

TRACE LEVEL ODOUR MONITORING

DANIELE MOROSINI¹ | AARON DAVIES² | LAURA MILES² | ERICKA HACHMEISTER²

¹SRA INSTRUMENTS SpA, Via alla Castellana 3, Cernusco sul Naviglio (MI), IT

²MARKES INTERNATIONAL LTD, 1000B Central Park, Western Avenue, Bridgend, CF31 3RT, UK



INTRODUCTION

Odour emissions are often associated with, but not limited to sulphur compounds due to their unpleasant, pungent odours, which are noticeable even at low concentrations. These compounds are difficult to analyse as they are thermally labile (sensitive to high temperatures), particularly when in contact with metals. Moreover, several of the compounds of interest are very volatile, such as hydrogen sulfide and methanethiol.



The detection of odorous compounds at trace levels is critically important in a number of air monitoring applications, including:

- industrial emissions testing;
- environmental monitoring of air toxics (US EPA TO-15A), off-odours, e.g. from sewage treatment plants and landfill sites;
- health and safety monitoring of toxic compounds, e.g. exposure to CS₂;
- flavour and fragrance testing; and
- food studies, e.g. shelf-life tests and off-odour profiling.

Thermal desorption (TD) is an ideal technique for the analysis of trace-level vapours. It provides both analyte concentration and efficient transfer/injection into the GC analytical system. Samples can be collected using sorbent tubes or canisters and analysed off-line by TD-GC. Alternatively, air/gas samples can be drawn directly into the TD-GC system and analysed on-line.



EXPERIMENTAL

On-line or canister analysis

On-line analysis is the method of choice for real-time monitoring of changes in the vapour concentration. On-line or canister sampling is also required when the compounds of interest are too volatile to be retained by sorbent tubes at ambient temperature, e.g. hydrogen sulfide.

On-line TD-GC method was developed¹ in response to the EPA off-odor regulations which came into force in February 2005.

Off-line analysis with sorbent tubes

Off-line monitoring with sorbent tubes involves sampling air (either actively or passively) onto tubes packed with one or more sorbents that are suitable for trapping/retaining the volatility range of the compounds of interest. Due to the labile nature of sulfur compounds, a specially prepared inert-coated sorbent tube is recommended for this application. It is typically packed with two inert sorbents designed to retain sulfur compounds over a range of volatilities. (Note that hydrogen sulfide cannot be reliably sampled using sorbent tubes at ambient temperature).

The performance of the Markes thermal desorber and inert-coated sorbent tubes is illustrated both by the analysis of a standard sulfur calibration solution and by the analysis of landfill gas.

Analytical conditions

A Markes International UNITY™-ULTRA-xr-KORI- CIA-HL-xr system was connected to a GC fitted with a pulsed flame photo-metric detector (PFPD).

ONLINE	OFFLINE
TD (UNITY™-ULTRA-xr-KORI- CIA-HL-xr): Sampling volume: 100–500 mL at 50 mL/min KORI dryer: In-line Focusing trap: Graphitised carbon black/silica gel Trap low: –15°C Trap high: 250°C Hold: 3 min Flow path temp.: 120°C	TD (UNITY™-ULTRA-xr): Prepurge time: 0.5 min (split on and trap in line) Primary desorb: 200°C for 3 min (split on) Trap low: –10°C Trap desorb: 200°C for 3 min (split on) Trap: U-T6SUL (porous polymer– carbonised molecular sieve) Flow path temp.: 120°C Carrier gas pressure: 10 psi Desorb flow: 3 mL/min Split flow: 45 mL/min Split ratio: 20:1
GC: Column: VF-1 MS, 60 m × 0.32 mm × 5.0 µm Column flow: 2.0 mL/min GC oven: 60°C (5 min), 8°C/min to 200°C	GC: Column: GS-Gaspro, 30 m × 0.32 mm Column flow: 1.2 mL/min Start temp: 60°C for 0 min End temp: 220°C for 6 min Ramp rate: 10°C/min
PFPD (square root function on): Fuel gas: Air: 17 mL/min, Air2: 10 mL/min, H2: 14 mL/min Temp.: 200°C (S filter)	MS: Source temp: 230°C Quadrupole temp: 150°C Transfer line temp: 150°C Mass scan range m/z 25–350

RESULTS AND DISCUSSION

Online sampling system

Detection limits²

Minimum achievable detection limits were 0.15 ppb for hydrogen sulfide, methanethiol and dimethyl sulfide, and 0.10 ppb for dimethyl disulfide. These limits were obtained with a sample volume of 200 mL and a split ratio of 4:1.

Linearity

The linearity of each compound was tested through the complete UNITY-Air Server-GC analytical system (see Table 2). The sampled volume was 100 mL and the split ratio was ~13:1.

Compound	Peak area				Linearity (r)
	0 ppb	20 ppb	40 ppb	100 ppb	
Hydrogen sulfide	0	82438	218215	619303	0.9973
Methanethiol	0	176790	370921	949516	0.9983
Dimethyl sulfide	0	166279	345939	864878	0.9999
Dimethyl disulfide	0	318125	639442	1479555	0.9993

Table 2: Linearity data for the four sulfur compounds specified in the Korean off-odor regulations.

Reproducibility

Each of three concentrations of calibration gas were sampled ten times in order to obtain reproducibility data (see Table A1 in the Appendix). The sampled volume was 100 mL and the split ratio was ~13:1.

Excellent reproducibility was observed across all four compounds, and at all three concentration levels. For the 40 ppb and 100 ppb standards, RSDs below 1.8% were observed across all four compounds. This was maintained for the 20 ppb standard, except for hydrogen sulfide, which showed a slightly higher RSD of 4.1%.

Recovery³

Recovery was assessed at various relative humidities (using purified nitrogen) to investigate any bias in the method (Table 3). In each case results were compared to those from direct GC injection of the same mass of analyte under identical split conditions.

Compound	Relative humidity (%)	Recovery rate (average of three replicates) (%)
Hydrogen sulfide	0	103
	60	98
	80	93
Methanethiol	0	114
	60	113
	80	108
Dimethyl sulfide	0	110
	60	109
	80	107
Dimethyl disulfide	0	115
	60	114
	80	108

Table 3: TD recovery rate at various relative humidities

Off-line

Detection limits

Figure 1 shows the extracted-ion chromatogram from a 2 ng standard. This equates to approximately 2 ppb in 1 L of air. This approaches the minimum detection limit for methanethiol under these analytical conditions. However, for dimethyl sulfide and dimethyl disulfide, the minimum detection limit is at least five times lower than this, i.e. 0.4 ppb in a 1 L air sample.

Linearity

Linearity data are shown in Figure 2. The response for all four sulfur compounds was found to be linear.

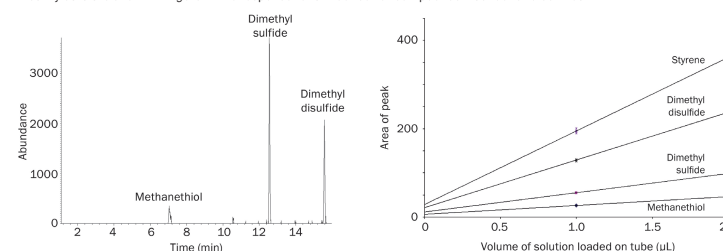


Figure 1: Extracted-ion chromatogram from a 2 ng standard solution – equivalent to approximately 2 ppb in 1 L of air.

Figure 2: Peak area versus sample volume for each component in the sample mix.

CONCLUSIONS

Markes' TD technology has been shown to be compatible with on- and off-line monitoring of trace sulfur compounds in both standards and real-world samples. This is due to the following key features of the system:

Totally inert sample flow path (i.e. constructed entirely of quartz, fused silica and inert-coated stainless steel). In some TD systems the heated valve connectors are metal, causing degradation of sulfur components and leading to the failure of this method.

Low-temperature valve and flow path (80–120°C). Some TD systems have minimum flow path temperatures of 150°C, which is too high for monitoring reactive sulfur species.

Use of highly specialised focusing technology for quantitative trapping and release of target sulfur compounds.

For off-line field monitoring of sulfur compounds using method-compliant sorbent tubes, it is also important for samples to be transferred to the laboratory as soon as possible and analysed within a few days.

REFERENCES

1. Method developed by Professor K.-H. Kim of Sejong University, Seoul, South Korea and ITC21, Seongnam City, South Korea.
2. K.-H. Kim, Some insights into the gas chromatographic determination of reduced sulfur compounds (RSCs) in air, *Environmental Science & Technology*, 2005, 39: 6765–6769, <http://dx.doi.org/10.1021/es050497l>.
3. K.-H. Kim, D.-W. Ju and S.-W. Joo, The evaluation of recovery rate associated with the use of thermal desorption systems for the analysis of atmospheric reduced sulfur compounds (RSC) using the GC/PFPD method, *Talanta*, 2005, 67: 955–959, <http://dx.doi.org/10.1016/j.talanta.2005.04.048>.