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Application

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Application Note 107

A simple sampling technique for the TD–GC–MS analysis of VOCs released from packaged meat

Summary

This Application Note describes the use of an easy-to-use grab-sampler for the rapid collection of volatile compounds in the headspace surrounding packaged meat. Analytes are collected directly onto sorbent tubes for analysis by thermal desorption (TD)–GC–MS. This approach offers particular advantages in terms of sensitivity enhancement and water management.

Introduction

In the food industry, considerable effort is devoted to ensuring product consistency and avoiding the presence of compounds that give rise to customer complaints. These compounds fall into two broad categories – *taints* arise from an external source such as packaging, and *off-flavours* result from processes taking place in the food itself, such as microbial action.

Although the chemicals giving rise to taints or off-flavours are rarely at levels that cause concerns for food safety, companies have a strong desire to identify the chemicals involved and their source as quickly as possible.

To achieve this, it is necessary to employ robust instrumental analysis in addition to the use of trained sensory panels. Gas chromatography–mass spectrometry (GC–MS) is inherently well-suited to the detection of the volatile compounds involved in taints and off-flavours. Combined with pre-concentration and thermal desorption, it can also easily achieve the very low detection limits required. However, sample preparation often remains a major bottleneck, and there remains a need for rapid and representative sampling techniques for odour profiles that are able to provide sufficient sensitivity, especially for key olfactory compounds.

In this Application Note, we use Easy-VOC™, a simple 'grab'-sampler for sorbent tubes that is ideally suited to capture volatiles from the headspace above food samples and within food packaging containers. As well as ensuring compatibility with the widest possible range of analytes, the use of sorbent tubes also allows selective elimination of water during the sampling phase, thus minimising interference during the subsequent TD–GC–MS analytical run.

Overview of Easy-VOC

Easy-VOC (Figure 1) is a hand-held manually operated device that 'grab'-samples small volumes of air (typically 50–200 mL) directly onto sorbent tubes.

Figure 1: Markes' Easy-VOC grab-sampler.

Sorbent tubes push into the end of the Easy-VOC, and air/gas is drawn steadily and directly into the tube over a period of several seconds. Air can be sampled in accurate aliquots of 50 or 100 mL, and larger volumes are collected by multiple samples onto the same tube in quick succession.

Easy-VOC is typically used for collecting ambient and workplace air samples or for sampling headspace and other gases in containers. As the air/gas volumes collected are significantly larger than those used in conventional headspace methods, detection limits are consequently much lower.

Background to thermal desorption

Thermal desorption (TD) is a versatile GC pre-concentration technology that is used to analyse volatile and semi-volatile organic compounds (VOCs and SVOCs) in a wide range of sample types. By concentrating organic vapours from a sample into a very small volume of carrier gas (Figure 2), TD maximises sensitivity for trace-level target compounds, helps to minimise interferences, and routinely allows analyte detection at the ppb level or below. It also greatly improves sample throughput, by allowing full automation of sample preparation, desorption/extraction, pre-concentration and GC injection.

The new 'xr' range of TD instruments from Markes International enhance these capabilities, offering a wide analyte range (C_2–C_{44} including reactive species), automated re-collection and re-analysis of split portions for method validation and compliance with standard methods, optional internal standard addition for improved confidence in results, and electronic/manual options for control of carrier gas.

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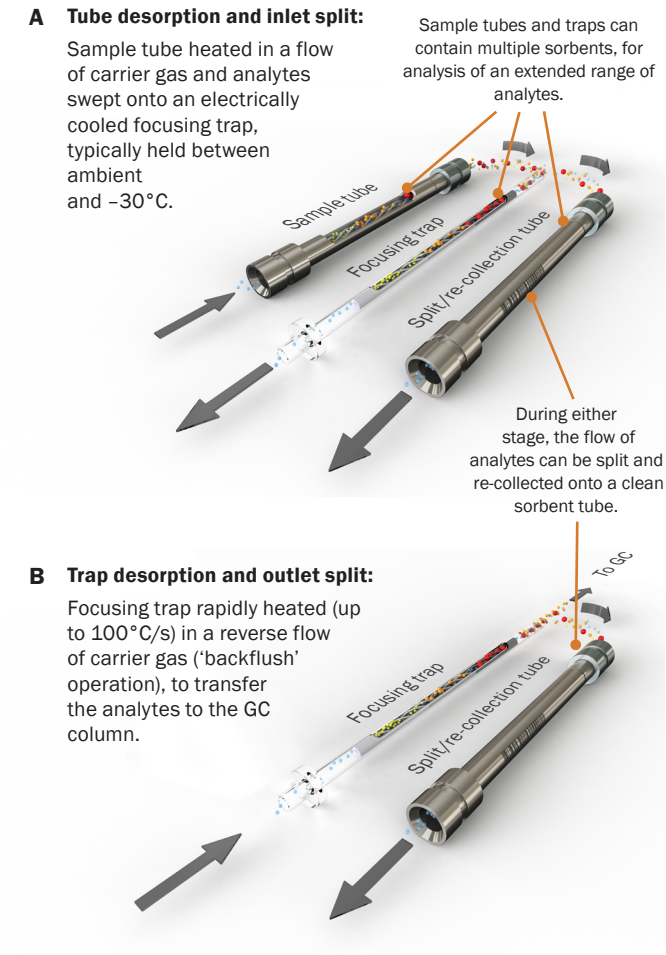


Figure 2: How two-stage thermal desorption works.

Notes on water management

The presence of water in GC–MS systems can cause broadened/split peaks, shifted retention times, and damage to the GC column and detector. In this study, the high humidity of the meat headspace was addressed using a three-fold approach:

- **Sample volume:** Using the Easy-VOC enabled a relatively small (100 mL) volume of air to be sampled accurately, limiting the mass of water drawn into the tube.
- **Dry-purging:** Two inert sorbents were used in each tube to optimise the volatility range of compounds that could be sampled simultaneously. The front sorbent was the hydrophobic porous polymer Tenax® TA, and this was backed up by the stronger more hydrophilic sorbent SulfiCarb™. As water would be retained by the SulfiCarb during sampling, the TD-100 was set up to automatically dry-purge each tube prior to desorption and analysis. This involved passing a controlled flow of clean, dry carrier gas through the sampled tubes, in the sampling direction, while they were still at ambient temperature. For more information on dry-purging, see Application Note 026.
- **Sample splitting:** Selection of a 21:1 split ratio further reduced the mass of water reaching the column and detector.

Experimental

Sampling:
An inert-coated headspace needle was connected to the sampling end of an industry-standard (3½″ long × ¼″ o.d.) inert-coated stainless steel sorbent tube packed with quartz wool, Tenax TA and SulfiCarb using a low-dead-volume connector. The tube–needle assembly was connected to an Easy-VOC and 100 mL of the packaged meat headspace was collected (Figure 3). The tubes were then analysed by TD–GC–MS.

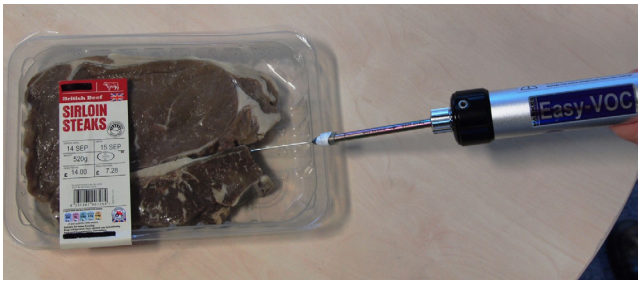


Figure 3: Sampling of the headspace of the packaged meat onto an inert-coated sorbent tube using the Easy-VOC grab-sampler.

TD:

Instrument:	TD-100™ (Markes International)
Flow path temp.:	160°C
Focusing trap:	Material Emissions trap (Markes International part number U-T12ME-2S)
Dry-purge:	2 min, 20 mL/min flow
Primary (tube) desorb:	120°C for 5 min then 260°C for 5 min; 40 mL/min trap flow
Pre-trap-fire purge:	2 min; 50 mL/min trap flow; 20 mL/min split flow
Secondary (trap) desorb:	Trap low: 25°C; trap high: 300°C; heating rate: 24°C/s; hold time: 5 min; split flow: 20 mL/min
TD split:	21:1 outlet split

Each sample was re-collected onto a clean tube containing the same sorbent combination, and this was then re-analysed using the same split conditions.

GC:

Column:	DB-5™, 60 m × 0.25 mm × 0.5 µm
Flow:	Constant-flow 1.0 mL/min
Temp. programme:	40°C (5 min), 10°C/min to 300°C (5 min)
Total run time:	36.0 min

Quadrupole MS:

Ion source:	230°C
Transfer line:	280°C
Quadrupole:	150°C
Mass range:	m/z 35–300

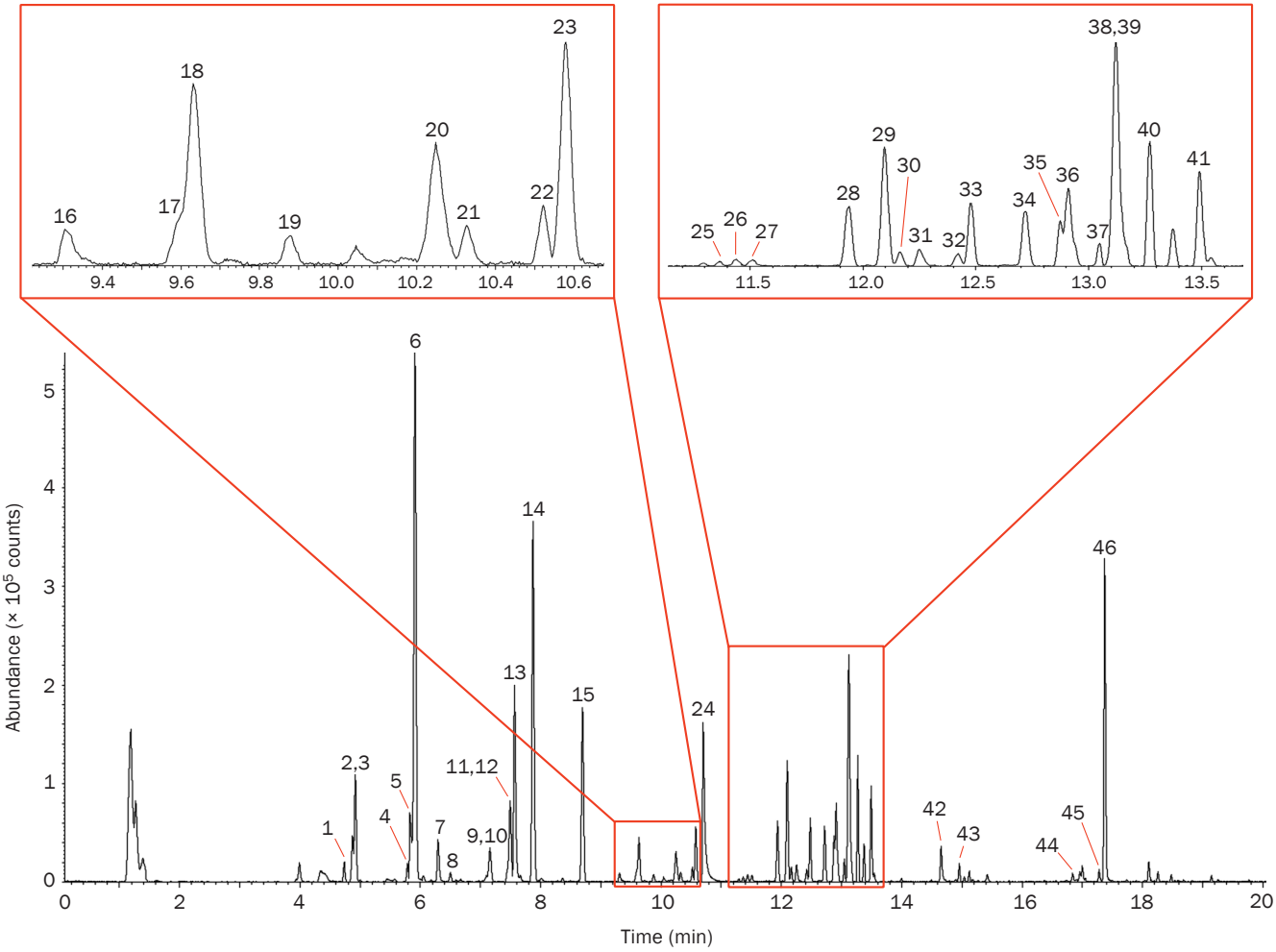
Software:
TargetView™ (Markes International) was used for background compensation and compound identification.

Results and discussion

The emission profile obtained from the packaged meat headspace was queried against the NIST 11 database using TargetView (see Figure 4). A list of 46 identified components was automatically generated (see Table 1).

The chromatogram demonstrates excellent peak shape, with no splitting or tailing of analyte peaks and minimal water or artefact interference. (Contrast this with conventional solid-phase extraction methods using PDMS sorbents, which generate high levels of background interference.)

Compounds of particular note include toluene, benzene and dichloromethane, which are possible migrants from the packaging, and unbranched short-chain alkanes and alkenes, which (along with the odorous sulfur compound dimethyl sulfide) are reported to be artefacts of the irradiation of beef.[1]



1	Isobutane	13	Butane-2,3-dione	25	2,5-Dimethylhexane	37	*trans*-Oct-4-ene
2	Isobutene	14	Hexane	26	2,4-Dimethylhexane	38	*cis*-Oct-4-ene
3	Butane	15	Methylcyclopentane	27	2,2-Dimethylhexane	39	Octane
4	Pent-1-ene	16	3-Methylbutanal	28	2,3,4-Trimethylpentane	40	*trans*-Oct-2-ene
5	Acetone	17	Benzene	29	2,3,3-Trimethylpentane	41	*cis*-Oct-2-ene
6	Pentane	18	Cyclohexane	30	2,3-Dimethylhexane	42	Hexan-1-ol
7	Dimethyl sulfide	19	3-Methylhexane	31	Pentan-1-ol	43	2,2,4-Trimethylheptane
8	Dichloromethane	20	2,2,4-Trimethylpentane	32	Toluene	44	Benzaldehyde
9	2,3-Dimethylbutane	21	Pentane-2,3-dione	33	3-Methylheptane	45	2-Pentylfuran
10	2-Methylpentane	22	Heptane	34	2,2,4-Trimethylhexane	46	2,2,4,6,6-Pentamethylheptane
11	Acetic acid	23	2-Ethylfuran	35	3-Methyleneheptane		
12	3-Methylpentane	24	3-Hydroxybutan-2-one	36	3-Ethylhex-3-ene		

Figure 4: Major peaks identified in the headspace of packaged meat following sampling using a quartz wool–Tenax TA–SulfiCarb tube and analysis by TD–GC–MS.

No.	Compound name	Retention time (min)	Match factor	Peak sum (TIC)
1	Isobutane	4.74	956	202 901
2	Isobutene	4.87	974	508 365
3	Butane	4.92	925	1 105 219
4	Pent-1-ene	5.79	932	196 117
5	Acetone	5.83	970	756 975
6	Pentane	5.91	968	7 060 134
7	Dimethyl sulfide	6.30	981	513 662
8	Dichloromethane	6.50	912	87 722
9	2,3-Dimethylbutane	7.10	808	58 946
10	2-Methylpentane	7.16	908	549 547
11	Acetic acid	7.48	923	134 699
12	3-Methylpentane	7.49	944	1 025 211
13	Butane-2,3-dione	7.56	949	2 302 276
14	Hexane	7.87	960	4 271 286
15	Methylcyclopentane	8.70	961	2 144 319
16	3-Methylbutanal	9.31	867	99 854
17	Benzene	9.59	870	113 173
18	Cyclohexane	9.63	957	505 199
19	3-Methylhexane	9.88	911	74 244
20	2,2,4-Trimethylpentane	10.25	914	368 074
21	Pentane-2,3-dione	10.33	860	92 633
22	Heptane	10.52	899	96 013
23	2-Ethylfuran	10.58	951	563 488
24	3-Hydroxybutan-2-one	10.70	890	2 224 690
25	2,5-Dimethylhexane	11.37	837	37 349
26	2,4-Dimethylhexane	11.44	879	70 279
27	2,2-Dimethylhexane	11.51	922	67 232
28	2,3,4-Trimethylpentane	11.94	941	682 644
29	2,3,3-Trimethylpentane	12.10	932	1 348 750
30	2,3-Dimethylhexane	12.17	906	130 971
31	Pentan-1-ol	12.25	941	190 713
32	Toluene	12.42	858	118 837
33	3-Methylheptane	12.48	957	597 153
34	2,2,4-Trimethylhexane	12.72	917	582 979
35	3-Methyleneheptane	12.87	884	396 256
36	3-Ethylhex-3-ene	12.91	881	591 423
37	*trans*-Oct-4-ene	13.05	894	160 213
38	*cis*-Oct-4-ene	13.11	882	1 027 245
39	Octane	13.12	906	1 743 796
40	*trans*-Oct-2-ene	13.27	958	1 014 413
41	*cis*-Oct-2-ene	13.49	946	809 337
42	Hexan-1-ol	14.65	936	399 941
43	2,2,4-Trimethylheptane	14.96	943	152 256
44	Benzaldehyde	16.84	927	91 811
45	2-Pentylfuran	17.28	855	99 913
46	2,2,4,6,6-Pentamethyl-heptane	17.37	943	3 032 792

Table 1: List of the major components identified in the headspace of the packaged meat with match factors >800.

A comparison with a blank tube analysed prior to sampling and a 100 mL sample of laboratory air taken immediately after sampling demonstrates that all the peaks identified in the emission profile were generated in the packaged meat headspace air (Figure 5).

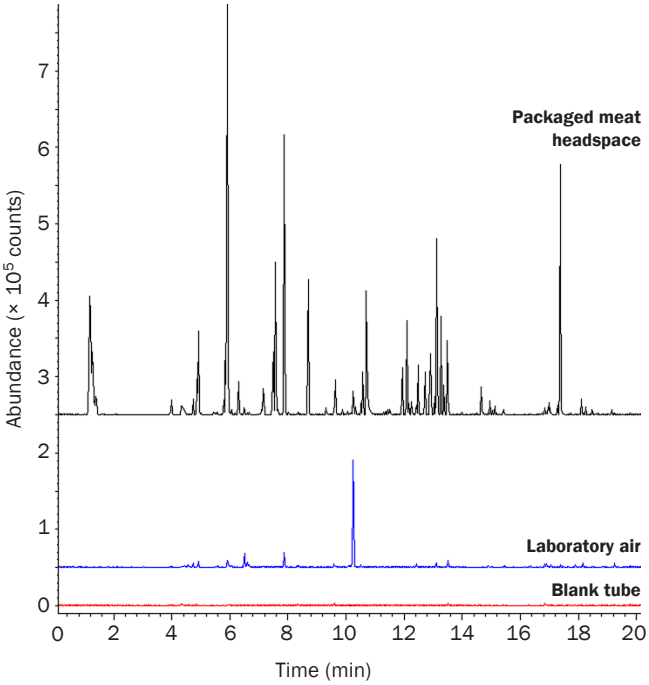


Figure 5: Emission profile of the headspace of packaged meat following analysis using a Tenax TA–SulfiCarb tube (black) compared to 100 mL of laboratory air (blue) and a blank tube (red), with analysis by TD–GC–MS.

Conclusions

This short study shows how an easy-to-use grab-sampler allows rapid collection of volatiles from packaged meat headspace onto thermal desorption tubes for analysis by TD–GC–MS.

Collection directly onto a TD tube allows the analyst to benefit from selective concentration of the compounds of interest combined with efficient and automatic transfer to the GC–MS system for optimum analytical sensitivity. It also provides a simple, one-step process, helping to ensure that the chromatogram is as representative as possible of the real sample profile.

This is a technique that could easily be employed to sample the headspace above a wide range of other packaged foodstuffs, and could be especially valuable in cases where the foods are prone to deterioration during storage, or to contamination during processing.

References

1. Y.H. Kim, K.C. Nam and D.U. Ahn, Volatile profiles, lipid oxidation and sensory characteristic of irradiated meat from different animal species, *Meat Science*, 2002, 61: 257–265, http://dx.doi.org/10.1016/S0309-1740(01)00191-7.

Trademarks

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

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