

Application Note 064

Simultaneous TD-GC analysis of VOCs and SVOCs

Summary

This Application Note shows that Markes' thermal desorption (TD) technology, incorporating a main heated valve and backflush desorption of the focusing trap, facilitates simultaneous analysis of VOC and SVOCs, such as those of relevance to material emissions testing. This capability is validated using the secure sample re-collection facility inherent to Markes' systems.

Definitions

Volatile and semi-volatile organic compounds (VOCs and SVOCs) are both present in the air in the vapour phase. VOCs are predominantly in the vapour phase at ambient temperature, and are variously defined as having similar or higher volatility than n-C₁₆, or as having a volatility in the range n-C₆ to n-C₁₆.

SVOCs, in contrast, are present in the air in both vapour-phase and particulate form, and are typically defined as being within the volatility range n-C₁₆ to n-C₄₀.

Some standard thermal desorption (TD) protocols, for example those for emissions testing, require evaluation of both VOCs and SVOCs. Analysing both of these groups of compounds simultaneously can therefore provide considerable savings of time and money.

Limitations of forward-flow desorption

Many TD systems desorb the focusing trap in 'forward-flow' mode, meaning that analytes have to pass through the entire sorbent bed on their way to the analyser. This restricts the sorbents to those weak enough to allow the highest-boiling compound of interest to pass through. This then makes it difficult to trap volatile species quantitatively, limiting the analyte volatility range that can be analysed simultaneously (even if liquid cryogen is used to reduce trapping temperatures below -100°C).

Extending the volatility range

Every Markes' TD system incorporates a patented, inert and uniformly-heated valve, in compliance with standard methods. This enables critical functions (leak test, purge to vent, etc.), and is fully compatible with 'sticky' semi-volatiles such as phthalate plasticisers.

Importantly, this component allows the flow of gas to be reversed through the focusing trap during trap desorption, flushing the compounds from the trap into the analyser. Figure 1 illustrates the flow path during tube desorption and trap desorption.

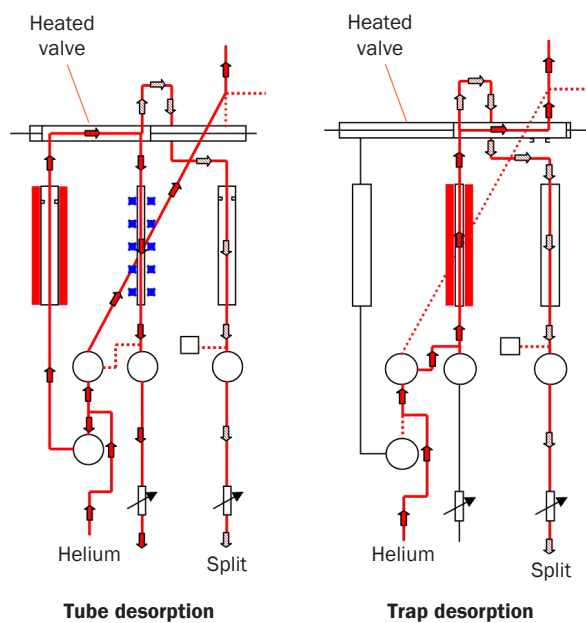


Figure 1: The heated main valve facilitates backflush desorption of the focusing trap during two-stage desorption on Markes' TD systems.

Focusing traps used in Markes' TD instruments (Figure 2) are constructed of quartz, and are narrower at their inlet/outlet end to optimise linear gas velocity and minimise band broadening. For simultaneous analysis of VOCs and SVOCs they are packed with a series of sorbents of increasing strength.

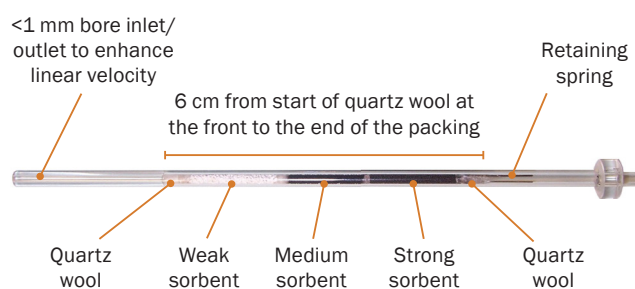


Figure 2: Design of Markes' focusing trap, in this case packed with three sorbent beds.

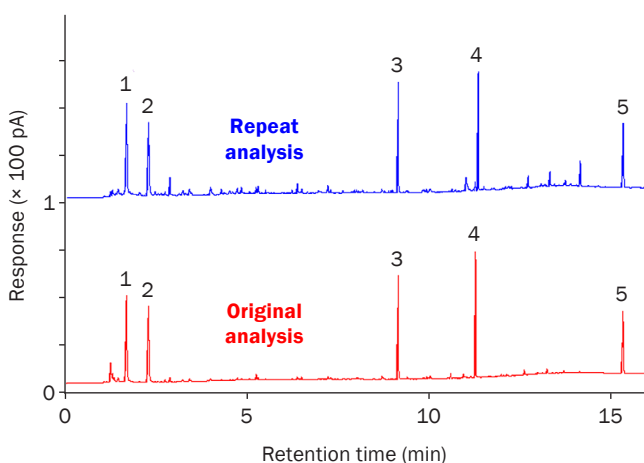
Semi-volatiles desorbed from the sample tube during tube desorption are retained by the weak sorbents at the front of the trap, whereas volatiles break through to the stronger sorbent(s) at the back.

During trap desorption, when the flow of carrier gas is reversed, volatiles are quantitatively released from the stronger (rear) sorbents and semi-volatiles are quantitatively released from the weaker (front) sorbents. The semi-volatiles are not impacted by the presence of the stronger sorbents at the back of the trap, because they never come into contact with them.

Validation of analyte recovery

Markes' TD systems are unique in offering quantitative re-collection for repeat analysis. This is invaluable for method development and validation, as described in ASTM D6196 (see [Application Note 024](#) for more information).

To demonstrate this capability, a Markes TD instrument was used to simultaneously analyse VOCs and SVOCs in a material emissions standard. The split portion of the original sample was then quantitatively re-collected and re-desorbed (Figure 3).



Peak no.	Compound	Peak area	
		Original	Repeat
1	Benzene	94.5	94.0
2	Toluene	90.4	95.9
3	Diethyl phthalate	60.7	64.5
4	Di-n-butyl phthalate	72.1	69.8
5	Di-n-octyl phthalate	60.2	60.7

Figure 3: Analysis of a material emissions standard with subsequent re-analysis of the re-collected sample.

Poor recovery of one or more compounds would have been observed as bias in the analysis of the re-collected sample. The results show quantitative recovery of analytes across the volatility range.

Similar results were obtained for an automated series of repeat analyses of a mix of phthalates with a range of volatilities, using an UNITY™ thermal desorber and ULTRA™ autosampler (Figure 4). As before, full recovery is demonstrated across the volatility range.

- 1 Dimethyl phthalate
- 2 Hexadecane
- 3 Diethyl phthalate
- 4 Di-n-butyl phthalate
- 5 Bis(2-ethylhexyl) phthalate

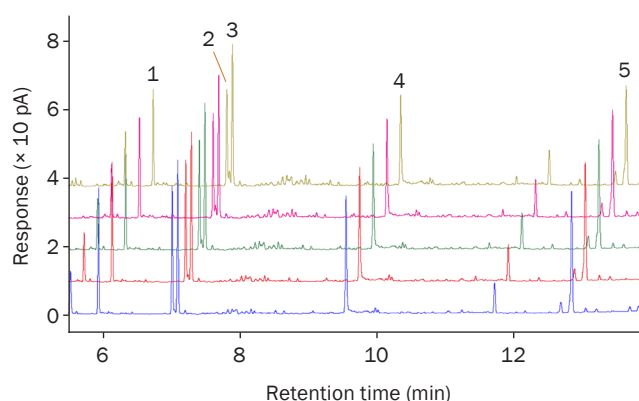


Figure 4: Primary and repeat analyses of a phthalate standard, demonstrating quantitative recovery.

Conclusions

These results show that Markes' TD technology, incorporating a main heated valve and backflush desorption of the focusing trap, facilitates simultaneous analysis of VOCs and SVOCs, such as those of interest to material emissions testing. In addition, it has been shown that this capability can be validated using the unique capability of Markes' instruments to quantitatively split and re-collect split flows.

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.

日本正規代理店
株式会社 ENVサイエンスレーディング
 本社
 〒270-2241 千葉県松戸市松戸新田 53-1-804
 ENVラボ
 〒277-0005 千葉県柏市柏 273-1 シャープ株式会社柏事業所内 35 研究室
 TEL: 04-7193-8501 FAX: 04-7193-8508
 e-mail: info@env-sciences.jp http://www.env-sciences.jp