

Application Note 521[†]

The advantages of a TD-GC-TOF MS approach for detecting trace-level odorants in polluted air

Summary

This Application Note describes the use of BenchTOF instruments in conjunction with thermal desorption-gas chromatography to analyse air taken from the outflow of a biological waste processing plant. At the same time, the value of TargetView software is demonstrated by applying it to a targeted search for odorous sulfur compounds.



Introduction

The release of odorous compounds into the environment can cause great nuisance to communities and have a negative impact on human comfort and health. Therefore, there is a need to determine the nature of airborne pollutants and measure the concentration of odorous components.

These compounds often have very low (low or sub-ppb) odor thresholds and can be difficult to identify within complex polluted air samples. Furthermore, labile species, particularly sulfur compounds and terpenes, can undergo decomposition during analysis unless appropriate conditions are used.

Traditionally, detection of odorous species has involved the use of olfactometry. However, detection thresholds for odorous compounds may vary substantially between individuals, and therefore it is desirable to back-up such methods with a

robust chromatographic approach. For environmental air samples, thermal desorption (TD)-GC, with or without MS detection, is a particularly suitable method, because it can achieve very high sensitivities for these dilute air streams.

In this study we describe the analysis of polluted air by pumped sampling onto sorbent tubes chosen to be compatible with sulfur compounds, with analysis by inert TD-GC. We then show how the inherent sensitivity of BenchTOF time-of-flight mass spectrometers allows automated detection of trace-level sulfur compounds, using TargetView software to speed up and simplify the process of compound identification.

Background to BenchTOF instruments

Markes' BenchTOF™ instruments are ideal for the analysis of trace-level compounds, particularly unknowns, because they offer a unique combination of three important features:

- **Sensitivity:** Highly efficient direct-extraction technology allows BenchTOF instruments to acquire full-range spectra with SIM-like sensitivity, allowing them to reliably detect trace-level analytes in a single run, which would be difficult or impossible on a quadrupole system.
- **Spectral quality:** The 'reference-quality' spectra produced by BenchTOF are a close match for those in commercial libraries such as NIST or Wiley. This enables quick and confident matching of both targets and unknowns.
- **Speed:** The ability to record full-range mass spectral information to extremely high densities (10,000 transient spectral accumulations per second) enables advanced spectral deconvolution and 'data-mining' algorithms to extract maximum information from weak, matrix-masked signals.

The high-definition mass spectrometry delivered by this combination of features makes BenchTOF ideal for the most demanding GC applications, as demonstrated by this work.

[†] Formerly ALMSCO Application Note 021.



Background to TargetView

The advantages of BenchTOF instruments are further enhanced by TargetView™, an innovative post-run data processing package that allows accurate and automated identification of trace compounds in complex GC–MS profiles.

TargetView uses sophisticated algorithms to eliminate background interference and deconvolve co-eluting components into individual analyte peaks. The mass spectra produced for each deconvolved component can then be rapidly matched against library spectra using advanced chemometric techniques, which allow both target and ‘unknown’ compounds to be identified confidently, even at trace levels. Total ion chromatographic (TIC) profiles can either be searched against a target library (a ‘target search’), or screened against the full NIST library (an ‘all-component search’).

TargetView is easy to learn, simple to operate, and compatible with GC–MS file types from most major vendors.

Experimental

Sampling:

A 5 L sample of air from the outlet of a biological waste processing plant was mixed with 15 L of clean nitrogen contained within a nalophane bag. From this, a sample volume of 1000 mL was pumped onto an inert-coated two-bed sorbent tube packed with a porous polymer (Tenax® TA) and a carbonised molecular sieve (SulfiCarb™). Combined, these inert sorbents are capable of retaining labile analytes over a wide volatility range (C₃ to n-C₃₀).

TD:

Instrument: TD-100™ (Markes International)
 Tube desorption: 120 °C for 5 min, then 260 °C for 8 min (50 mL/min desorb flow)
 Focusing trap: Sulfur trap
 Trap low: 25 °C
 Trap desorption: 300 °C for 3 min (heating rate: 40 °C/s)
 Split flow: High split: 50 mL/min; Low split: 5 mL/min
 Overall TD split ratio: 4:1 – 30:1

GC:

Column: VF-624ms, 60 m × 0.32 mm × 1.8 µm
 Constant flow: 1.7 mL/min
 Oven program: 40 °C (0.5 min), then 5 °C/min to 230 °C (5.0 min)

MS:

Instrument: BenchTOF (Markes International)
 Transfer line: 240 °C
 Ion source: 240 °C
 Mass range: m/z 15–350
 Acquisition rate: 2 Hz (5000 spectral accumulations per data point)

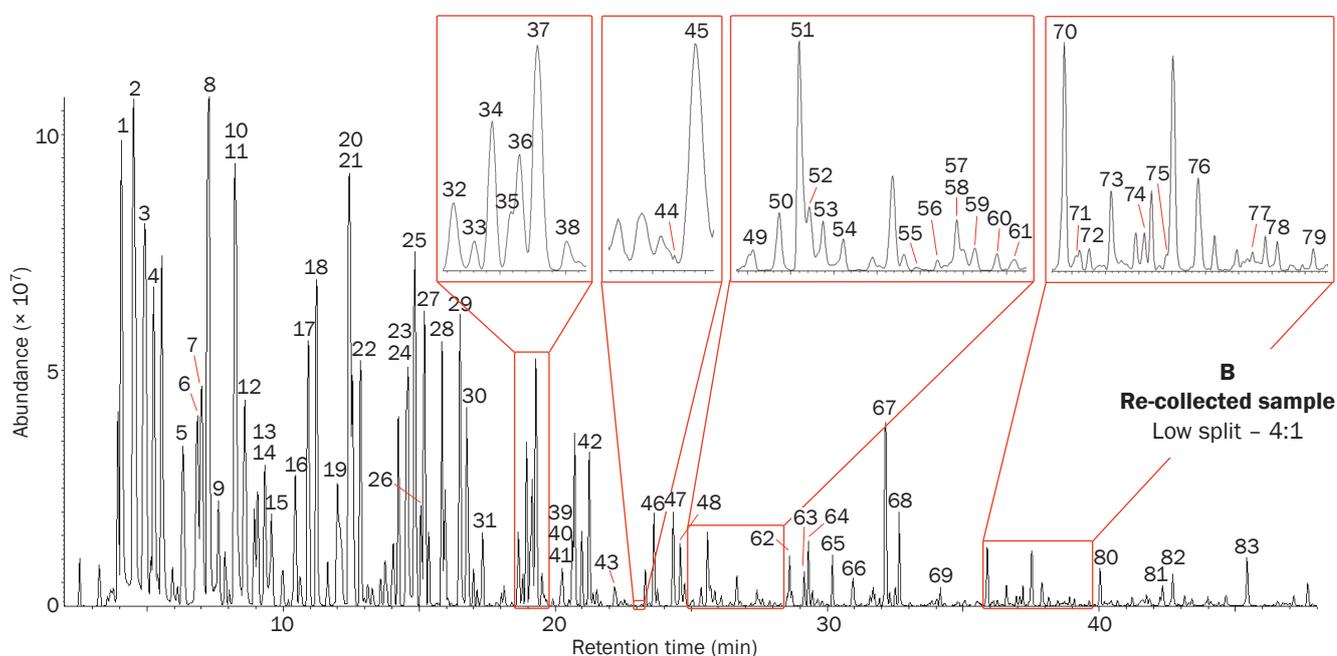
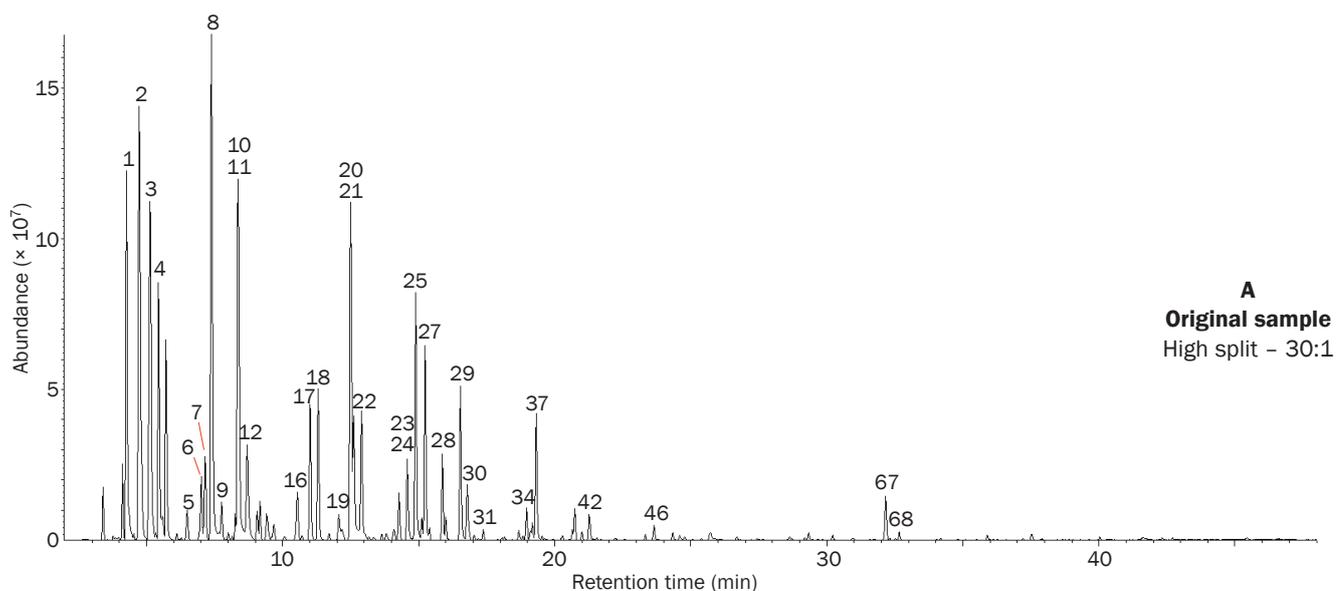
Results and discussion

Detecting trace-level analytes

Initially, a high split was used to avoid overloading the column for this unknown sample (Figure 1A). The split was automatically re-collected onto a sorbent-packed tube using the TD-100 thermal desorber, and subsequently re-analysed at a lower split ratio to increase the sensitivity for trace-level components (Figure 1B). The increase in the dynamic range is evident, particularly in the 20–30 min region.

The chromatogram resulting from the low-split analysis was processed using an ‘all-component’ search in TargetView, which compares every deconvolved peak spectrum against the NIST spectral library. A lower limit of 800 was placed on the match factor in order to ensure that only high-quality matches were reported.

A total of 165 compounds were identified by this process, and 83 are presented in Figure 1B. Approximate analyte concentrations (calculated in terms of toluene equivalents) ranged from 2 ppm for ethanol (#8) to 20 ppt for 1-chloro-4-(trifluoromethyl)benzene (#44).



1 Propane	19 Butane-2,3-dione	37 Toluene	53 Pentanoic acid	70 Decanal
2 Isobutane	20 Butan-2-one	38 n-Octane	54 Menthol	71 α -Terpineol
3 n-Butane	21 Methylglyoxal	39 Pentan-1-ol	55 Propylbenzene	72 Naphthalene
4 Acetaldehyde	22 Tetrahydrofuran	40 Ethyl butanoate	56 3-Ethyltoluene	73 Benzoic acid
5 2-Methylbutane	23 Benzene	41 Tetrachloroethene	57 β -Phellandrene	74 Tridecane
6 Pent-1-ene	24 Acetic acid	42 3-Methylpentanal	58 n-Decane	75 2-Methyl-3-phenylpropanal
7 n-Pentane	25 3-Methylbutanal	43 Butanoic acid	59 β -Pinene	76 2-Phenoxyethanol
8 Ethanol	26 n-Heptane	44 1-Chloro-4-(trifluoro- methyl)benzene	60 2-Pentylfuran	77 1-Methoxy-4-(prop-1-enyl)- benzene
9 Furan	27 2-Methylbutanal	45 Ethylbenzene	61 1-Ethyl-4-methylbenzene	78 4-Methoxybenzaldehyde
10 Propanal	28 Trichloroethene	46 1-Ethyl-3-methyl- cyclohexane	62 6-Methylhept-5-en-2-one	79 1-Methylnaphthalene
11 Acetone	29 Pentanal	47 2-Methylbutanoic acid	63 β -Pinene	80 n-Tetradecane
12 Ethyl formate	30 n-Propyl acetate	48 o-Xylene	64 Dimethyl sulfone	81 3,4-Di(<i>tert</i> -butyl)phenol
13 Dichloromethane	31 Methyl butanoate	49 Heptan-2-one	65 2-Ethylhexan-1-ol	82 n-Pentadecane
14 2-Methylpentane	32 Dimethyl disulfide	50 Propylcyclohexane	66 Phenol	83 Dodecan-1-ol
15 <i>tert</i> -Butanol	33 Hexan-2-one	51 Dimethyl sulfoxide	67 2,2'-Azobis- (2-methylpropanenitrile)	
16 Butyraldehyde	34 3-Methylbutan-1-ol	52 α -Pinene	68 Nonanal	
17 Propan-1-ol	35 2-Methylbutan-1-ol		69 n-Dodecane	
18 2-Methylfuran	36 2-Methylbut-2-enal			

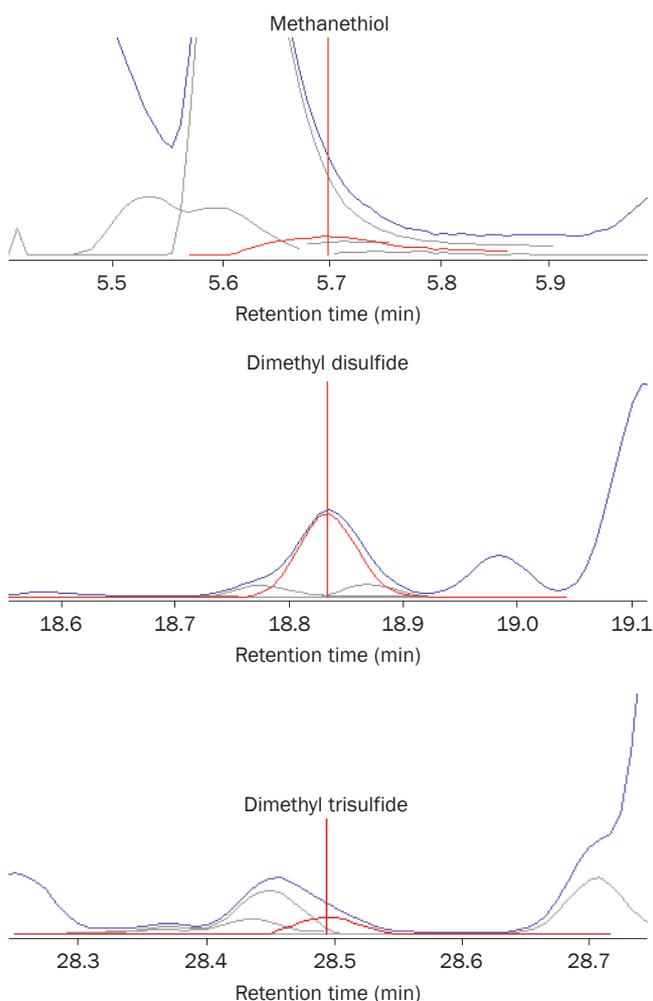
Figure 1: Analysis of 1000 mL of polluted air under (A) high-split and (B) low-split conditions. The insets show detection of trace-level analytes.

Detection of sulfur compounds

The re-collected sample analysed with a low split ratio was then interrogated against a 22-compound library of sulfur compounds using TargetView. Eight sulfur compounds were identified (Table 1), including odorous compounds such as methanethiol, dimethyl disulfide and dimethyl trisulfide. Each show strong agreement with the NIST library (Figure 2), confirming the quality of the spectra produced by BenchTOF.

Note that these labile compounds are very difficult to detect if the analytical system is not completely inert and if excessive heat is applied to the analytes during the desorption process. Methanethiol is a case in point, made more challenging in this case by its low abundance and co-elution with methanol. In this study the analytical conditions were selected for compatibility with the widest analyte range and not optimised for complete recovery of the most reactive sulfur compounds. Nevertheless, the combination of the sensitivity of BenchTOF and peak deconvolution using TargetView makes it possible to detect this compound without recourse to a modified chromatographic method.

N.B. See Application Note 032 for more information on the TD-GC analysis of sulfur compounds.



Target compound	Retention time (min)	Match coefficient	Peak sum (TIC)	Sample conc. (ppb) ^a
Methanethiol	5.70	0.871	5 721 349	28.3
Carbon disulfide	8.81	0.903	65 913 011	206
Dimethyl disulfide	18.83	0.951	58 058 383	146
3-Methylthiophene	20.22	0.877	683 730	1.7
Methyl ethyl disulfide	22.76	0.783	660 682	1.4
Dimethyl sulfoxide	25.78	0.905	74 781 209	227
Dimethyl trisulfide	28.50	0.891	1 556 681	2.9
Dimethyl sulfone	29.81	0.852	26 855 373	67.7

Table 1: Identification of eight sulfur compounds in the air sample using TargetView. ^a Concentrations determined in terms of toluene equivalents by comparison with the peak area of a toluene standard.

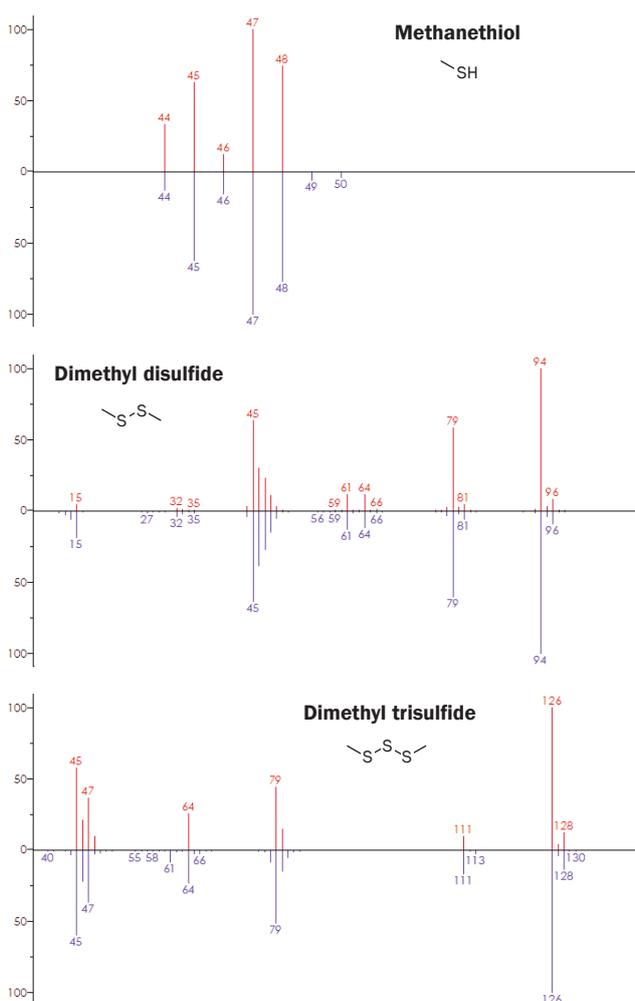


Figure 2: Left: Detection of the deconvolved peaks for three sulfur compounds using TargetView (blue trace, baseline-compensated TIC; red trace, target; grey traces, closely eluting compounds). Right: The corresponding mass spectra (top, red) compared to those in the NIST library (bottom, blue).

Conclusions

In this Application Note, we have shown that it is possible to detect thermally labile trace-level sulfur components in a complex air sample by combining the inherent sensitivity of BenchTOF instruments with thermal desorption pre-concentration.

We have also shown that, because TOF MS technology monitors all ions without scanning, it generates full spectral information at much lower mass/concentration levels than conventional quadrupole MS instruments. This is of particular benefit in high-throughput environmental monitoring laboratories, as it allows trace-level unknowns to be detected and identified, which would not be possible using selected ion monitoring (SIM).

It is also worth pointing out that the 'reference-quality' spectra and data density produced by BenchTOF instruments provide TargetView with the data quality needed for rapid and reliable compound identification.

A particular feature of this study is the re-collection capability of the TD system, which offers an exceptionally wide dynamic range. Initial high-split analysis enables quantitative measurement of the most abundant species, and subsequent low-split analysis allows trace-level constituents to be measured in the same sample.

Trademarks

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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.