



Application Note 262

Comprehensive VOC profiling of meat using dynamic headspace extraction and automated TD-GC-MS analysis

This study shows that data acquired using the Centri® sample extraction and enrichment platform for gas chromatography-mass spectrometry (GC-MS) can be used to generate useful insights into the aroma profiles of foods. In the example investigated, the dynamic headspace profiles of two cuts of lean steak were extracted at elevated temperature onto sorbent tubes, with subsequent preconcentration on Centri. Over 140 VOCs and SVOCs from a variety of chemical classes were identified, with the detection of a range of sulfur species demonstrating the inertness of the Centri flowpath and the use of optimised sorbent tubes and desorption conditions.

Introduction

Amongst other organoleptic properties such as tenderness, the aroma/flavour of cooked meat is an important contributor to consumer sensory experience, and is a consequence of the presence of a broad range of volatile and semi-volatile organic compounds (VOCs and SVOCs). These are generally the result of biochemical processes during cooking, such as Maillard and Strecker reactions and lipid oxidation. In addition, the components of cattle feed may influence the aroma profile, while the development of a microbial flora can confer off-odours. Correlating the presence of all these volatiles with sensory data is an important aspect of understanding the factors involved in consumer experience and maintaining the quality of cooked meat.

In this study we examine the headspace aroma profiles of bulk samples of sirloin and rump steak, sampled onto industry-standard sorbent-packed tubes using a stand-alone dynamic headspace instrument. Tube desorption and analyte preconcentration were carried out on the Centri® sample extraction and enrichment platform, in conjunction with analysis by GC-MS.

Experimental

Sample:

Fresh diced lean sirloin and rump steak (10 g each) obtained from a supermarket.

Dynamic headspace extraction:

Instrument: μ -CTE™ dynamic headspace sampler (Markes International). Two models are available – one with four chambers and a maximum temperature of 250°C, and one with six chambers and a maximum

Background to Centri®

Markes International's Centri system for GC-MS is the first platform to offer high-sensitivity unattended extraction and enrichment of VOCs and SVOCs in solid, liquid and gaseous samples.

Centri allows full automation of immersive and headspace extraction using HiSorb™, high-capacity sorptive extraction probes. It also offers full automation of headspace, SPME and tube-based thermal desorption with enrichment. Leading robotics and analyte-trapping technologies are used to improve sample throughput and maximise sensitivity for a range of applications – including profiling of foods, beverages and fragranced products, environmental monitoring, clinical investigations and forensic analysis.

In addition, Centri allows samples from any injection mode to be split and re-collected onto clean sorbent tubes, avoiding the need to repeat lengthy sample extraction procedures and improving security for valuable samples, amongst many other benefits.



For more on Centri, visit www.markes.com.

temperature of 120°C.
 Chamber temp.: 70°C
 Purge flow: 50 mL/min air for 40 min
 Moisture-capture tube: Na₂SO₄ (~1.5 g, granular, Sigma Aldrich part no. 798592)¹
 Sampling tube: 'Bio-monitoring' (Markes International part no. C2-CAAXX-5149)

TD:

Instrument: Centri (Markes International)
 Focusing trap: 'Material emissions' (part no. U-T12ME-2S)
 Tube desorption: 150°C (5 min), then 300°C (10 min)
 Trap purge: 50 mL/min for 2 min
 Trap desorption: 30°C to 300°C (5 min)
 Inlet split: 11:1
 Outlet split: 2:1
 Flowpath: 180°C

GC:

Column: DB-624ms™, 60 m × 0.32 mm × 1.8 μm
 Carrier gas: Helium, constant-flow, 2.0 mL/min
 Oven program: 40°C (5 min), 5°C/min to 250°C (35 min)

Quadrupole MS:

Scan mode: m/z 35–350
 Source: 220°C
 Transfer line: 250°C

Software:

ChromSpace® GC-MS software (Markes International) was used to selectively remove unwanted background noise and to deconvolve analyte peaks. This improved the identification of lower-level analytes during subsequent automated comparison against a customised library generated from spectra in the NIST 2014 database, using a high match-factor filter of >900.

Results and discussion

Figure 1 compares the aroma profiles for the sirloin and rump steaks, and indicates in both cases a broad range of compounds, from volatile species such as acetaldehyde to semi-volatile C₁₆ compounds. The use of multiple sorbent beds in the sampling tube and focusing trap allows the collection of a wide variety of compound types in a single run – including aliphatics, aromatics, acids, alcohols, esters, lactones, aldehydes, ketones, furans, pyrazines and sulfur species. Over 140 compounds were identified in total across the two samples, and Table A1 (see appendix) lists the top 50 components in each.

With regard to the sampling conditions, an elevated temperature of 70°C was used, to allow correlation to

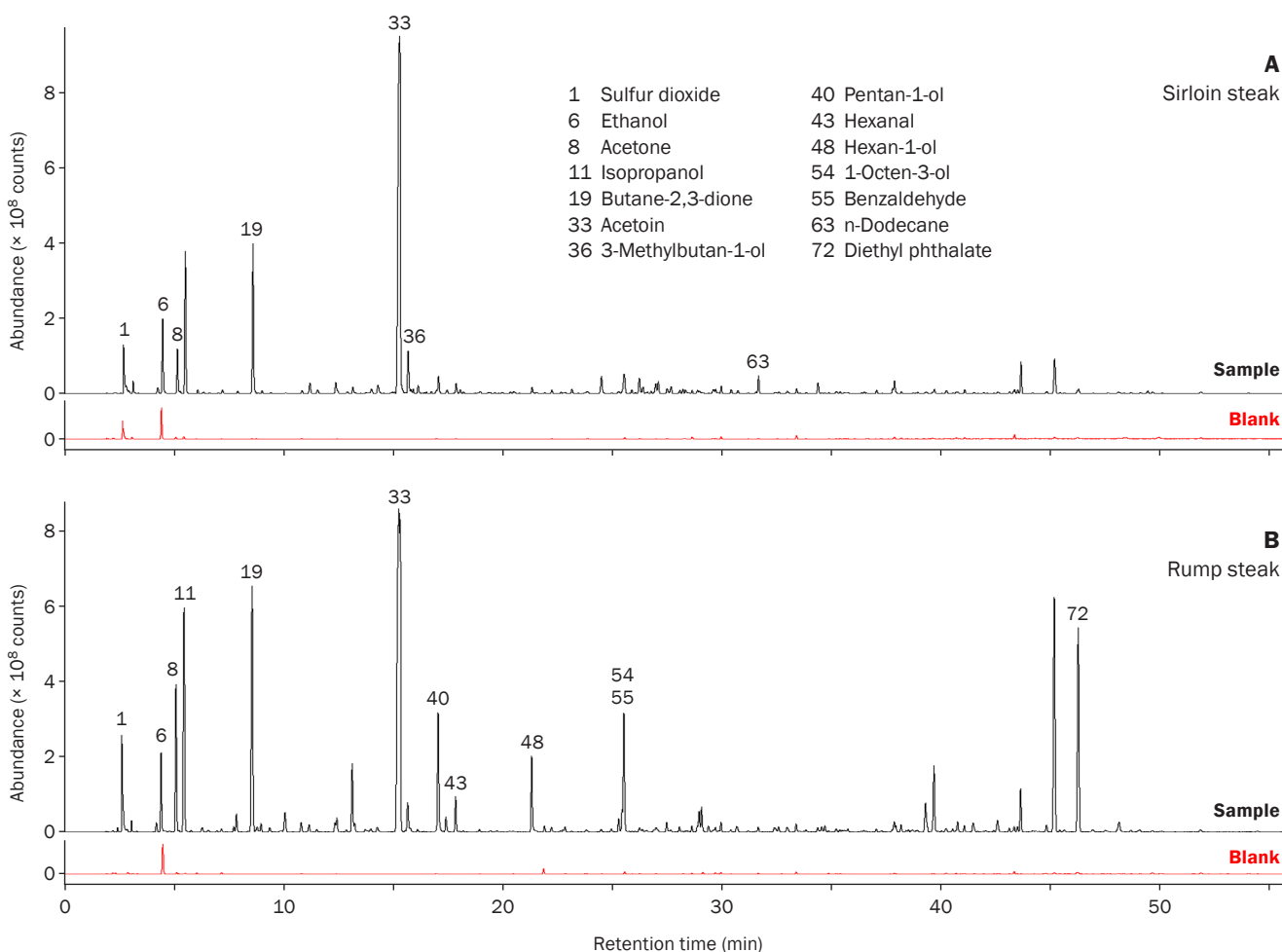


Figure 1: Aroma profiles (TIC) of (A) sirloin steak and (B) rump steak, followed in each case by a blank run (red trace). Major compounds are indicated.

separate olfactory experiments and to simulate the effect of cooking upon the aroma profile.

Optimum column loading for these samples was achieved by use of appropriate inlet and outlet split ratios on the Centri system. Although the relatively high analyte concentrations in this case allowed an overall split ratio of 22:1 to be used, use of very low ratios or even full splitless injection is possible on Centri, for maximum sensitivity. An additional benefit of sample splitting is the option to re-collect the split flow onto a second TD tube, allowing repeat analysis of the same sample using a different split ratio, within the same analytical sequence.

Although the two profiles are similar, they differ in the relative proportions of several compounds. The most abundant VOC in both samples is acetoin (#33), which in combination with butane-2,3-dione (#19), and 3-methylbutan-1-ol (#36), is indicative of the presence of the meat spoilage bacterium *Brochothrix thermosphacta*.²

Volatile sulfur species are also significant contributors to meat aroma and flavour, generating (in combination with carbonyl compounds) the desirable 'meaty' characteristics of steak at low levels, but causing off-odours at elevated concentrations. These sulfur species are primarily formed by the action of heat and antioxidants, but are also indicative of bacterial activity. Six sulfur compounds with match factors >900 were found across the two samples (highlighted in Table A1). The fact that these are identified demonstrates the inertness of the Centri flowpath, as well as the optimised choice of sorbents and desorption settings. In addition, two sulfur compounds – ethanethiol and ethyl methyl disulfide – were found with lower match factors.

Finally, compounds such as 2,2,4-trimethylpentane-1,3-diyl diisobutanoate (#71) and diethyl phthalate (#72) are plasticisers, which probably originate from contact of the sample with polymers during processing or packaging.

Conclusions

In summary, we have shown the ability of Centri to generate useful insights into the aroma profiles of meat, using a versatile analytical setup that could easily be applied to other sample types. In particular, the combination of large-volume dynamic headspace extraction with automated preconcentration on a focusing trap using Centri offers enhanced sensitivity. Furthermore, the use of multi-bed tubes and traps enables analytes across a broad boiling-point range to be detected, while maintaining chromatographic performance.

The TD-tube capability of Centri is complemented by its other extraction and enrichment modes – HiSorb high-capacity sorptive extraction, headspace and SPME – all of which can benefit from cryogen-free trapping for enhanced sensitivity. By allowing unattended sequential analysis of multiple sample types using these different injection modes, Centri greatly improves efficiency for high-throughput laboratories.

Acknowledgements

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Notes and references

1. The very high moisture content in meat samples required precautions to be taken to reduce water transfer into the analytical system. An Na₂SO₄-packed TD tube was therefore positioned between the μ-CTE chamber lid and sampling tube, with the flow rate monitored to ensure that the flow was not interrupted during sampling.
2. R.H. Dainty, R.A. Edwards and C.M. Hibbard, Time course of volatile compound formation during refrigerated storage of naturally contaminated beef in air, *Journal of Applied Bacteriology*, 1985, 59: 303–309, <http://doi.org/10.1111/j.1365-2672.1985.tb03324.x>.

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

Appendix

Sirloin steak

No.	Compound	t _R (min)	NIST match factor	NIST prob. (%)
1	Sulfur dioxide	2.67	950	53.40
2	But-2-ene	2.90	919	40.42
3	Acetaldehyde	3.11	979	77.85
4	Methanethiol	3.33	984	98.39
5	n-Pentane	4.23	931	77.47
6	Ethanol	4.45	936	78.61
8	Acetone	5.12	986	90.15
9	Dimethyl sulfide	5.26	952	60.19
13	Dichloromethane	6.05	944	98.75
15	n-Hexane	7.18	948	69.49
16	Methacrolein	7.40	921	78.47
18	Propan-1-ol	7.87	951	95.97
19	Butane-2,3-dione	8.57	964	77.03
22	Ethyl acetate	8.98	961	95.48
25	3-Methylbutanal	11.17	948	81.68
26	1-Methoxypropan-2-ol	12.35	931	83.87
27	Butan-1-ol	12.43	934	68.77
28	n-Propyl acetate	13.48	948	98.04
29	3-Methyltetrahydrofuran	14.06	921	6.93
30	2,3,3-Trimethylpentane	14.27	958	68.02
32	Dimethyl disulfide	15.03	946	96.33
33	Acetoin	15.25	901	71.04
34	2,2,5-Trimethylhexane	15.37	949	45.34
36	3-Methylbutan-1-ol	15.65	920	45.46
37	Toluene	15.73	954	53.55
38	n-Octane	16.10	946	52.06
39	Oct-2-ene	16.49	921	23.19
40	Pentan-1-ol	17.03	955	72.97
41	Ethyl butanoate	17.27	915	98.07
43	Hexanal	17.83	953	87.53
44	Ethylcyclohexane	18.02	916	61.23
46	Ethylbenzene	19.97	959	42.34
47	1,3-Dimethylbenzene	20.31	952	29.96
48	Hexan-1-ol	21.30	935	53.77
49	Bicyclo[4.2.0]octa-1,3,5-triene	21.52	915	39.22
50	Heptanal	22.20	926	86.33
56	Limonene	26.36	929	33.56
58	2,6,6-Trimethyloctane	27.98	915	30.12
60	Octan-1-ol	28.93	932	43.21
61	Nonanal	29.92	923	68.80
62	3-Methylundecane	30.69	926	26.34
63	n-Dodecane	31.62	968	48.78
65	1,3-Bis(1,1-dimethylethyl)benzene	34.34	965	90.10
66	4-Methoxy-3-buten-2-one	37.39	960	10.98
67	2-Hydroxyisobutyrophenone	37.51	930	97.76
68	n-Tetradecane	37.83	925	30.26
70	Ethyl 4-ethoxybenzoate	43.59	944	90.32
71	2,2,4-Trimethylpentane-1,3-diyl diisobutanoate	45.12	925	89.46
72	Diethyl phthalate	46.21	946	83.73
73	n-Hexadecane	49.60	915	11.88

Rump steak

No.	Compound	t _R (min)	NIST match factor	NIST prob. (%)
1	Sulfur dioxide	2.61	982	51.97
3	Acetaldehyde	3.06	971	76.64
4	Methanethiol	3.29	941	98.60
5	n-Pentane	4.19	961	81.48
6	Ethanol	4.41	943	87.46
7	Prop-2-enal	4.79	935	91.40
8	Acetone	5.08	962	87.99
9	Dimethyl sulfide	5.22	938	52.21
10	Carbon disulfide	5.44	964	97.44
11	Isopropanol	5.46	950	74.88
12	Methyl acetate	5.77	946	76.19
14	2-Methylpropan-2-ol	6.28	955	73.17
15	n-Hexane	7.16	940	66.13
17	Prop-2-en-1-ol	7.72	938	86.67
18	Propan-1-ol	7.84	953	95.91
19	Butane-2,3-dione	8.55	957	80.46
20	1,3,5-Trifluorobenzene	8.74	936	44.98
21	Butan-2-one	8.79	939	86.73
22	Ethyl acetate	8.96	935	94.94
23	Cyclohexane	10.05	949	66.82
24	Benzene	10.80	956	73.15
25	3-Methylbutanal	11.15	934	81.96
27	Butan-1-ol	12.42	948	73.13
30	2,3,3-Trimethylpentane	14.26	946	59.70
31	Pyrazine	14.81	934	78.23
32	Dimethyl disulfide	15.02	935	95.46
33	Acetoin	15.27	910	68.00
35	Pyridine	15.52	942	84.41
38	n-Octane	16.10	929	47.37
40	Pentan-1-ol	17.04	960	71.66
42	cis-Pent-2-en-1-ol	17.39	934	72.36
43	Hexanal	17.83	965	85.75
45	1-Propoxypropan-2-ol	19.71	936	93.22
46	Ethylbenzene	19.96	950	53.44
47	1,3-Dimethylbenzene	20.31	958	30.59
48	Hexan-1-ol	21.30	955	64.78
50	Heptanal	22.20	946	87.62
51	2-Butoxyethanol	22.73	944	83.54
52	Cyclohexanone	22.82	943	71.44
53	Dimethyl trisulfide	25.18	909	97.58
54	1-Octen-3-ol	25.50	943	85.45
55	Benzaldehyde	25.53	932	77.70
57	2-Ethylhexan-1-ol	27.45	931	34.6
59	Phenol	28.60	954	64.22
61	Nonanal	29.93	927	71.12
64	1-Methyl-4-(1-methylethyl)cyclohexanol	32.94	943	18.00
65	1,3-Bis(1,1-dimethylethyl)benzene	34.34	927	87.01
69	Dodecan-1-ol	41.42	936	19.74
70	Ethyl 4-ethoxybenzoate	43.59	942	89.93
72	Diethyl phthalate	46.22	948	81.30

Table A1: The top 50 components identified in the two samples with NIST match factors >900. Sulfur compounds are shaded grey.