

Application Note 032

Analysis of Sulfur Compounds Using On-line and Off-line TD–GC

Application Note

MARKES
international

Abstract

This application note shows how Markes' TD technology is compatible with trace-level sulfur compounds, both in standard mixes and in real-life samples.

Introduction

Sulfur compounds are associated with unpleasant, pungent odors that are noticeable even at low concentrations. These compounds are difficult to analyze, as they are thermally labile (sensitive to high temperatures), particularly when in contact with metals. Moreover, several of the compounds of interest, such as hydrogen sulfide and methanethiol, are very volatile.

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

- Industrial emissions testing
- Environmental monitoring of off-odors, for example, from sewage treatment plants and landfill sites
- Health and safety monitoring of toxic compounds, for example, exposure to CS₂
- Flavor and fragrance testing
- Food studies, for example, shelf-life tests and off-odor profiling

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



Agilent Technologies

In May 2016, Markes International launched the xr series of thermal desorption instruments, which offer extended recollection capability, extended analyte range, and extended reliability.

On-line or canister analysis

On-line analysis is the method of choice for the real-time monitoring of changes in vapor 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, for example, hydrogen sulfide.

The following on-line TD–GC method was developed in response to the Korean off-odor regulations that came into force in February 2005 [1]. The regulations state maximum allowable concentrations for four sulfur compounds (Table 1).

Table 1. Sulfur compound regulation limit levels (Korean off-odor regulations).

Compound	Industrial area (ppb)	Other areas (ppb)
Hydrogen sulfide	60	20
Methanethiol	4	2
Dimethyl sulfide	50	10
Dimethyl disulfide	30	9

Analytical conditions

A Markes International UNITY–Air Server system was connected to a GC fitted with a pulsed flame photometric detector (PFPD). Figure 1 presents a schematic of the system setup.

Note that it is important to keep sampling flow rates above 50 mL/min, and flow path temperatures below 100 °C to prevent degradation or loss of these labile analytes. It is also critical that the entire flow path is short and narrow-bore, and is constructed entirely of inert materials (for example, PTFE or quartz).

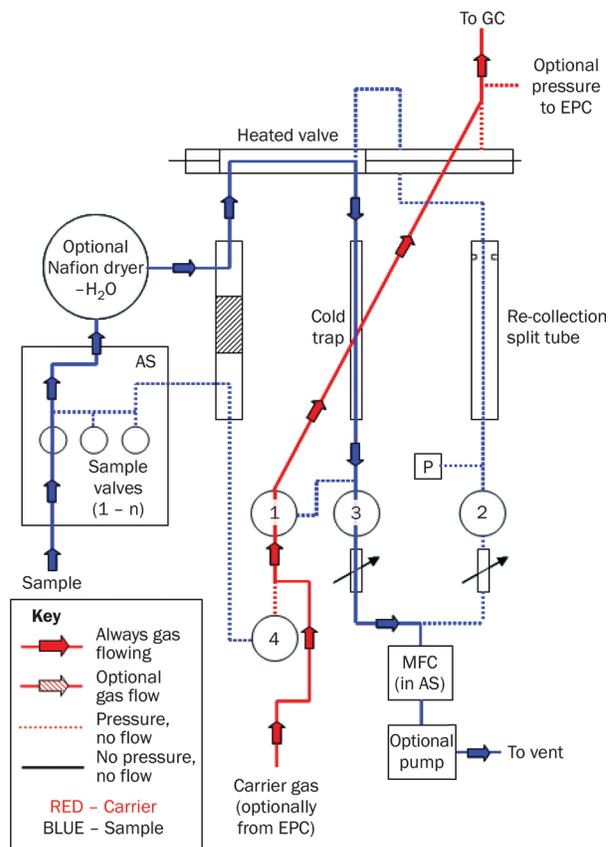


Figure 1. Schematic of UNITY–Air Server setup.

Analytical conditions

Parameter	Value
TD (UNITY–Air Server)	
Sampling volume:	100-500 mL at 50 mL/min (critical)
Nafion dryer:	In-line
Focusing trap:	Graphitized carbon black/silica gel
Trap low:	–15 °C
Trap high:	250 °C
Hold:	5 minutes
Flow path temperature:	80 °C (critical)
GC	
Column:	VF-1 MS, 60 m × 0.32 mm, 5.0 μm
Column flow:	2.0 mL/min
GC oven:	60 °C (5 minutes), 8 °C/min to 200 °C
PFPD (square root function on)	
Fuel gas:	Air1: 17 mL/min Air2: 10 mL/min H ₂ : 14 mL/min
Temperature:	200 °C (S filter)

Calibration

Figure 2 shows the analysis of 10 ppb and 20 ppb gas standards, together with a typical QA/QC check-sample.

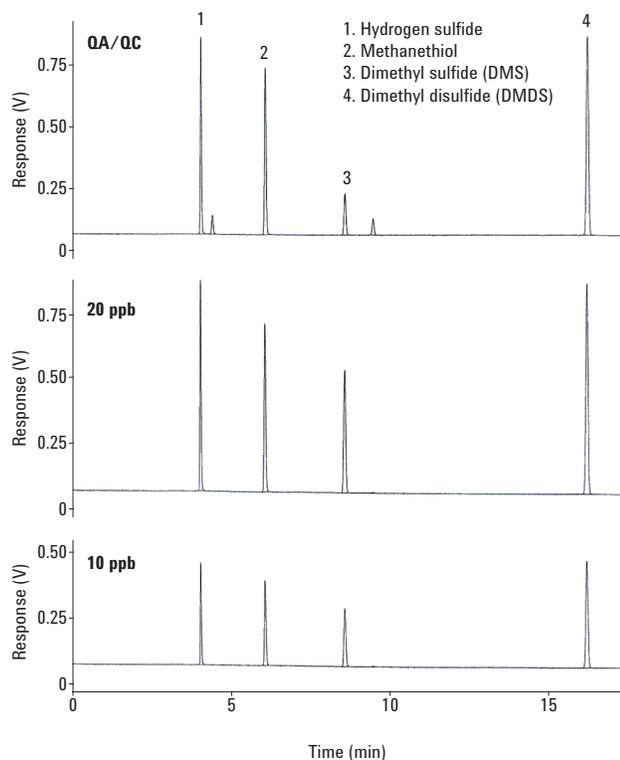


Figure 2. On-line chromatograms for 10 ppb and 20 ppb calibration standards and a QA/QC check-sample.

Detection limits [2]

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 (Table 2). The sampled volume was 100 mL and the split ratio was ~13:1.

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

Compound	Peak area				Linearity (r)
	0 ppb	20 ppb	40 ppb	100 ppb	
Hydrogen sulfide	0	82,438	218,215	619,303	0.9973
Methanethiol	0	176,790	370,921	949,516	0.9983
Dimethyl sulfide	0	166,279	345,939	864,878	0.9999
Dimethyl disulfide	0	318,125	639,442	1,479,555	0.9993

Reproducibility

Each of three concentrations of calibration gas were sampled 10 times to obtain reproducibility data (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%.

Recovery [3]

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.

Table 3. TD recovery rate at various relative humidities.

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

Korean Odor Monitoring network data

The excellent analytical performance shown during method development is reproduced in routine field operation.

A report [4] presenting data from on-line odor monitoring systems (UNITY–Air Server–GC) in operation in seven Korean cities shows:

- Peak area precision consistently below the guideline value of 10% RSD, with values for hydrogen sulfide between 0.5 and 4.3% across all laboratories
- Stable retention times: <0.1% RSD for all compounds at all field monitoring sites
- Excellent recovery across all analytes, with >87% recovery for the most volatile component (hydrogen sulfide) in all cases. This is well above the 80% performance criterion.

Results and Discussion

The excellent system performance data, obtained in both laboratory trials and subsequent field operation, clearly show the inertness of the UNITY–Air Server flow path.

This system has also been shown to be compatible with the most volatile sulfur compounds such as hydrogen sulfide, with no breakthrough during sampling, nor loss during analysis.

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 reliably be 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.

Analysis of the sulfur standard

The standard solution (1% in methanol) contained methanethiol, dimethyl sulfide, acetaldehyde, dimethyl disulfide, and styrene. Three different sample volumes (0.5 μ L, 1 μ L, and 2 μ L) were injected onto a sorbent tube in a flow of helium at 50 mL/min using Markes' Calibration Solution Loading Rig (CSLR). The samples were then desorbed using the UNITY thermal desorber linked to a GC/MS.

Analytical conditions

Parameter	Value
TD (UNITY)	
Prepurge time:	0.5 minutes (split on and trap in line)
Primary desorb:	200 °C for 3 minutes (split on)
Trap low:	-10 °C
Trap desorb:	200 °C for 3 minutes (split on)
Trap:	U-T6SUL (porous polymer – carbonized molecular sieve)
Flow path temperature:	80 °C
Carrier gas pressure:	10 psi
Desorb flow:	3 mL/min
Split flow:	45 mL/min
Split ratio:	~400:1
GC	
Column:	GS-Gaspro, 30 m \times 0.32 mm
Column flow:	~2 mL/min
Start temperature:	60 °C for 0 minutes
End temperature:	220 °C for 6 minutes
Ramp rate:	10 °C/min
MS	
Source temperature:	230 °C
Quadrupole temperature:	150 °C
Transfer line temperature:	150 °C
Mass scan range	<i>m/z</i> 25-350

Figure 3 shows the chromatograms obtained from varying injection volumes of the standard solution.

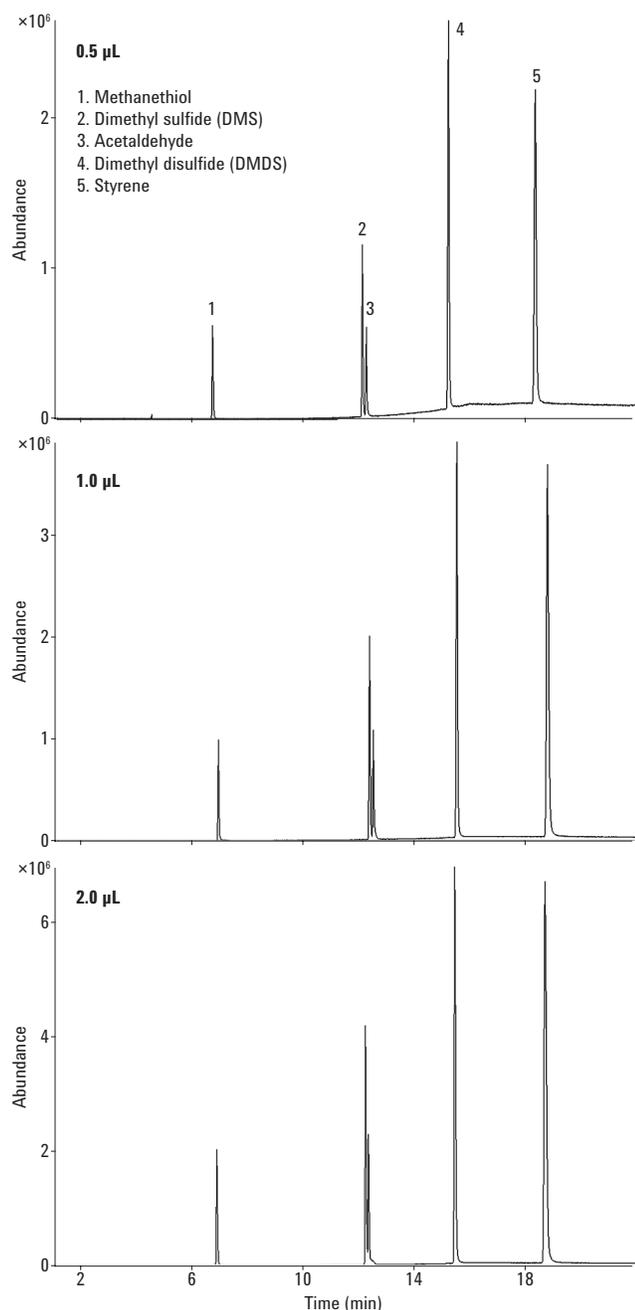


Figure 3. Injections of three different volumes of a standard solution.

Linearity

Figure 4 shows linearity data. The response for all four sulfur compounds was found to be linear.

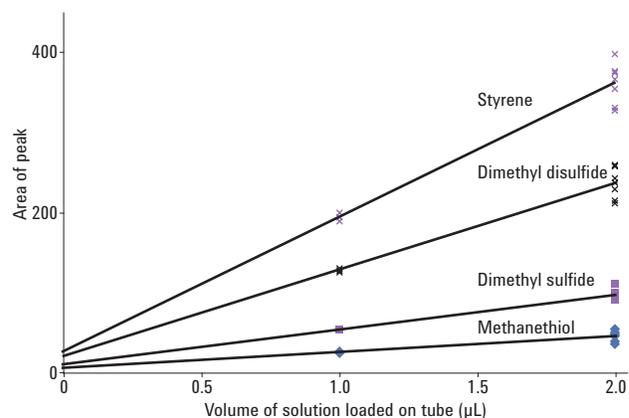


Figure 4. Peak area versus sample volume for each component in the sample mix.

Detection limits

Figure 5 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 (MDL) for methanethiol under these analytical conditions. However, for dimethyl sulfide and dimethyl disulfide, the MDL is at least five times lower than this, that is, 0.4 ppb in a 1 L air sample.

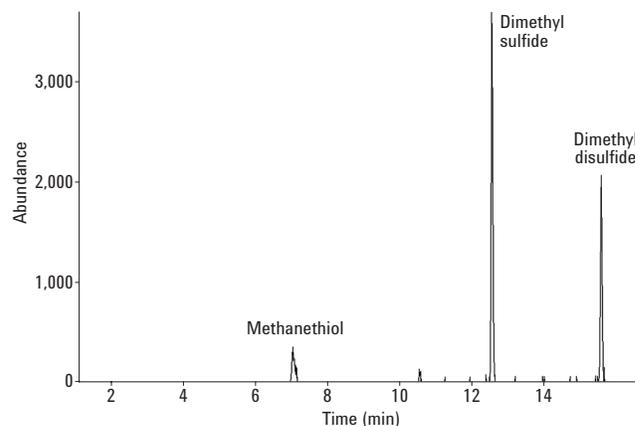


Figure 5. Extracted ion chromatogram from a 2 ng standard solution, equivalent to approximately 2 ppb in 1 L of air.

Analysis of sulfur compounds in landfill gas

Levels of odorous and toxic vapors in landfill gas are controlled under European legislation on the landfill of waste (EC Directive – 1999/31/EC). This requires the concentration of priority pollutants in landfill gas emissions to be measured, and includes the following sulfur compounds:

- Methanethiol
- Ethanethiol
- Propanethiol
- Butanethiol
- Carbon disulfide
- Dimethyl sulfide
- Dimethyl disulfide

In the UK, a standard sampling and analytical protocol for compliance with the monitoring requirements of this directive is available [5]. It specifies active sampling of a small volume (~100 mL) of landfill gas onto inert-coated sorbent tubes followed by TD–GC/MS analysis. Note that this method cannot be used for monitoring hydrogen sulfide.

The nature of landfill gas poses a number of problems when sampling onto sorbent tubes for TD–GC analysis. These include humidity and reactivity.

Humidity

Landfill gas is usually at very high humidity, and is often at elevated temperatures. This can complicate sampling and analytical procedures. It is essential to ensure that sorbent tubes are allowed to equilibrate to the same temperature as the landfill gas before sampling, and that all sampling lines are kept as short as possible.

If sampling of humid gas takes place onto tubes that are at a lower temperature than the gas, condensation will occur, and liquid water will collect in the sorbent tubes. This can lead to breakthrough during sampling, and inefficient desorption during analysis.

Reactivity

The labile nature of the compounds of interest requires the use of inert sample tubes and sorbents (note that not all glass tubes are suitable for sulfur compound analysis). The sorbents used must also be compatible with analytes over a wide volatility range. A combination of Tenax TA (suitable for trapping the less volatile compounds such as benzene) backed up by UniCarb (a carbonized molecular sieve sorbent, suitable for trapping volatiles such as methanethiol) packed in inert-coated stainless steel tubes was tested by the UK Environment Agency, and found to work well. Both sorbents are inert, and have very low background artefact levels.

For further information on the analysis of landfill gas compounds, see application note 047.

Practical recommendations for landfill gas analysis

To minimize the amount of water vapor trapped on the tube and simplify sampling, samples are typically collected by pulling 100 mL of landfill gas through the tube using a large gas syringe. The tubes are then dry-purged prior to analysis. Dry-purging the sample tube simply involves passing a volume (typically ~400 mL) of pure, dry air or inert gas through the tube from the sampling end at a rate of ~50 mL/min. Do not exceed the breakthrough volumes for any of the retained analytes during the dry-purge process.

Due to the labile nature of the sulfur compounds and the nature of the two-bed sorbent tube (that is, weak sorbent backed by extremely strong sorbent), it is essential to analyze the tubes as soon as possible after sampling, and certainly within 4 days.

Figures 6 and 7 show example chromatograms.

Analytical conditions

Parameter	Value
TD (UNITY)	
Prepurge time:	1 minute (split on) – trap in-line
Primary desorb 1:	200 °C for 5 minutes (split on)
Primary desorb 2:	300 °C for 5 minutes (split on)
Trap low:	30 °C
Trap desorb:	220 °C at 40 °C/s for 5 minutes (split on)
Trap	U-T6SUL (porous polymer–carbonised molecular sieve)
Flow path temperature:	120 °C
Carrier gas pressure:	25 psi
Desorb flow:	20 mL/min
Split flow:	80 mL/min
Split ratio:	~100:1

Parameter	Value
GC	
Column:	DBVRX, 60 m × 0.25 mm, 1.4 µm
Column flow:	~1 mL/min
Start temperature:	40 °C
End temperature:	225 °C
Ramp rate:	10 °C/min
MS	
Mode:	Scan
Mass range:	<i>m/z</i> 35-260
Threshold:	50
Rate:	3.25 scans/s

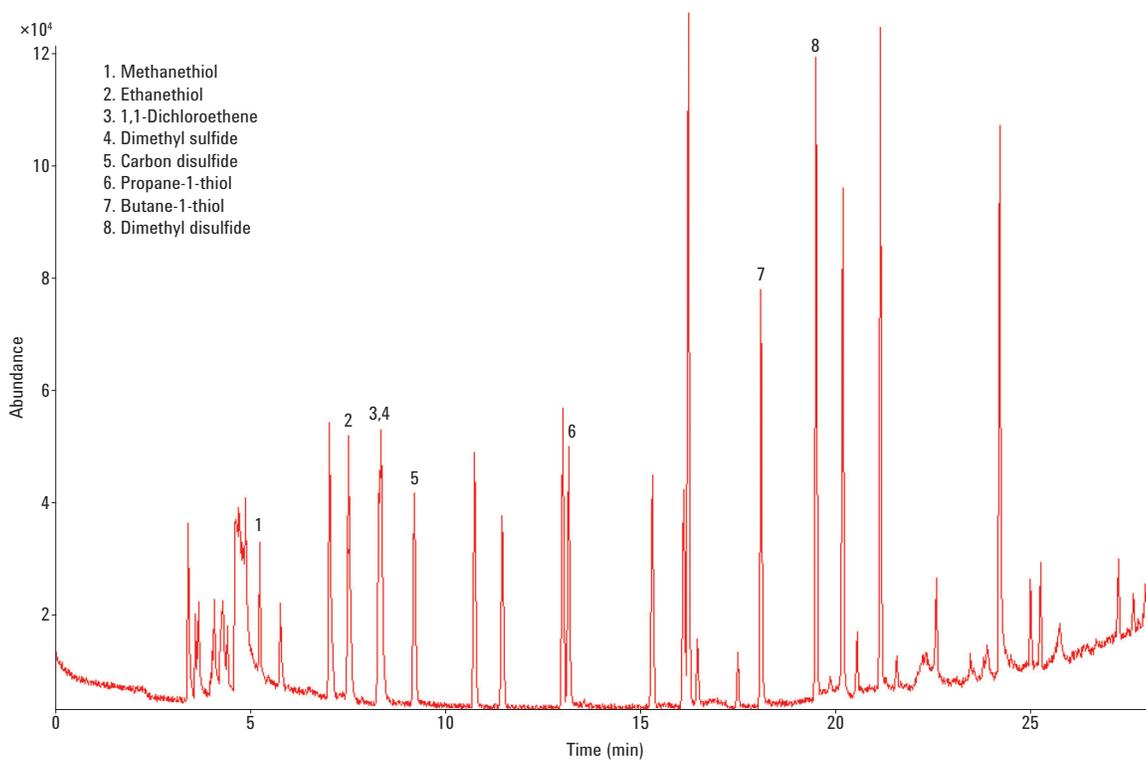


Figure 6. A 1 µL injection of a 50 ppm standard mix (~50 ng of each component), showing the seven key sulfur compounds (and 1,1-dichloroethene) on the landfill gas priority list.

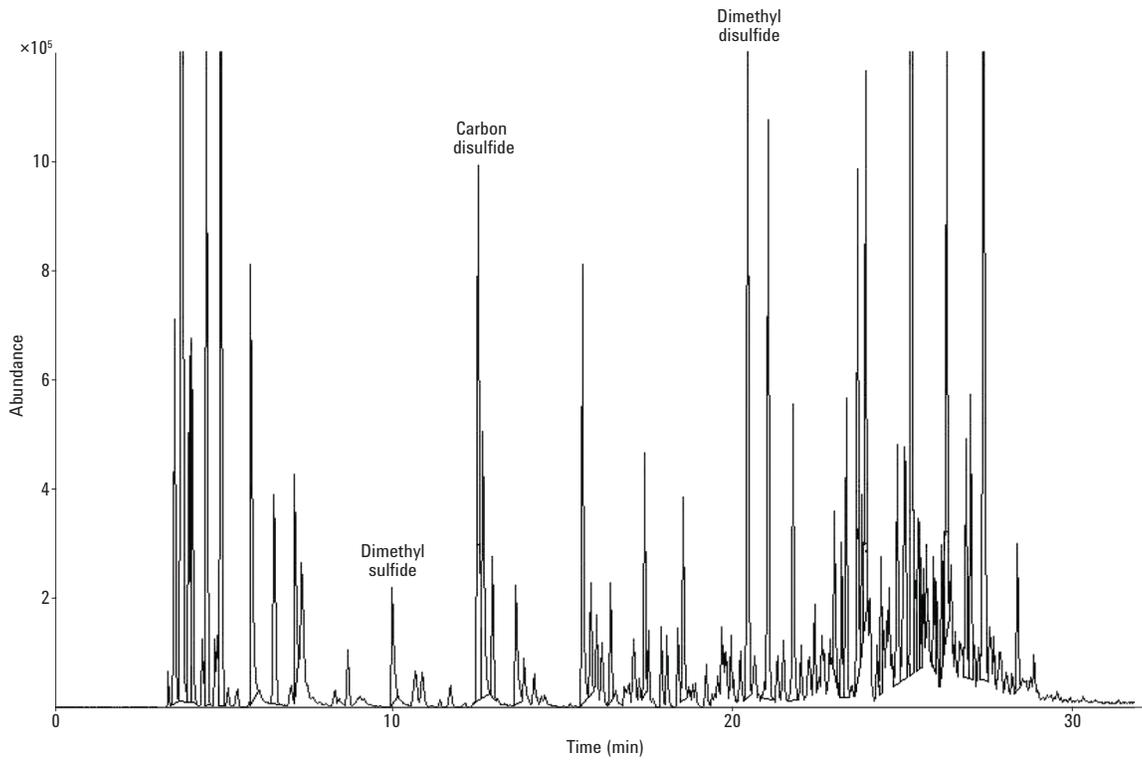


Figure 7. A 100 mL sample of landfill gas showing detection of trace levels of three key sulfur compounds.

Conclusions

Markes' TD technology has been shown to be compatible with on-line 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:** (that is, 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 specialized 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 analyzed within a few days.

Acknowledgements

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References

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Trademarks

Air Server™, CSLR™, UniCarb™, and UNITY™ are trademarks of Markes International.

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Appendix

Table A1. Reproducibility data over 10 replicate injections.

20 ppb

Compound	Injection										Av.	SD	RSD (%)
	1	2	3	4	5	6	7	8	9	10			
Hydrogen sulfide	76460	79036	82056	80372	82262	83807	83113	85978	83025	88271	82438	3350	4.1
Methanethiol	178052	182005	180246	174585	174370	180054	175625	172700	176003	174257	176790	3113	1.8
Dimethyl sulfide	165430	165550	167582	166836	164237	167215	167313	167183	167147	164300	166279	1285	0.8
Dimethyl disulfide	322276	320646	321332	314792	319151	317320	315838	314978	318441	316475	318125	2680	0.8

40 ppb

Compound	Injection										Av.	SD	RSD (%)
	1	2	3	4	5	6	7	8	9	10			
Hydrogen sulfide	214768	214999	218966	219496	219740	217208	216217	222580	220169	218003	218215	2465	1.1
Methanethiol	375418	371806	370029	370483	374777	372415	370784	368924	367694	36680	370921	2786	0.8
Dimethyl sulfide	341996	337985	345363	345658	343218	348081	347328	351048	348833	349884	345939	3989	1.2
Dimethyl disulfide	642067	633164	637461	641081	644071	643528	644157	634946	641445	632500	639442	4542	0.7

100 ppb

Compound	Injection										Av.	SD	RSD (%)
	1	2	3	4	5	6	7	8	9	10			
Hydrogen sulfide	607029	602222	621621	614785	615481	621670	618770	627965	629519	633963	619303	9905	1.6
Methanethiol	950364	649117	953585	942689	944820	954597	942524	951135	956390	949935	949516	4840	0.5
Dimethyl sulfide	857252	852854	862116	862870	862856	872753	866397	869007	870955	871724	864878	6529	0.8
Dimethyl disulfide	1484243	1480388	1479072	1475582	1483793	1491751	1478730	1473567	1475154	1473266	1479555	5782	0.4

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