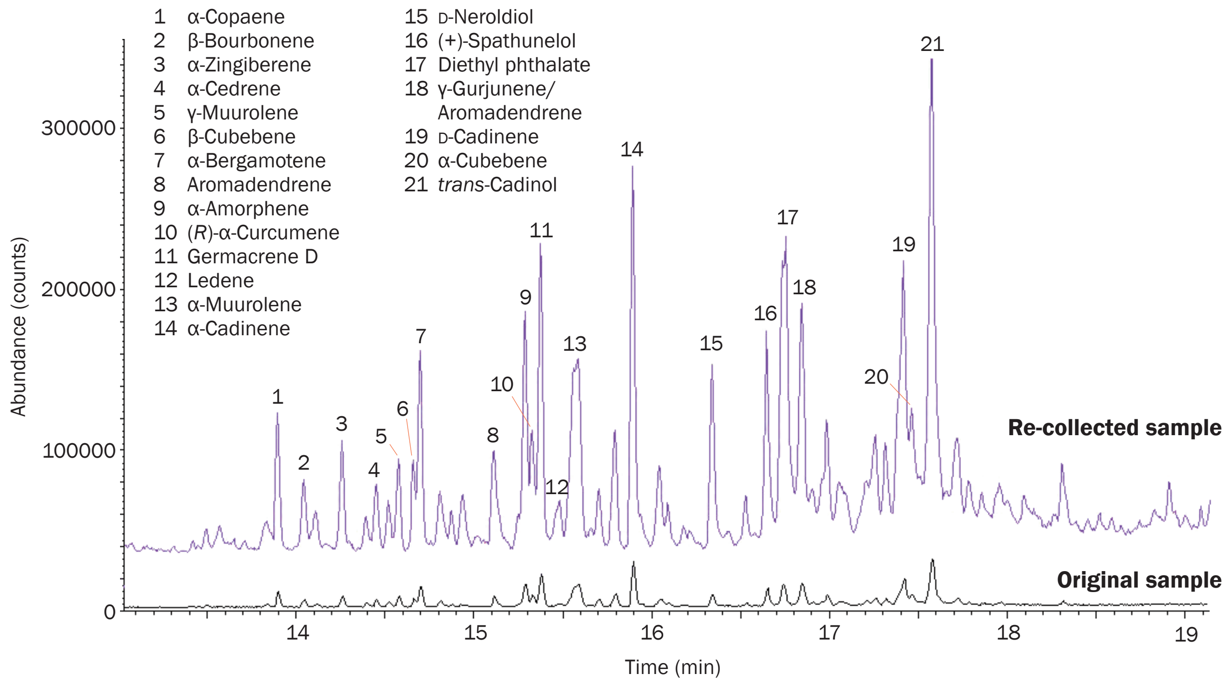

Figure 13: Direct desorption of volatiles from a sample of leaf, followed by analysis of the re-collected sample with a decreased split ratio to enhance sensitivity.

A further benefit of SecureTD-Q is that, during method development, the sample can be re-collected in order to repeat the analysis with optimised conditions. This is illustrated in Figure 14 for the analysis of volatiles from a leaf by direct desorption. The initial analysis, re-collected onto an inert-coated tube packed with Tenax TA and UniCarb, did not result in the required sensitivity, so the analysis was repeated by desorbing the re-collected sample with a reduced split ratio. This enabled enhancement of the sensitivity to identify the components of interest.

Conclusions

The examples presented in this Application Note demonstrate the power and versatility offered by thermal desorption to the food, flavour, fragrance and consumer product industries, as well as to the field of biological research.

The key advantages described include:

- Reduction in sample preparation (cost saving)
- Enhanced automation (productivity)
- Elimination of matrix interference and system contamination
- Wide range of sampling options to suit different sample types
- Selective concentration of target olfactory components with purging of water and volatile interferents, enhancing profiling and improving sample-to-sample discrimination.

Acknowledgements

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