

The use of high-definition TD-GC-TOF MS for challenging analyses in the food industry

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Introduction

Aroma profiles of food contain a wide variety of components at a range of concentrations. Detection and identification of keynote compounds with a low odour threshold and those responsible for off-odours is a challenging prospect, and one that demands a highly sensitive and selective detector, to maximise the prospects for analyte detection and identification.

The use of high-definition gas chromatography with time-of-flight mass spectrometry (GC-TOF MS) combined with thermal desorption offers an ideal solution for routine analysis. Fast acquisition speeds and low detection limits allow trace components, including adulterants, to be identified even within the most challenging of matrices. Thermal desorption (TD) can bring the added advantage of retaining part of the sample for re-analysis, which allows confident and secure repeat analysis, especially when combined with tagged TD tubes that reliably store and transfer valuable information on the provenance of each sample.

An overview of this novel TD-GC-TOF MS system is presented using case-studies on aroma profiling of food products.

Thermal desorption

TD is widely used in the food, flavour and fragrance industry to preconcentrate volatile organic chemicals (VOCs) prior to analysis by gas chromatography-mass spectrometry (GC-MS).

TD works by passing an air/gas stream through a bed of solid sorbents, typically packed into a 3½" x ¼" sample tube. Analytes retained on the sorbents are released by heat and a flow of inert gas, and pass onto a narrower focusing trap, where the process is repeated to inject the analytes into the GC in a very narrow band of vapour.

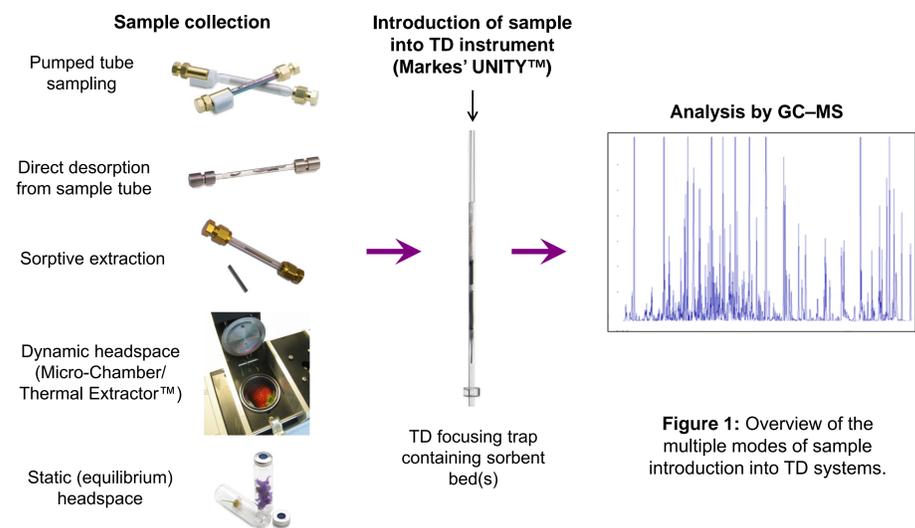


Figure 1: Overview of the multiple modes of sample introduction into TD systems.

TD provides enhanced sensitivity for a wide range of analytes, enabling comprehensive odour profiling of foods, beverages or cosmetics. Such analyses allow product quality, shelf life, or contamination issues to be assessed.

Experimental

Aroma profiles from bulk food samples were extracted using a Micro-Chamber/Thermal Extractor (μ-CTE™). A regulated flow of purge gas is supplied to each sealed, temperature-controlled chamber. This extracts the volatiles by a dynamic headspace process, allowing them to be collected on a TD sample tube inserted into the μ-CTE lid. The μ-CTE facilitates minimal sample preparation, saving both time and expense.

The TD system used for this work was the TD-100™ (Markes International). This automated tube sampling system can accommodate up to 100 tubes, enabling high sample throughput. It also allows samples to be split prior to analysis, with the split part of the sample being re-collected onto another sample tube, allowing reliable repeat analysis.

VOCs desorbed from the TD tube were analysed by GC-TOF MS (BenchTOF™, Markes International). BenchTOF mass spectrometers are compact instruments delivering maximum sensitivity at high data rates. BenchTOF generates 'classical' EI spectra, enabling easy comparison with commercial libraries, while its innovative design provides excellent sensitivity for the analysis of trace compounds in complex matrices. The workflow is shown in Figure 2.



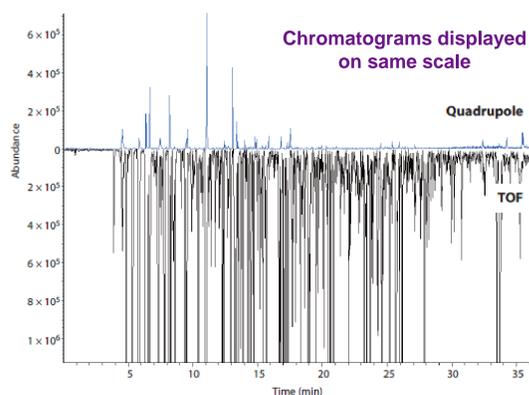
Figure 2: Workflow for the μ-CTE-TD-GC-TOF MS system.

Results

Odour profiling of strawberries

Analyses of strawberry headspace samples were run using a μ-CTE-TD-GC-quadrupole MS system and a μ-CTE-TD-GC-BenchTOF system. The emission profiles of a whole strawberry for each system are compared in Figure 3.

Figure 3: Comparison of the VOC profiles for strawberries as acquired by quadrupole MS and the BenchTOF. Analytical conditions were the same in both cases.



Clearly, these results demonstrate the greater number of trace compounds that can be detected and identified using BenchTOF compared to quadrupole MS. An example of this is shown for the target analysis of trace sulfur compounds (Figure 4).

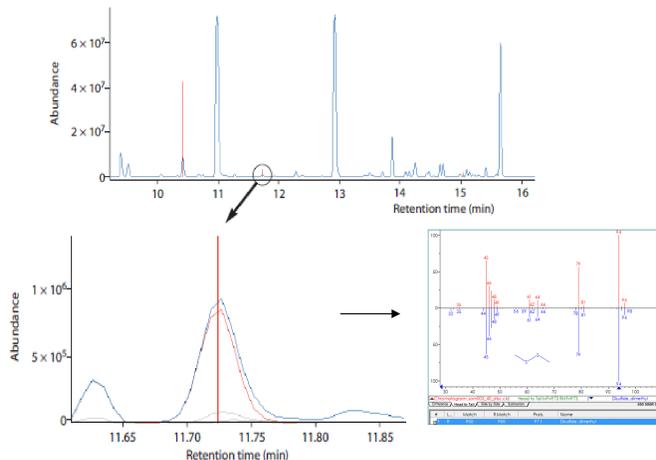


Figure 4: Detection of the deconvolved peak for dimethyl disulfide (red trace) alongside a co-eluting peak (grey trace), with corresponding mass spectra (top, red) compared to those in the NIST library (bottom, blue).

The collection of full spectral information at low detection levels also enables users to re-examine stored data for new target species (such as allergens, toxins and olfactory components) should the need arise.

Aroma profiling of cheese

The aroma profile is an important part of the consumer experience of cheese, and investigations have shown that a range of compounds combine to create their distinctive odours. Cheese samples were analysed by the μ-CTE-TD-GC-BenchTOF system described above.

An advantage of Markes' TD systems is the ability to 'split' samples (*i.e.* just part of the sample can be transferred to the GC) and the remainder collected and re-analysed under the same or different conditions, as required. An example of this process, first using a high split (low loading, for primary compounds) followed by a low split (high loading, for trace-level compounds) is shown in Figure 5 for a Cheddar sample. This 'High/Low' process enables robust quantitation, and can be completely automated using the TD-100 autosampler.

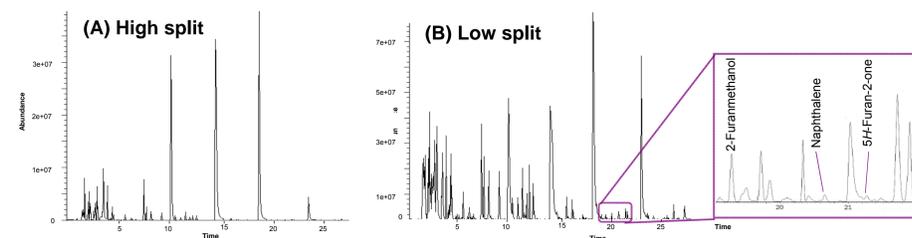


Figure 5: Analysis of the VOC profile of full-fat (extra-mature) Cheddar. Sampling used the μ-CTE, with analysis by TD-GC-MS under (A) high-split (51:1) conditions, to provide an indication of the quantities of high-concentration components, and (B) low-split (6:1) conditions, to aid identification of trace-level components.

In this example, the high sensitivity of the BenchTOF combined with low-split analysis enables identification of many trace 'unknowns'.

The TIC profile in Figure 5B is complex, with multiple co-eluting compounds. However, Markes International's powerful data acquisition and analysis software can be used to deconvolve co-eluting spectra, to enable fast analysis of complex mixtures with no compromise in sample information. In the example shown in Figure 6, four compounds are identified within one chromatographic peak. Of these four compounds, two are highly odour-active (namely (B) limonene and (C) pentyl acetate), while two are not. Deconvolution therefore uncovers additional information on the aroma profile.

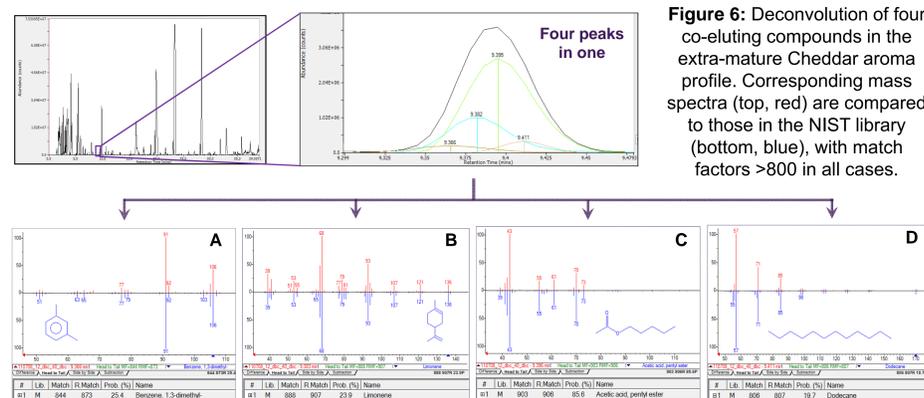


Figure 6: Deconvolution of four co-eluting compounds in the extra-mature Cheddar aroma profile. Corresponding mass spectra (top, red) are compared to those in the NIST library (bottom, blue), with match factors >800 in all cases.

Conclusions

This work has demonstrated the versatility of the μ-CTE-TD-GC-TOF MS system for analysis in the food industry. The system minimises sample preparation steps whilst also providing fast analysis of the resulting complex mixtures. Thermal desorption provides pre-concentration of VOCs, enabling confident quantitation of ultra-trace analytes. Furthermore, with SecureTD-Q™ technology, TD is no longer a 'one-shot' technique, with repeat re-collections now possible. Re-collection can aid analysis of samples with a wide dynamic range by allowing repeat analysis under different analytical conditions, for example, with a different split.

The high sensitivity of BenchTOF mass spectrometers delivers detection limits typical of quadrupole in SIM mode, while collecting full spectral information for retrospective data interrogation. This combined with the generation of 'classical', library-searchable spectra, the ability to provide sub-unit mass resolution, and the advanced deconvolution and data-mining provided by BenchTOF's TOF-DS™ software, means that trace-level analytes often not identified with conventional quadrupole detectors can be confidently assigned.