MARKES international

TDTS

Thermal Desorption Technical Support

Note 95: Food decomposition analysis using the Micro-Chamber/Thermal Extractor and TD-GC/MS

Keywords:

VOC, food, flavour, fragrance, dynamic headspace, shelf life

Introduction

The shelf life of food products is of huge interest to the food industry. The main factor governing the period of shelf life is the rate of decomposition. As food decomposes, the emission profile changes such that the desirable flavour compounds diminish while unfavourable off-odours and hazardous compounds are emitted.

Valuable information regarding the rate of decomposition and release of undesirable compounds can be obtained by sampling and analysing the vapours emitted by a product over time. Markes International's Micro-Chamber/Thermal Extractor™ (µ-CTE™) provides industry with a compact dynamic headspace extraction instrument, which allows accurate control of an atmosphere and extraction of emissions from multiple samples simultaneously.

The µ-CTE has been designed for simplified dynamic headspace sampling of product emissions with minimal sample preparation. Two versions of the µ-CTE are manufactured by Markes; one comprising four individual chambers of 114 mL capacity and one comprising six chambers of 44 mL capacity (figure 1). All chambers are inert-coated stainless steel to minimise sink effects and aid the recovery of very reactive species. Samples including foods, drinks, ingredients, packaging, *etc.* may be placed into the individual chambers within the unit, incubated at a selected temperature and purged with a constant flow of pure air or inert gas.

Following an equilibration period, clean sorbent tubes are connected to the outlet of each individual micro-chamber to collect the organic vapours purged from the sample in the flow of pure air or gas. Sorbents may be chosen to retain all emitted headspace vapours or to selectively retain key olfactory compounds while potential interferences such as water, ethanol or acetic acid are purged to vent. The sorbent tubes are subsequently analysed by thermal desorption (TD) with GC(MS).

Figure 1: The Micro-Chamber/Thermal Extractor (µ-CTE) units

TD is a GC-specific sample concentration technique used to significantly increase the sensitivity of organic analysis. Markes' leading-edge TD technology benefits from several key innovations pioneered by Markes International over recent years. Examples relevant to this application include:

- Compatibility with every TD application (including reactive species; amines, thiols, *etc.*) using a single valve/flowpath configuration.
- The ability to quantitatively re-collect samples for repeat analysis and method validation. Available on manual and automated models.
- World's most effective cryogen-free focusing offers maximum uptime (no risk of ice blockage) without compromising retention of ultra-volatiles.
- Efficient backflush desorption of the sorbent tube and focusing trap offers simultaneous analysis of compounds over a wide boiling range combined with optimum sensitivity.

For further information see Markes' Series 2 UNITY™ and TD-100™ brochures.

Figure 2: TD-100 autosampler

For the investigation into food decomposition and shelf life, three samples of bacon were obtained; unsmoked and smoked economy brand bacon and dry-cured premium brand bacon. Each was incubated in the µ-CTE for 10 days and the emissions sampled at defined intervals. Following vapour extraction, the Markes International TD-100 (figure 2) was used to automate TD-GC/MS analysis of multiple sorbent tubes.

Experimental

~8 g of each bacon sample (economy brand, unsmoked [A]; economy brand, smoked [B]; and premium brand, dry-cured [C]) was placed into separate chambers of the µ-CTE held at 30 °C with a 5 mL/min flow of dry air. A sorbent tube containing Tenax® TA and Carbopack™ X was attached to each chamber and vapours (900 mL) were sampled at 0, 1, 2, 3, 6, 8, 9 and 10 days followed by TD-GC/MS analysis. The TD-GC/MS conditions used in this study are described below.

TD

Flow path:	140°C
Oven temperature:	280°C
Oven hold:	10 min
Prepurge time:	1 min
Focusing trap:	General purpose (U-T11GPC-2)
Trap low:	25°C
Trap high:	320°C
Trap hold:	5 min

GC/MS

Column:	VF-624 ms, 60 m, 0.32 mm, 1.8 µm
Constant pressure:	10.26 psi
Initial flow:	1.7 mL/min
Temperature programme:	40°C hold 2 min, 10°C/min to 230°C hold 15 min
Total run time:	39 min
Carrier gas:	He
Mass scan range:	m/z 35–200
MS source temperature:	230°C
MS quad temperature:	150°C

Results and discussion

The chromatograms of the two economy brand bacon samples (A and B) at zero days are compared in figure 3. The emission profiles are extremely similar. This is an interesting observation as the two samples are intended to taste very differently. This implies that either minimal flavour compounds have been added by the smoking method used by the manufacturer or, alternatively, those that give a smoked flavour are well bound within the matrix of the bacon.

Figure 4 shows the chromatogram of the unsmoked economy brand bacon (A) overlaid with that of the premium brand dry-cured bacon (C). It is clear from the complexity of the chromatogram that the premium brand bacon releases many more compounds to the atmosphere (*e.g.* 4-hexen-3-one and hexenal) than the economy brand bacon.

Figures 5–7 show overlaid chromatograms of each sample (A, B and C) at t=0 days, t=1 day and t=10 days. It is apparent from these that the odour profile of each bacon sample has changed significantly over time; *i.e.* many complex reactions have occurred and VOCs emitted differ vastly between day 0 and day 10.

A more detailed analysis of several nominated compounds was then carried out. Figures 8–10 show the concentration profiles for these compounds in each sample over time.

Note: the optimised design of the TD sample flow path enabled recovery of the important sugar levoglucosan at flow path temperatures that were still low enough to prevent breakdown of thermally labile components like methane thiol (methyl mercaptan).

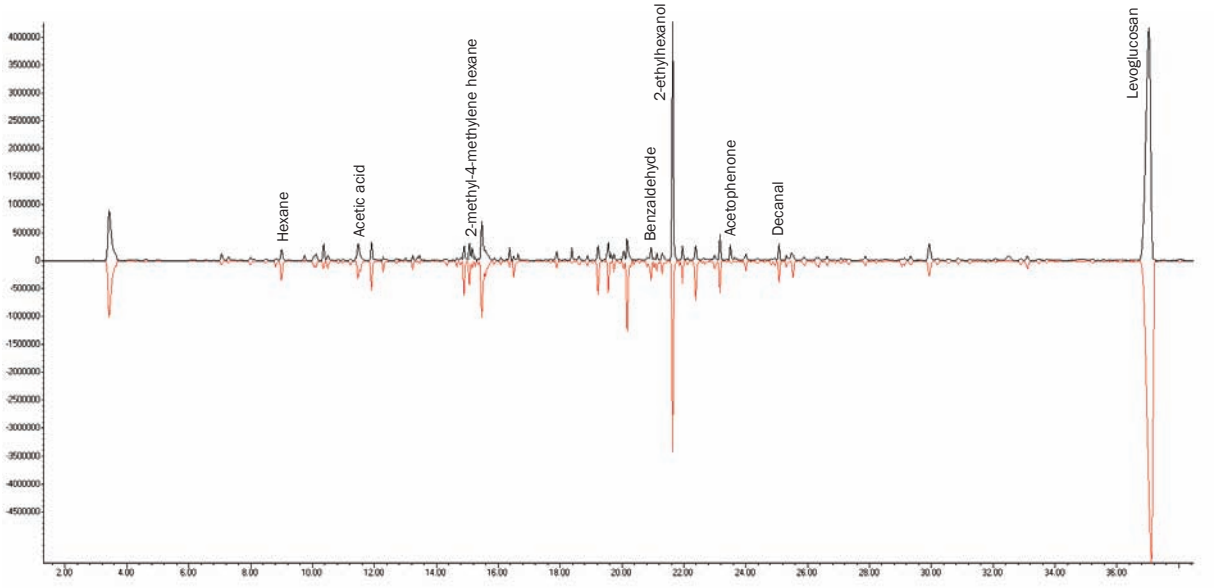

Figure 3: Overlaid chromatogram of sample A (economy brand, unsmoked; red) and sample B (economy brand, smoked; black) at t = 0 days

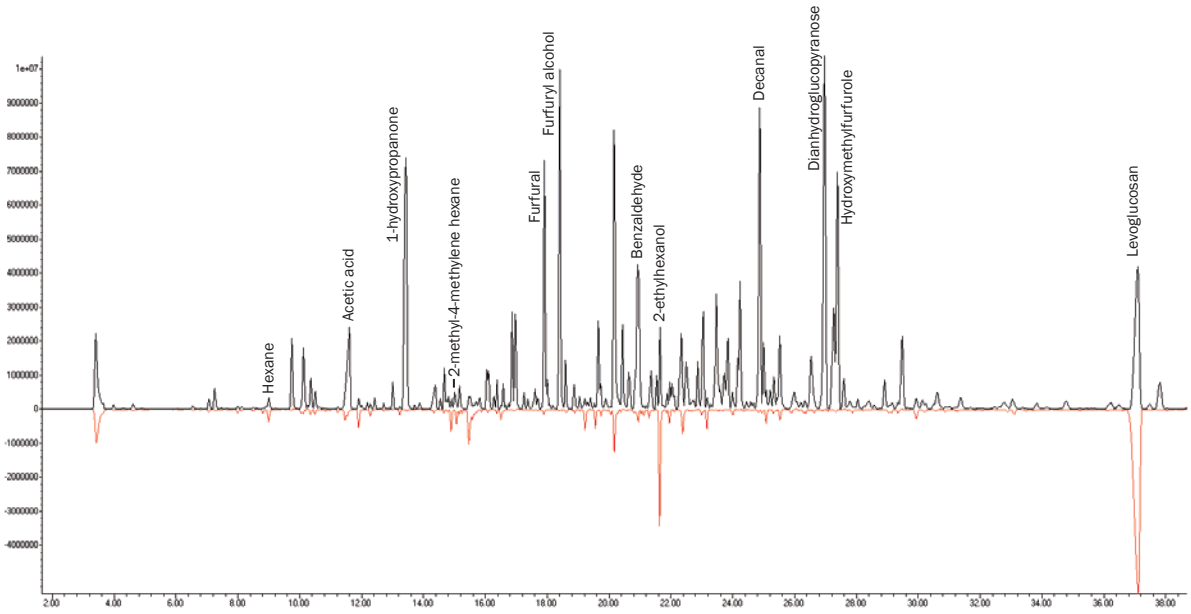

Figure 4: Overlaid chromatograms of sample A (economy brank, unsmoked; red) and sample C (premium brand, dry-cured; black) at t = 0 days

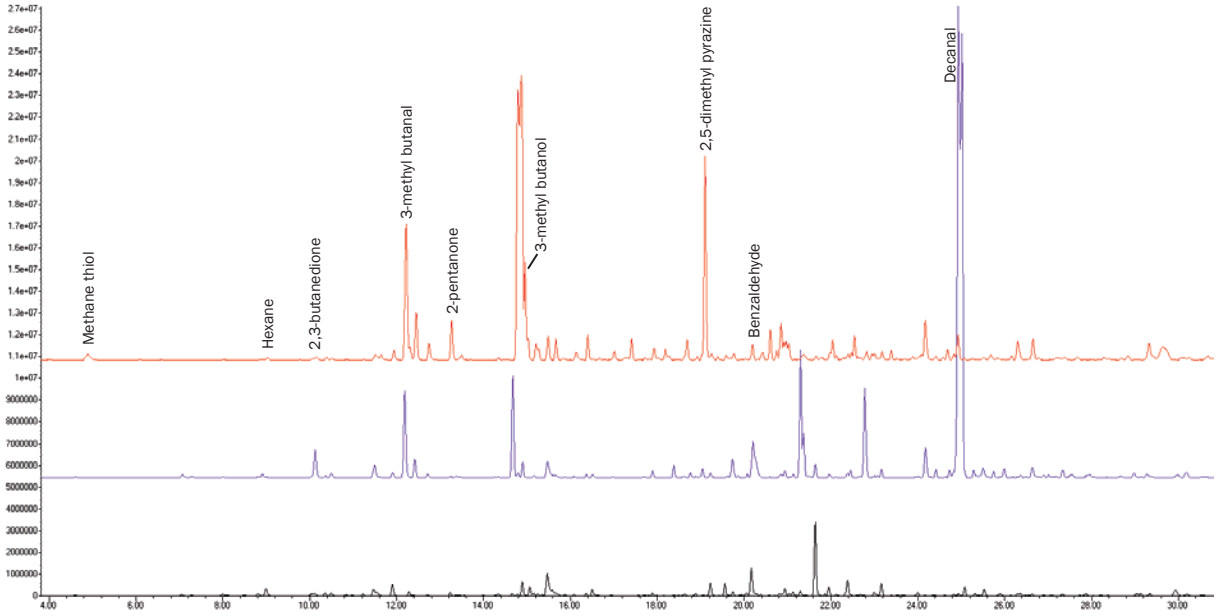

Figure 5: Overlaid chromatograms of sample A (economy brand, unsmoked) at t = 0 days (black) and t = 1 day (blue) and t = 10 days (red)

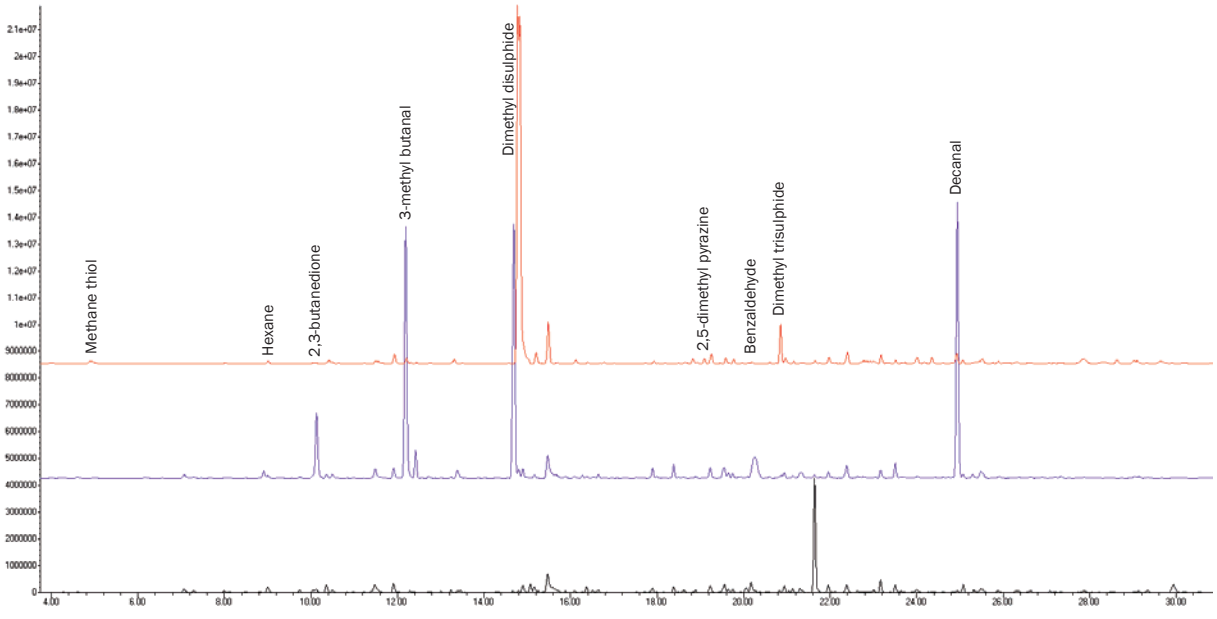

Figure 6: Overlaid chromatograms of sample B (economy brand, smoked) at t = 0 days (black) and t = 1 day (blue) and t = 10 days (red)

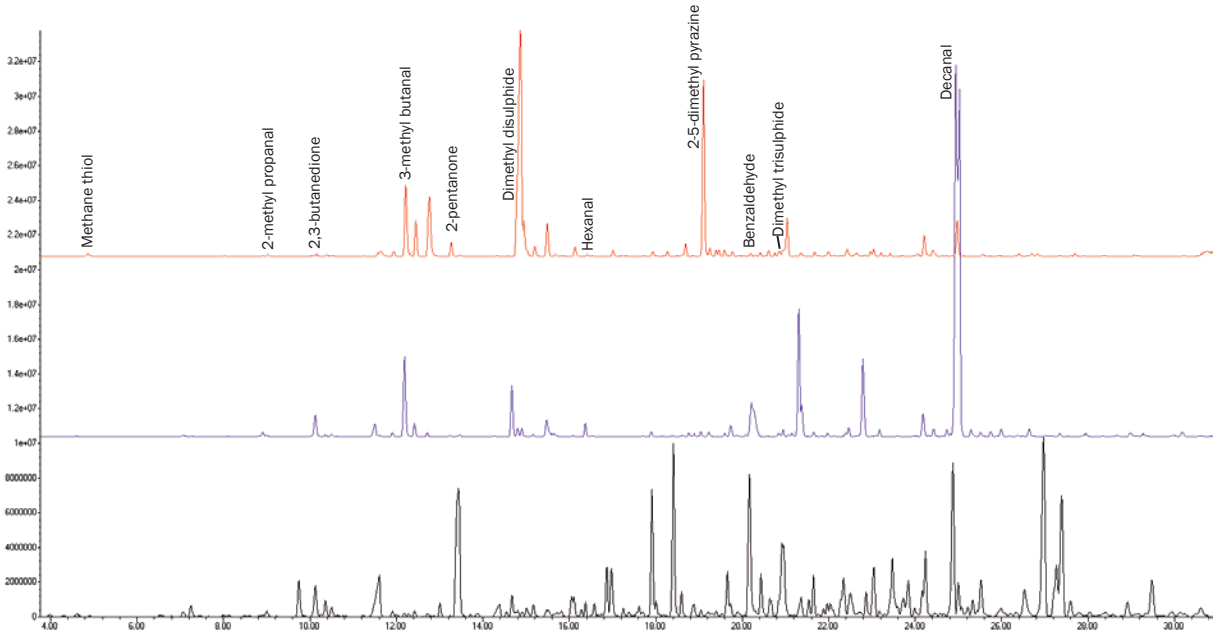

Figure 7: Overlaid chromatograms of sample C (premium brand, dry-cured) at t = 0 days (black) and t = 1 day (blue) and t = 10 days (red)

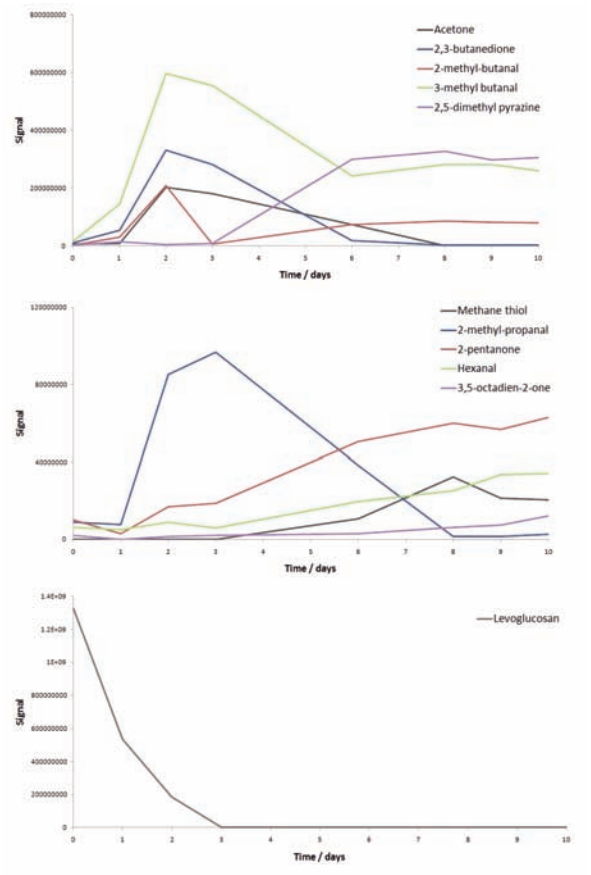

Figure 8: Concentration profiles of selected compounds vs. time for sample A (economy brand, unsmoked)

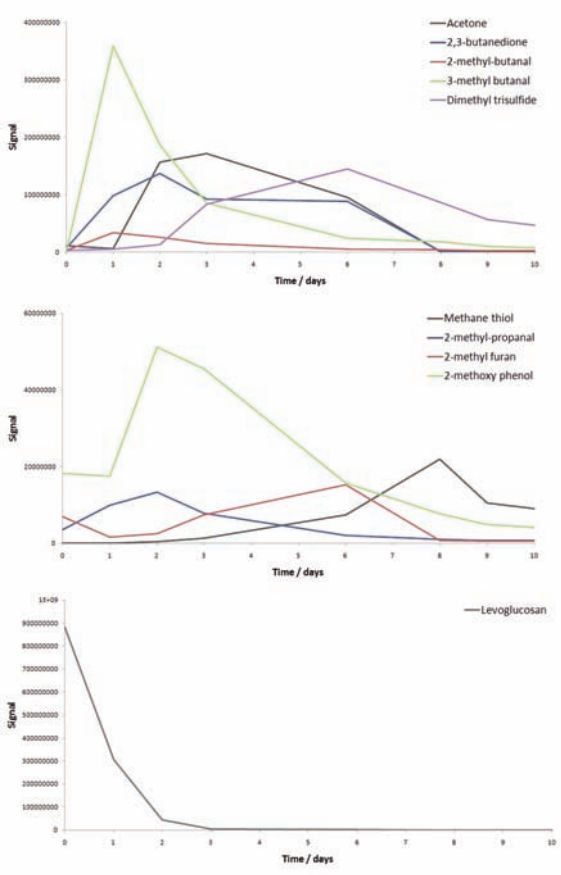

Figure 9: Concentration profiles of selected compounds vs. time for sample B (economy brand, smoked)

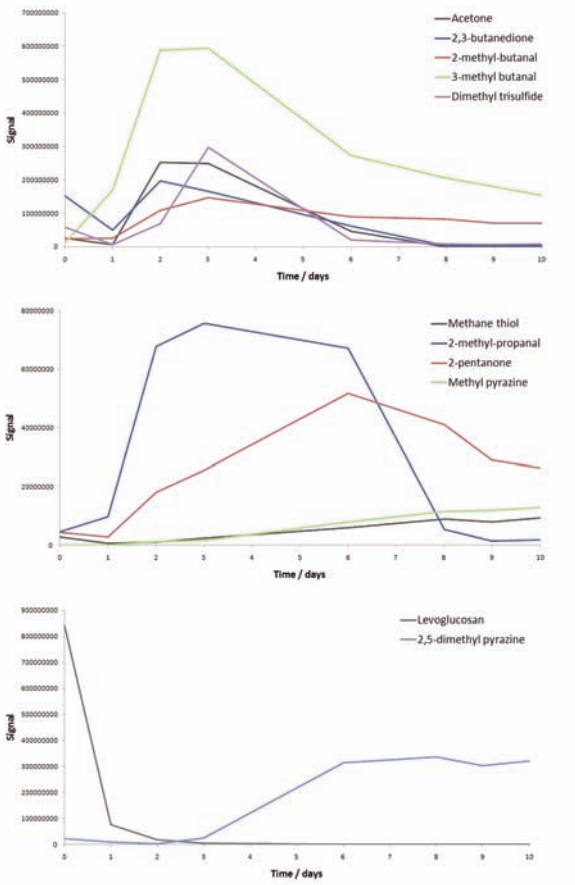

Figure 10: Concentration profiles of selected compounds vs. time for sample C (premium brand, dry-cured)

Figure 11 compares the signals of five interesting compounds for each sample over the 10 days.

Levoglucosan is a sugar that was found to decrease rapidly over time for all three samples, possibly *via* enzyme consumption. The level of this compound is lowest in the dry-cured bacon sample (C). In all three, the level became undetectable within five days.

Methane thiol is a breakdown product of many organic compounds and has a characteristic off-odour. Although sample C has a slightly higher initial concentration of this compound, the level did not increase as much with time as samples A and B. This is probably due to dry curing being a more even technique than wet curing.

Acetone is a common breakdown product of organic matter and its level seemed to increase sharply then decrease over a period of eight days in all samples. The dry-cured sample, C, is shown to produce a greater amount of acetone overall than the other samples.

2,3-butanedione is a natural by-product of many enzymatic reactions but can be harmful if high levels are ingested. This compound was found to be highest in

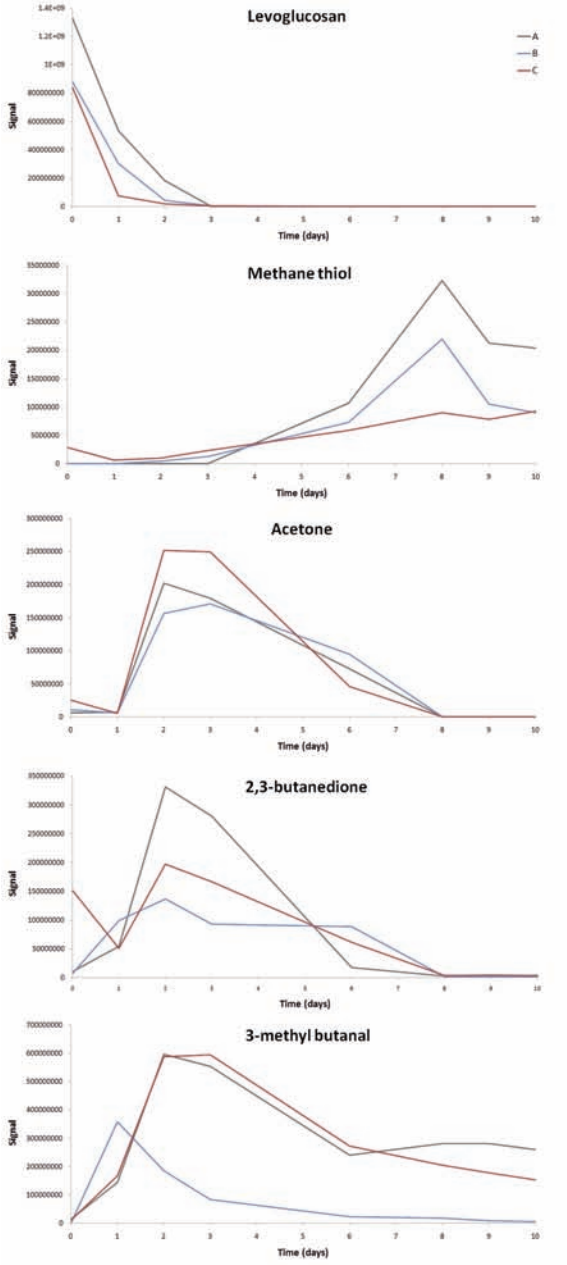

Figure 11: Specific compound concentration plots for samples A, B and C over 10 days

sample A. The concentration of 2,3-butanedione for all three samples follows a similar trend to that observed with acetone; a rise and fall over eight days.

3-methyl butanal is a compound released by the reaction of 3-methyl butanol with the enzyme 3-methyl butanal reductase. This compound is mainly found in samples A and C. This implies that the smoking process inhibits the action of 3-methyl butanal reductase in sample B.

Visually, the smoked economy brand bacon was the only sample to be completely covered in mould after 10 days; the two unsmoked samples displayed no visible mould.

Conclusion

This application highlights the novel use of Micro-Chamber/Thermal Extractor sampling with TD-GC/MS analysis for food shelf life studies. Such analysis permits comprehensive characterisation of the emission profile of a food sample over a long period of time, allowing observation of the chemical changes occurring at the various stages of decomposition under different conditions of temperature, purge gas type/flow, *etc*.

A wide volatility range of organic compounds, including reactive sulphur species, are quantitatively retained and analysed using one simple method. Minimal sample preparation is required and the individual chambers can be held at a defined temperature over weeks, if necessary, to ensure consistency of data.

Trademarks

Applications were performed using the stated analytical conditions. Operation under different conditions, or with incompatible sample matrices, may impact the performance shown.