MARKES international LIMITED

Unit D3 Llantrisant Business Park Pontyclun RCT CF72 8YW United Kingdom

Tel: +44 (0) 1443 230 935 **Fax:** +44 (0) 1443 231531

http://www.markes.com

Thermal desorption technical Support

Note 32: Analysis of sulphur compounds using TD-GC(MS)

Introduction

Sulphur compounds are probably best associated with their unpleasant, pungent odours, noticeable even at low concentrations. These compounds, especially when in contact with metals, become increasingly sensitive to high temperatures. However, despite the limitations this property brings to analysis, the detection of such compounds is of particular importance to a wide range of industries such as flavour and fragrance testing, the purification of water and food studies.

The following method was developed to analyse a standard sulphur solution obtained from Chemservice and consisting of methylmercaptan, methyl sulphide, acetaldehyde, dimethyl-disulphide and styrene (1% in methanol). The standard solution was introduced onto a Silcosteel® coated stainless steel thermal desorption tube containing a 40 mm bed of Tenax™ backed up by a 15 mm bed of UniCarb™. Four different volumes of sample were injected (5 ng, 0.5 µl, 1 µl and 2 µl) respectively, in a flow of inert gas (helium) at a rate of 50 ml/min and using the calibration standard solution loading rig from Markes International. The samples were then desorbed using the UNITY™ thermal desorber from Markes International linked to an Agilent 6890 GC and 5973 MS. The analytical conditions are given below.

The analytical conditions and results obtained from a similar application carried out in the field and using a UNITY - Air server system from Markes International are also given. On this occasion the calibration gas used consisted of hydrogen sulphide, methylmercaptan, ethylmercaptan, dimethyl sulphide, carbon disulphide and dimethyl-disulphide with a concentration of approximately 150-400 ppb. The standard was sampled for 3 minutes at a rate of 30 ml/min resulting in a total sample volume of 90 ml. Since the sampling was carried out on-line, no sorbent tube was required - the standard was sampled directly onto the focusing trap of UNITY.

Analytical Conditions

UNITY:	Prepurge time:	0.5 min (split on and trap in line)
	Primary desorb:	200°C for 3 mins (split on)
	Trap low temp:	-10°C
	Trap desorb:	200°C for 3 mins (split on)
	Trap:	U-T6SUL containing Tenax and Unicarb
	Flow path temp:	80°C
	Carrier gas pressure:	10 psi
	Desorb flow:	3 ml/min
	Split flow:	45 ml/min
	Split ratio:	~ 400:1
GC:	Column flow:	~ 2 ml/min
	Start temp:	60°C for 0 mins
	End temp:	220°C for 6 min
	Rate of temp increase:	10°C/min
	Column:	30 m, 0.32 mm i.d. with a GS-Gaspro phase

MS:	MS Source temp:	230°C	MSD transfer line temp:	150°C
	MS Quadrupole temp:	150°C	Mass Scan Range:	25 to 350 amu

Results

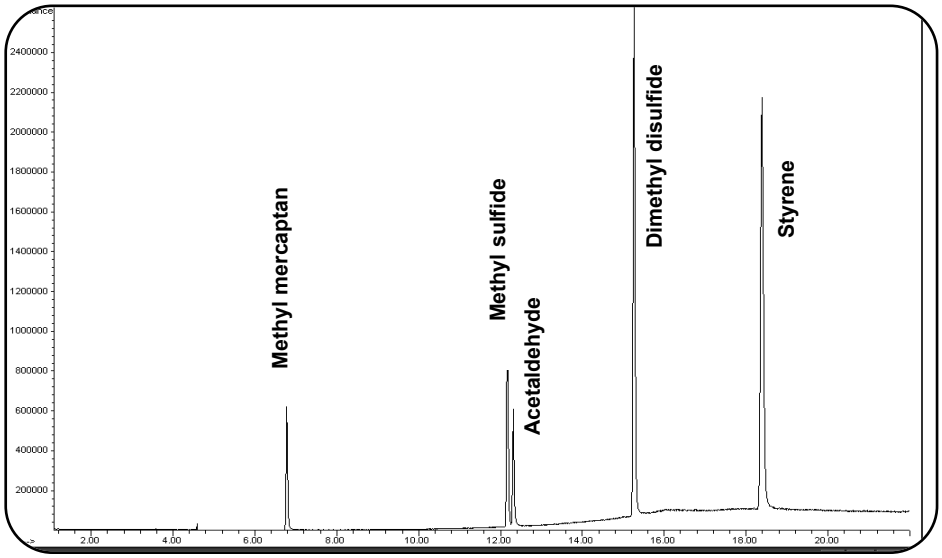

Figure 1. 0.5 µl sample of standard solution

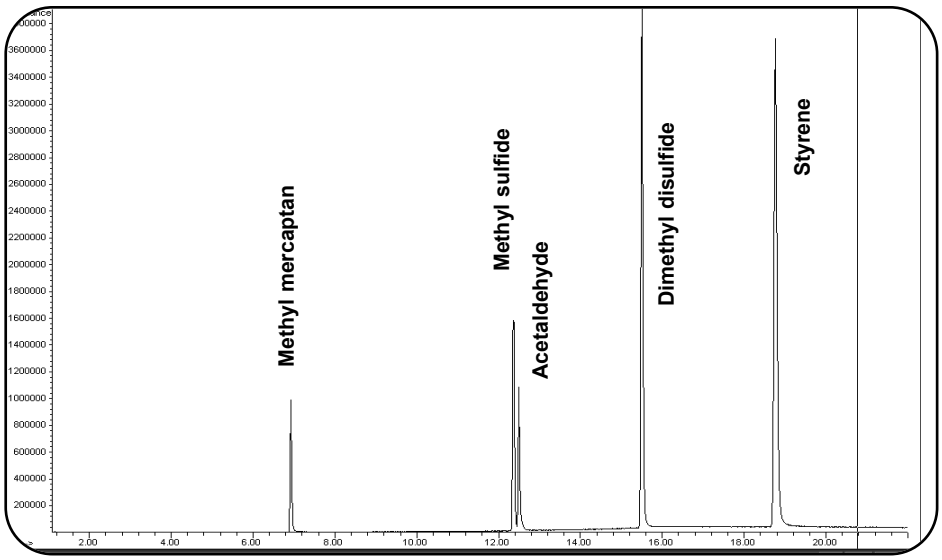

Figure 2. 1 µl sample of standard solution

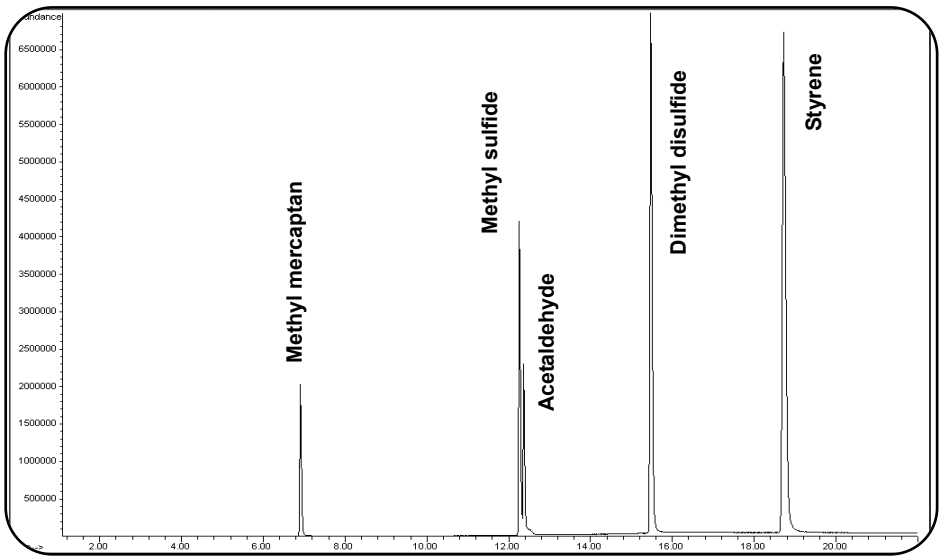

Figure 3. 2 µl sample of standard solution

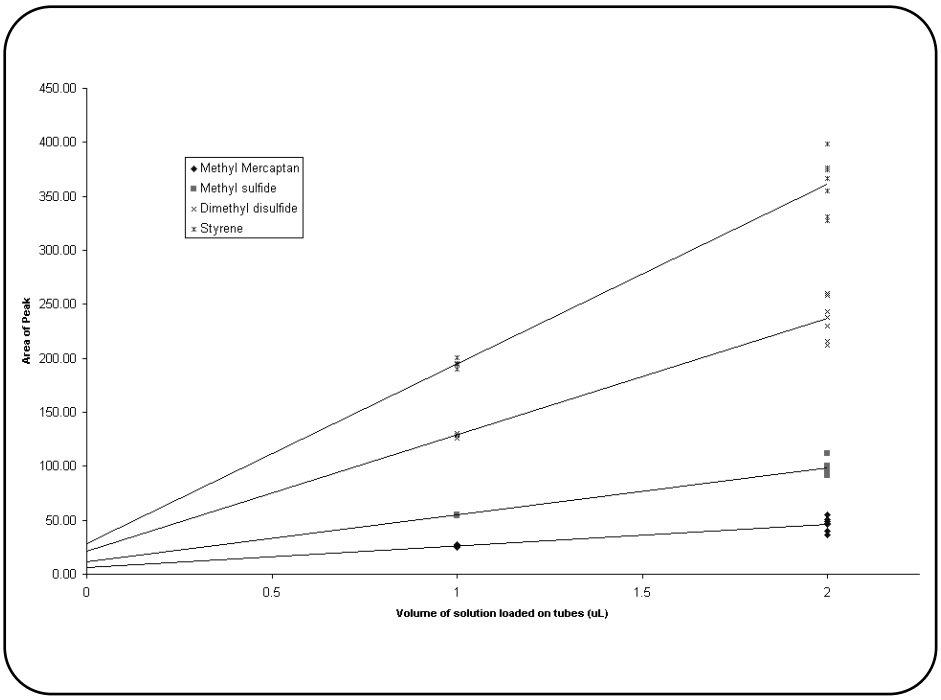

Figure 4. Plot of peak area against sample volume for each component

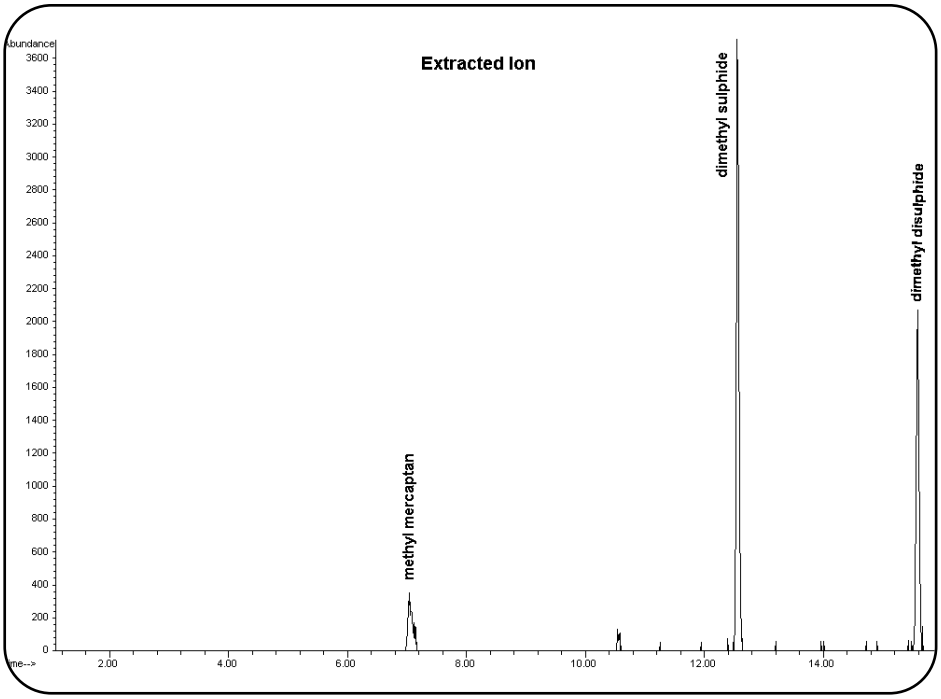

Figure 5. 2 ng sample of standard solution. This equates to approximately 2 ppb per litre of air

Analytical Conditions: On-Line Sampling - See figure 6 overleaf

UNITY-Air Sever:

Trap low temp:	-15°C
Trap desorb:	200°C for 5 mins (split on)
Flow path temp:	80°C
Carrier gas pressure:	10 psi
Sample flow:	30 ml/min for 3 mins
Split flow:	45 ml/min
Trap:	H2S Trap containing Tenax and Carboxen 1000

GC:

Column flow:	0.9 ml/min
Start temp:	40°C for 4 mins
End temp:	200°C for 5 min
Rate of temp increase:	10°C/min
Column:	DB-1, 0.32 mm, 4.0 µm thickness

Results

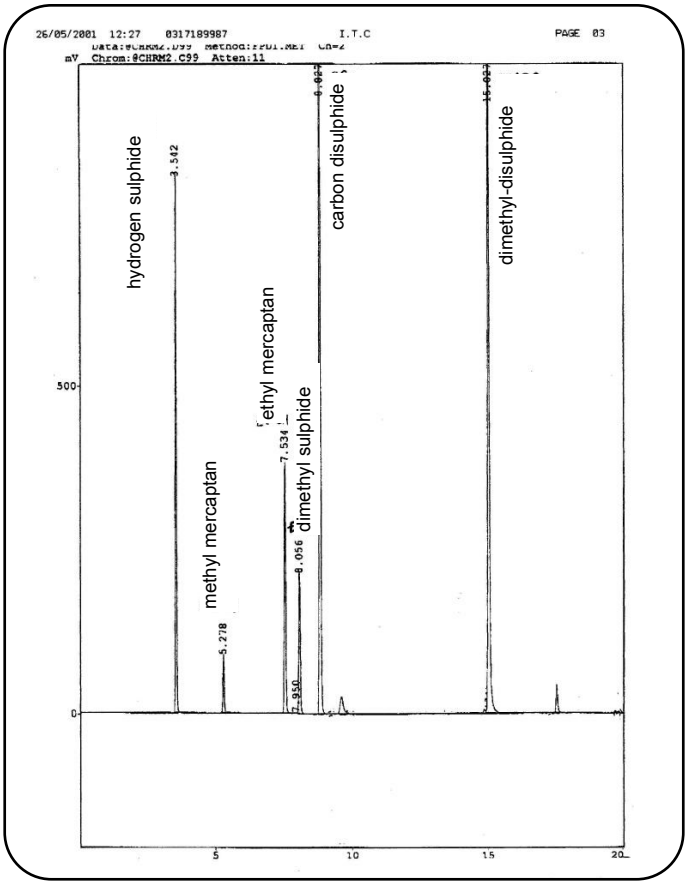

Figure 6. Analysis of a sulphur compound standard gas mixture using UNITY-Air Server-GC.

Summary

Both sets of experiments demonstrated the ability of UNITY to successfully thermally desorb a mixture of sulphur compounds, despite their sensitivity to heat and reaction with metals. This clearly confirms the inertness of the flow path in UNITY. From Figure 4 it is evident that there is a linear relationship between the amount of sample introduced to the tube and the peak area produced. Again this emphasizes the inertness of the UNITY and UNITY-Air Server flow path since all the sample was desorbed and subsequently passed onto the GCMS. From the low level standards (Figure 5), it also appears that quantitation limits in the order of 1 ppb can be readily achieved from as little as 1 L of air.

Sulphur compounds can therefore be analysed successfully using an on-line sampling method via the UNITY-Air Server system, or the more conventional passive/diffusive method via sorbent tubes and a UNITY thermal desorber.

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