Thermal Desorption Technical Support

Note 84: Using thermal desorption to enhance aroma profiling by GCMS – featuring example applications from the tobacco industry

Key Words:

Air sampling, sorbent tubes, sample identification, RFID, TubeTAG

Abstract

Flavour and fragrance profiles typically comprise contributions from hundreds of volatile organic compounds (VOCs) and those at lowest concentration are often the most important i.e. have the most profound effect on perceived aroma. Historically, this has made it difficult to carry out meaningful aroma tests using standard GCMS instrumentation. Conventional sample preparation methods (solvent extraction, steam distillation, etc.) simply don't offer the sensitivity required and may also distort the vapour profile so that it is no longer representative of the flavour/fragrance perceived by consumers. Odour experts and aroma assessment panels have therefore continued to play a significant role in product testing with respect to flavour and fragrance.

This TDTS Note examines the potential of two recent GCMS-related technological developments for allowing more odour profiling applications to be carried out by automated laboratory instrumentation thus reducing costs. The first of these relates to Markes' latest analytical thermal desorption technology for gas extraction and selective concentration of aroma constituents. The second is a complementary innovation in GCMS reprocessing software which further enhances the measurement of trace olfactory compounds in complex aroma profiles.

The applications and potential advantages of both these technologies for automated aroma profiling are described using applications from the tobacco industry as an example.

Introduction

Flavour and fragrance profiles typically comprise contributions from hundreds of volatile organic compounds (VOCs) and those at lowest concentration can be the most significant olfactory components i.e. have the most profound effect on perceived aroma. Historically, this has made it difficult to carry out meaningful aroma tests using standard GC/MS instrumentation.

Conventional sample preparation methods (solvent extraction, steam distillation, *etc.*) simply don't offer the sensitivity required and may also distort the vapour profile so that it is no longer representative of the flavour/fragrance perceived by consumers. Odour experts and aroma assessment panels have therefore continued to play a significant role in product testing with respect to flavour and fragrance.

These olfactometry procedures work well; however, they are to some extent subjective, are rarely able to identify the precise cause of a problem and are also, by definition, manual and consequently expensive/time-consuming to carry out.

In recent years, analytical thermal desorption (TD) has provided a useful complement to GCMS enabling more aroma profiling applications to be carried out using quantitative, automatic instrumentation. TD combines automated sample preparation with selective analyte enrichment allowing organic compounds to be injected into the GCMS as a narrow concentrated band of vapour, free of most/all sample matrix effects. The technology is available in on- and off-line configurations and is now widely used for vapour profiling in the food, flavour, fragrance and consumer product industries.

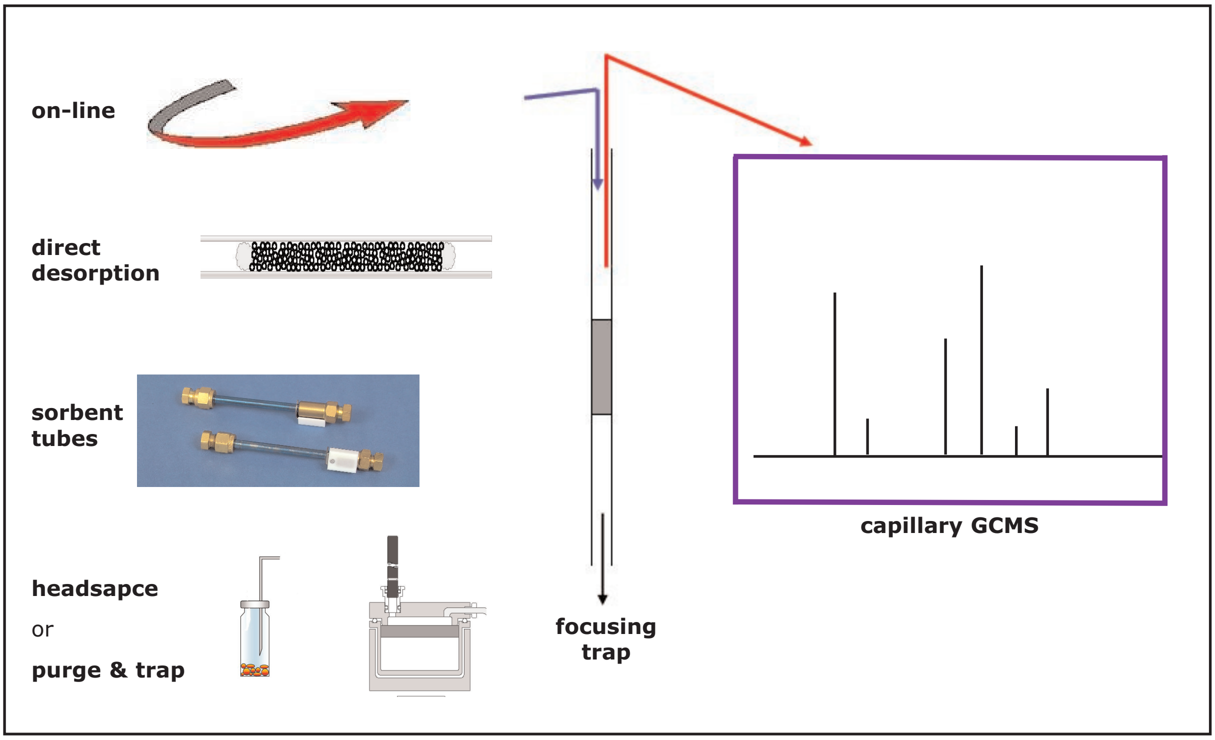


Figure 1: Overview of sample introduction methods compatible with thermal desorption analysis

Sampling options for thermal desorption

One of the strengths of thermal desorption for food, flavour and fragrance profiling is that it offers a versatile range of sampling methodologies (Figure 1).

TD sampling options include:

- **Sorbent tubes/traps**. Used for off-line concentration of organic vapours. The tubes may be packed with multiple sorbents for collecting the complete vapour profile or with a single sorbent that retains key olfactory compounds but allows volatile interferences (*e.g.* water, ethanol and acetic acid) to be purged to vent. Example applications include; profiling the fragrance of consumer products, tracking taint in warehouse air or shipping containers, breath profiling and monitoring crop volatiles.

- **On-line sampling** *i.e.* discontinuous sampling/concentration and analysis - used for monitoring changes in odour profile over time. Example applications include food shelf life studies, diurnal variation in natural (biogenic) fragrances, process gas purity and monitoring the profile of perfume products, such as air fresheners, as they decay with time.

- **Direct, low-temperature desorption of materials** weighed into empty TD tubes – used for screening the odour profile of dry, homogeneous materials such as spices, instant coffee, soap powder, *etc.* Example applications include quality control of spice blends, identifying taint/off-odour in consumer products, validating the quality of natural products (checking for cheap synthetics), QC of packaging and screening the vapour profile of medicinal pastes/creams.

- **Off-line thermal extraction or dynamic sampling of headspace vapours with in-line sorbent trap.** Used for monitoring the vapour profile of a wide range of inhomogeneous products and raw materials. Aroma profiling applications carried out this way include; tobacco and other vegetable products, shampoo and cleaning products, prepared foods (pizza, pet foods, meat products, *etc.*), dairy products, biogenic emissions (insect pheromones, plant volatiles, *etc.*), drinking water odour, taint from packaging, potable spirits and GM foods.

Thermal desorption and repeat analysis

Whichever of these approaches is used to introduce the sample to the TD-GCMS, the compounds of interest end up separated from the sample matrix and focused on a small, electrically-cooled sorbent trap (see figure 1). The focusing trap is subsequently desorbed by heating it rapidly in a reverse flow of carrier gas causing the organic compounds to be injected/transferred into the GCMS analytical system as a narrow band of vapour. Trap desorption efficiency and system inertness are key to ensure optimum sensitivity and quantitative recovery of the widest range of compounds – including odorous, reactive species like mercaptans. Series 2 TD systems from Markes International incorporate a short, totally inert flowapth and a quartz focusing trap which is capable of heating at rates over 100°C/sec. This ensures maximum desorption efficiency and best possible detection limits. Markes TD systems also feature SecureTD-Q - the unique facility to quantitatively re-collect any/all split flow during primary (tube) or secondary (trap) desorption. This allows repeat analysis and simple validation of component recovery through the analytical system (Figure 2).

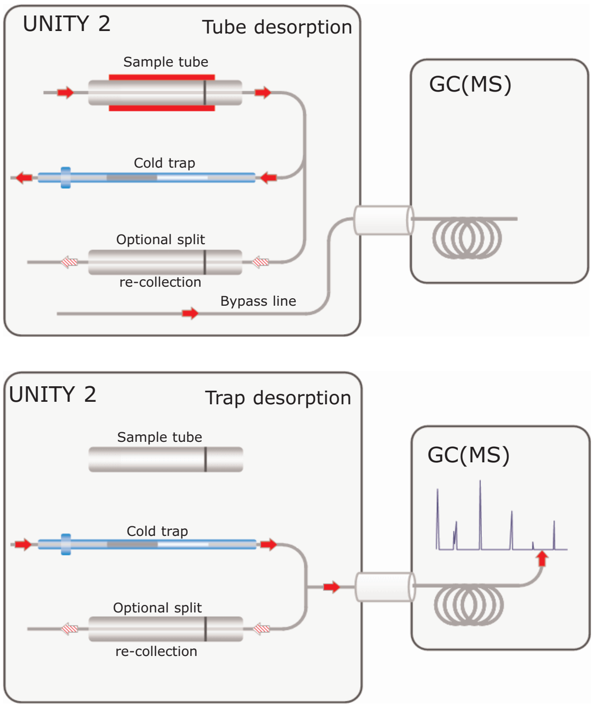


Figure 2: SecureTD-Q: Two-stage thermal desorption with quantitative re-collection of any/all split flow onto a single sorbent tube. Allows repeat analysis and validation of analyte recovery

Pioneered by Markes International, the innovation of SecureTD-Q™ is key for aroma profiling by TD-GC/MS, both in the method development phase and for monitoring system stability/performance long term. Many key olfactory constituents (*i.e.* compounds with the lowest odour thresholds) are very reactive *e.g.* amines, oxygenates and mercaptans. The ability to re-collect a portion of the sample, after it has been through the TD flow path, and then repeat the analysis to check recovery, gives greatly enhanced confidence that target compounds are being quantitatively transferred through the analytical system. If there was a loss of one or more reactive compounds in the profile, this would become apparent by a change in the relative responses in the repeat analysis data.

In both of the cases shown in figure 3 successful recovery of every component tested was demonstrated using the SecureTD-Q re-collection and repeat analysis technique.

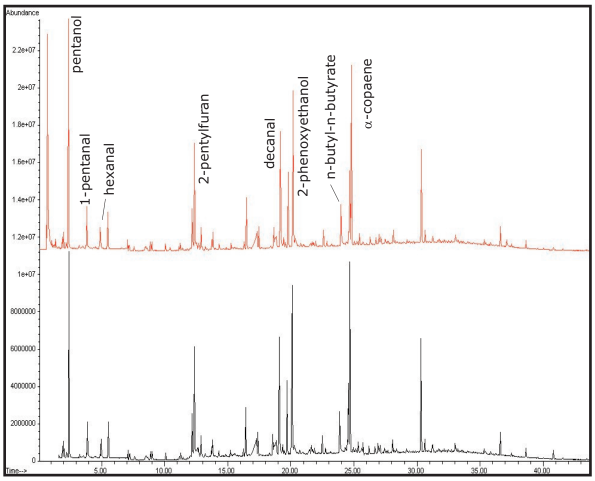


Figure 3a: Vapour profile from boiling potatoes. Original data (black). Analysis of re-collected sample (red) shows identical profile indicating quantitative recovery across the analyte range

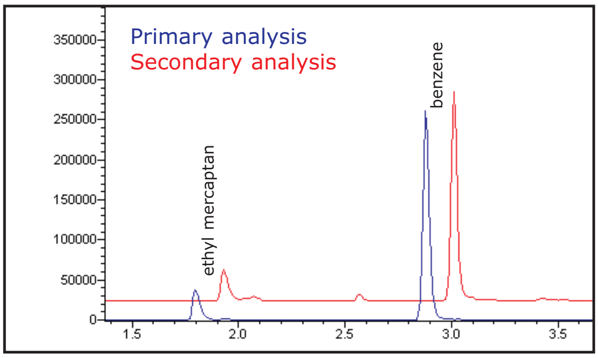


Figure 3b: Primary and repeat analysis of ethyl mercaptan & benzene using SecureTD-Q shows quantitative recovery of this highly reactive compound through the Markes UNITY™ 2 thermal desorber

A fundamental advantage of thermal desorption and its associated sampling methods is that compounds of interest are extracted straight into the GC carrier gas stream. No manual sample preparation steps are required and problems associated with the use of solvents are eliminated *e.g.* masking of peaks of interest, loss of volatiles and variable extraction efficiency. The vapour profile produced is thus more likely to be representative of the aroma perceived by consumers.

The latest Markes TD systems, as described above, are also capable of transferring the vapour profile constituents into the GC capillary column in much smaller volumes of carrier gas than was possible before. Transfer volumes can be as low as 100 µL of carrier gas. This means that very significant concentration enhancement factors can be achieved – typically from 10^3 to 10^6 depending on the number of concentration/desorption steps (Figure 4).

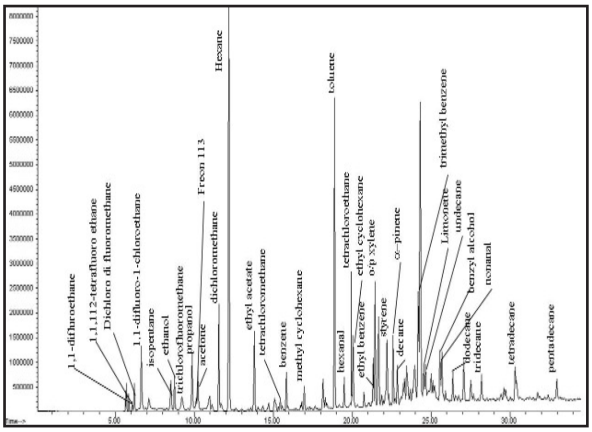


Figure 4: TIC profile of an indoor air sample with ppt level contaminants analysed by TD-GCMS(scan)

Thermal desorption also allows volatile interferences such as water and ethanol to be selectively purged to vent prior to analysis thus making it easier to discriminate between samples according to the key olfactory components (Figure 5).

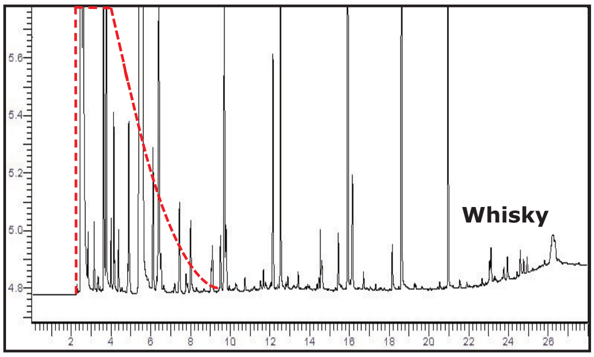


Figure 5: Typical VOC profile from whisky headspace, with illustration (dotted line) of how the ethanol peak would mask key aroma compounds if it was not selectively purged from the trap prior to desorption

Thermal desorption-GCMS in the tobacco industry

Automated thermal desorption was introduced to the tobacco industry in the early 1980's in response to growing public awareness of environmental tobacco smoke[1-3]. However, as cigarette manufacturers invested in TD-GCMS equipment for monitoring trace levels of nicotine and other target compounds in the environment, it gave staff in the product development and quality control departments an additional, versatile analytical tool to apply to the challenges they faced every day. The range of new applications successfully developed included:

A. 'Fingerprinting' the aroma of tobacco raw materials and products.

Tobacco fingerprinting is typically carried out using low temperature thermal extraction of a few grammes of material. Automated headspace-trap[4] or off-line thermal extraction are two typical sampling options in this case.

Markes Micro-Chamber/Thermal Extractor (µ-CTE™) with 6 separate sample chambers and a temperature range of ambient to 120°C is ideal for tobacco profiling. Vapours from the tobacco are collected on sorbent tubes attached to each micro-chamber and are subsequently analysed using 2-stage thermal desorption with GC/MS. Example data are shown in figure 6.

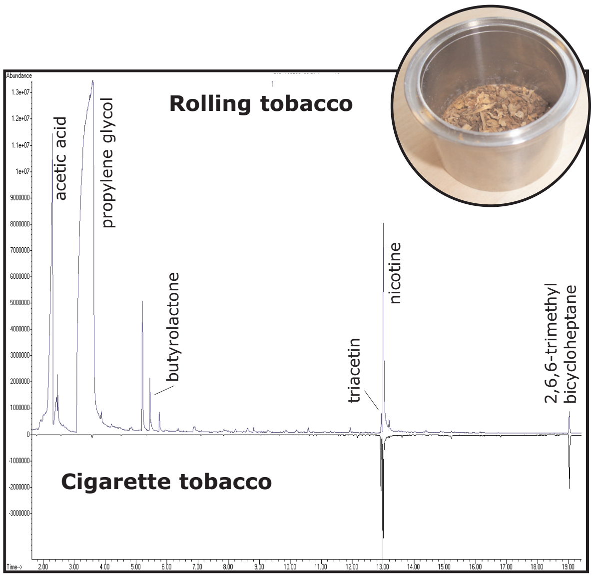


Figure 6: Comparison of rolling tobacco and cigarette tobacco, sampled using the Micro Chamber/Thermal Extractor. Inset shows individual micro-chamber containing tobacco

Direct thermal desorption of smaller samples of tobacco weighed into empty TD tubes is also used occasionally *e.g.* to measure flavour additives such as menthol or vanillin or for screening the total vapour profile (Figure 7).

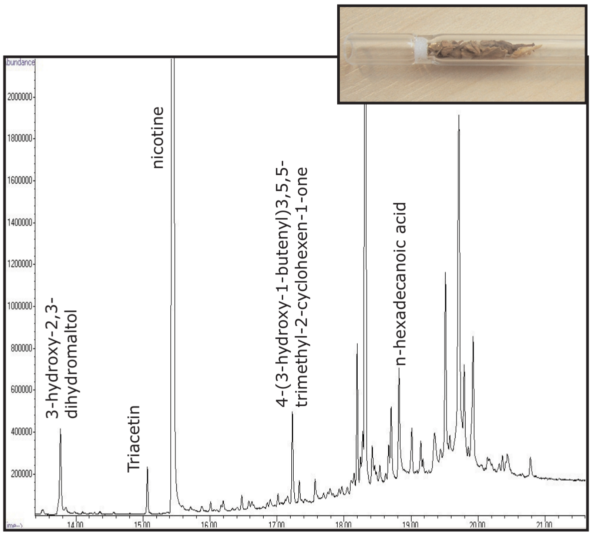


Figure 7: Analysis of tobacco by direct desorption

Both of these approaches (figures 6 and 7) are cost-effective, easy-to automate and not prone to the limitations of conventional extraction methods *e.g.* insensitivity and masking of compounds of interest with the solvent.

B. Identifying and tracking the cause of off-odour and taint complaints.

Cigarette taint can be an expensive issue to deal with if large quantities of product are affected and it is imperative that the cause of the contamination is identified and dealt with promptly. In one actual case, a chemical contaminant causing a raft of consumer complaints was identified and its source determined entirely using thermal desorption with GC/MS. First samples of the tobacco, filter tips and paper from contaminated and control cigarettes were directly desorbed. When the GC/MS data obtained from contaminated samples was compared with that from the controls the chemical culprit was quickly identified. Then direct thermal desorption was used to track the source of the contamination through the cardboard of the cigarette packaging until it was ultimately found that the contaminant had originated from the wooden pallets used to ship the cardboard that made the cigarette packets.

C Assessing the profile of VOCs inhaled by smokers.

"Smoking rigs" are used in the tobacco industry to draw air through lit cigarettes and onto sorbent tubes. In this case the sampling process mimics the actual smoking process by drawing several small volume "puffs" onto the sorbent tube, at specified time intervals, thus allowing the performance of cigarette filters to be monitored. Example TD-GC/MS data are shown in figure 8.

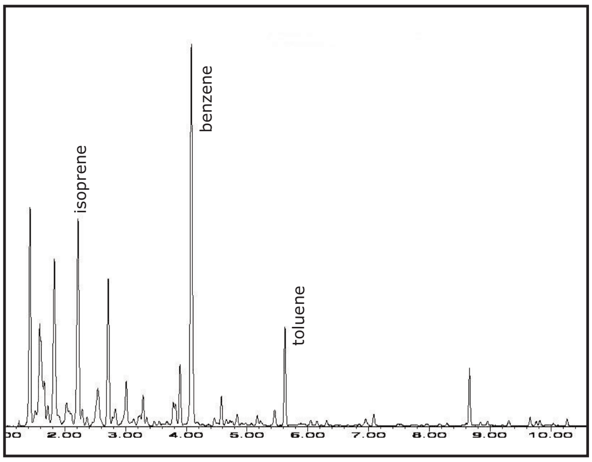
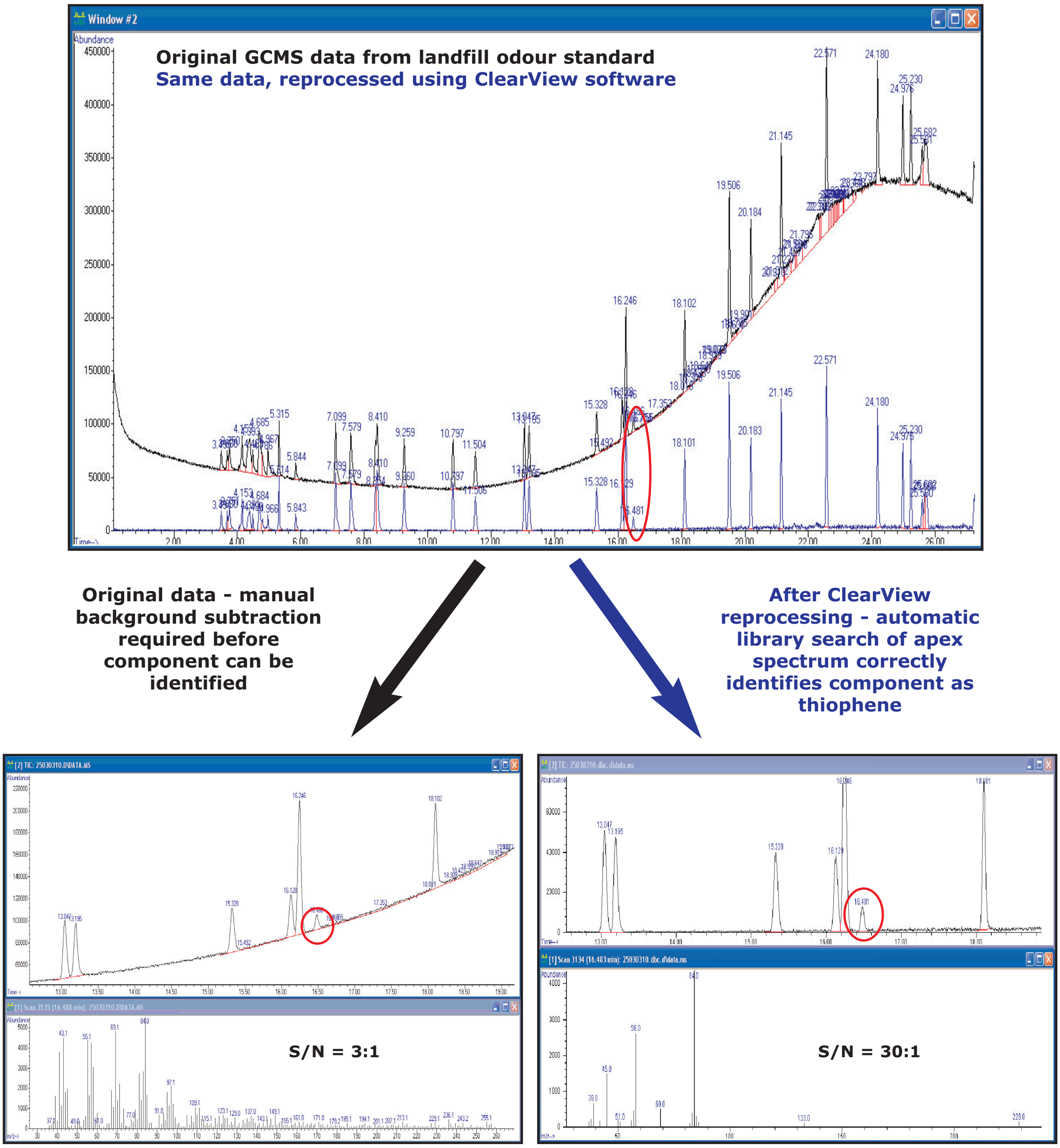


Figure 8: VOCs sampled from a cigarette using a "Smoking engine"

This data enables researchers to refine filter design – minimizing the breakthrough of toxic compounds while optimising consumer perception of aroma.

Enhancing automatic aroma profiling using innovative (TD-) GCMS data reprocessing software

While the latest innovations in analytical thermal desorption technology have provided a major breakthrough in allowing meaningful aroma profiling using automated laboratory instrumentation, TD-GC/MS does not always provide the complete answer. Aroma profiling often relates to natural products or complex composite manufactured products which can result in a high background signal in the total ion chromatogram (TIC) produced (see figure 7). Thick-film high-bleed columns may also be required to separate volatile polar components in the profile and this can also compromise subsequent analysis of trace components. See top chromatogram, figure 9.



Original GCMS data from landfill odour standard

Same data, reprocessed using ClearView software

Original data - manual background subtraction required before component can be identified

After ClearView reprocessing - automatic library search of apex spectrum correctly identifies component as thiophene

S/N = 3:1

S/N = 30:1

Figure 9: A chromatogram of trace-level landfill gas odour standard, reprocessed using ClearView software. This demonstrates the improved spectral quality and increase in signal to noise ratio for trace level components

A new dynamic background compensation (DBC) algorithm called ClearView has been developed by Markes to address this issue. ClearView distinguishes and eliminates mass ions originating from the chromatographic 'background' from those in real peaks, however small. This has great potential for many real-world GC/MS applications including odour and aroma profiling. To summarise how it works; the software reprocesses stored GC/MS data files (singly or in batches) distinguishing mass ions from the background (column bleed, sample matrix, solvent tail, air/water interference, *etc.*) and eliminating their contribution from the mass ion fragmentation pattern of chromatographic peaks. A separate reprocessed data file is then produced with lower interference, better signal to noise and enhanced spectral purity (see figure 9). This boosts sensitivity and aids automatic identification of trace compounds. It also improves integration and the repeatability of TIC and extracted ion data.

NOTE 1: The original data file is left intact for separate analysis if required.

NOTE 2: The GCMS reprocessing software is described in more detail elsewhere[5].

To evaluate the potential of ClearView for enhancing detection of trace olfactory components in complex vapour profiles, the TD-GCMS aroma data from direct desorption of tobacco (Figure 7) was reprocessed using the new software. The reprocessed data is shown in figure 10. The compounds highlighted in red were not detected at first in the original data file but were readily identified and measured after reprocessing using dynamic background compensation. Similarly, those compounds identified in blue gave a library match quality significantly better after reprocessing which was the data using ClearView.

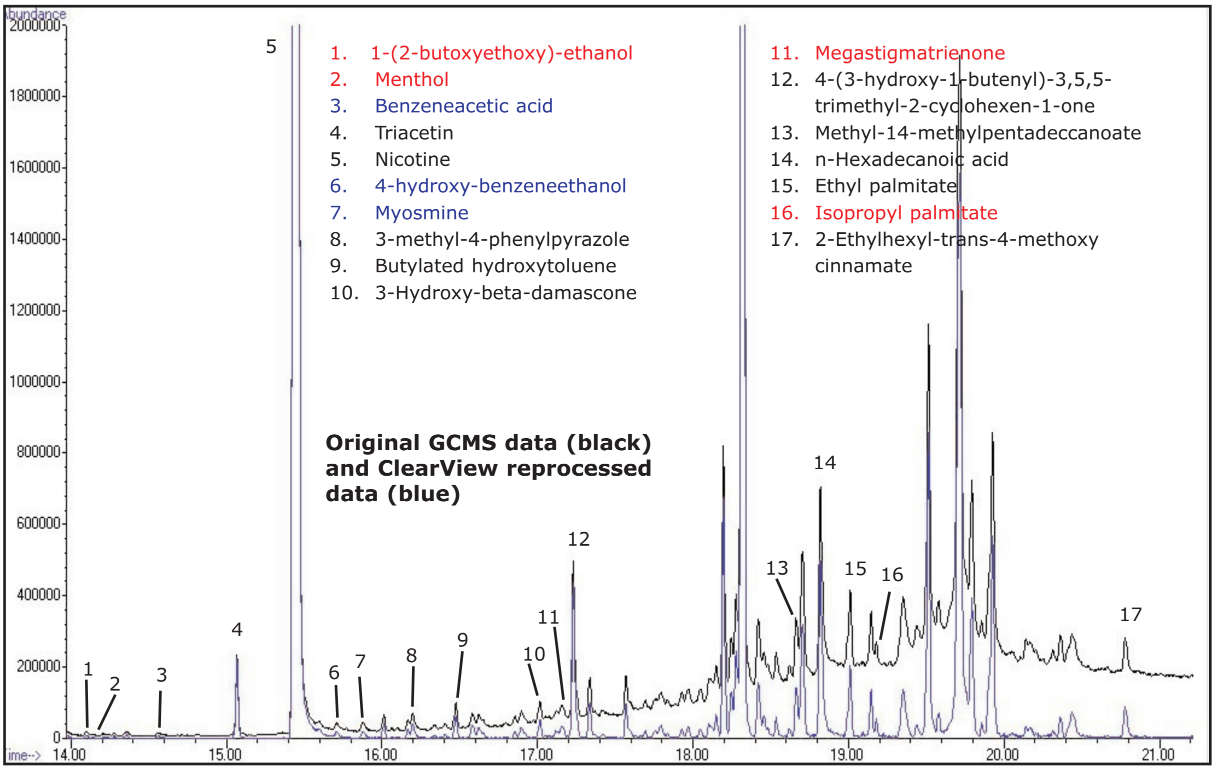


Figure 10: Clearview reprocessing direct tobacco desorption data shown in figure 7. Significant removal of unwanted background enables better qualification of trace aroma compounds present in the tobacco

Items in blue displayed a greatly improved library match quality after ClearView reprocessing, while those in red were not identified at all until ClearView reprocessing was applied

TD conditions for direct desorption of tobacco

Prepurge:	1min, trap and split in-line
Desorption:	8 mins @120°C, split on. desorb flow ~30 ml/min, split flow ~50 ml/min
Cold trap:	-10°C to 300°C for 3 mins split on
Flow path	150°C
GC programme:	40°C for 5 min, then 20°C/min up to 300°C.
Column:	HP1MS, 60 m x 0.25 mm x 0.25 µm

Summary

Markes recent innovations in thermal desorption technology have been shown to offer a readily-validated, automatic and high-sensitivity alternative to conventional liquid extraction methods for enhanced aroma profiling by GC/MS. TD allows vapour profile constituents to be cleanly extracted from the sample matrix into the gas phase and facilitates selective purging of volatile interferences in many cases. This helps to ensure that the vapour profile analyzed by the GC/MS system is as representative as possible of the aroma perceived by consumers and makes it easier to automate control of product quality.

The complementary potential of Markes' new ClearView software for reprocessing GCMS data files and enhancing the detection and identification of trace target olfactory analytes has also been demonstrated.

A combination of both of these technologies – thermal desorption to enhance sample introduction and ClearView reprocessing to enhance data analysis – should mean that more and more aroma profiling applications can be transferred to automated laboratory instrumentation, thus reducing costs and enhancing routine quality control for a wide range of foods, drinks and consumer goods.

References

1. Bell, R.E; *Intern. J. Environ. Anal. Chem.* (1987), 33, pp219-232
2. Proctor *et al; Environ. Inter.* (1991), 17, pp287-297
3. Burrefors, G & Petersson, G; *J. Chromatog.,* (1993), 643, PP71-76
4. Markes International TDTS note #78
5. Markes International TDTS note #83

Trademarks

ClearView™, SecureTD-Q™, UNITY™ and µ-CTE™ are trademarks of Markes International Ltd., UK