

Thermal Desorption Technical Support

Note 64: Simultaneous TD-GC(-MS) analysis of VOCs and semi-VOCs

Keywords

Phthalates, Re-collection, Validation, Sorbents, Trapping

Introduction

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 that is within the range n-C₆ to n-C₁₆.

SVOCs 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 (e.g. AgBB¹ and AFSSET² protocols), require evaluation of both VOCs and SVOCs. If both of these groups of compounds can be analysed simultaneously, it would save considerable laboratory time and cost.

Thermal desorber design - key considerations for extending the volatility range

Markes manual and automated TD systems (UNITY 2™ and series 2 ULTRA™-UNITY) offer state-of-the-art two-stage thermal desorption. The primary sorbent/sample tube is heated in a flow of inert gas which sweeps the vapours onto an electrically-cooled focusing trap. This is then heated rapidly (at rates approaching 100°C/sec) in a reverse flow of carrier gas to transfer/inject the analytes into the GC(MS) analytical system as a narrow band of vapour.

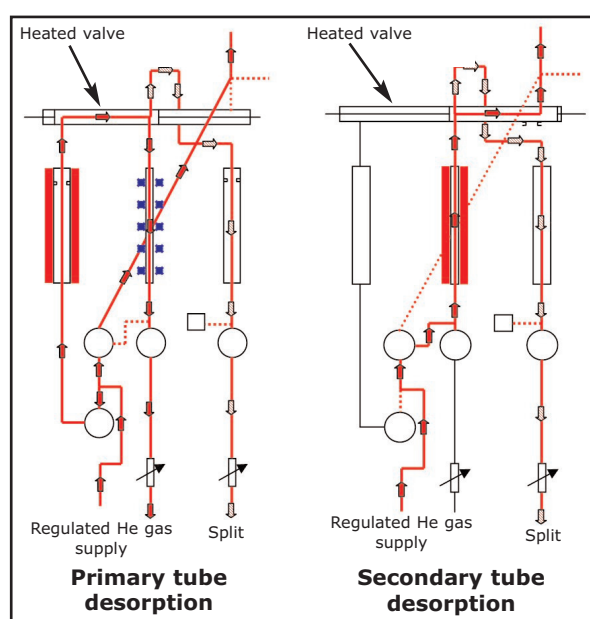


Figure 1: Heated main valve facilitates backflush desorption of the focusing trap during 2-stage TD on a Markes series 2 (ULTRA)-UNITY system

This multi-step process allows vapour concentrations to be enhanced by up to 6 orders of magnitude (TDTS 17).

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

¹ AgBB protocol. "Health-related evaluation procedure for volatile organic compound emissions (VOC & SVOC) from building products" (2008) (<http://www.umweltbundesamt.de/building-products/agbb.htm>)

² AFSSET protocol. "Relatif à une procédure d'évaluation des risques sanitaires concernant les composés organiques volatils (COV) et le formaldéhyde émis par les produits de construction" (<http://www.afsse.fr>)

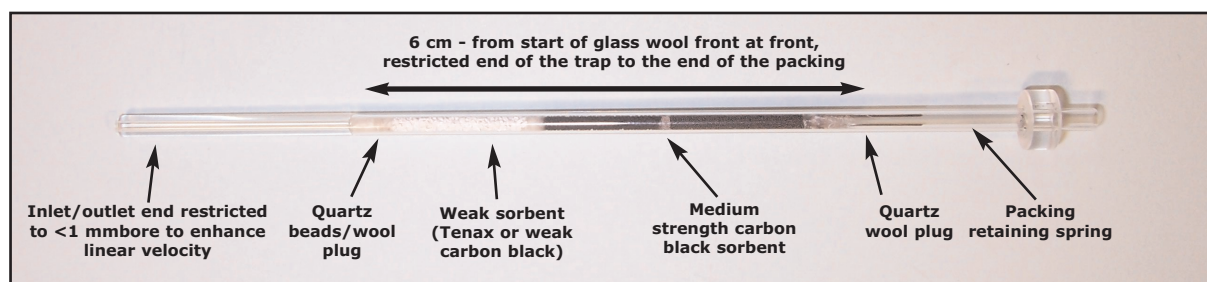


Figure 2: Markes focusing trap packed with two sorbent beds

It is this component which allows the flow of gas to be reversed through the focusing trap during secondary (trap) desorption such that the compounds are backflushed from the trap and transferred/injected into the analyser. Figure 1 illustrates the Markes TD flow path during primary (tube) desorption and secondary (trap) desorption.

The Markes focusing trap (Figure 2) is constructed of quartz and has a restricted internal diameter at its inlet/outlet end to optimise linear gas velocity and minimise band broadening. For simultaneous analysis of VOCs and SVOCs it is packed with a series of sorbents of increasing strength as shown.

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

Limitations of forward flow desorption of the focusing trap

Thermal desorption systems which do not contain an inert heated valve in the sample flow path cannot offer backflush desorption of the focusing trap. In this case the focusing trap is desorbed in 'forward flow' mode and analytes have to pass through the entire sorbent bed en route to the analyser. (Figure 3) Forward flow desorption therefore restricts the selection of sorbents to those which are weak enough to allow the highest boiling compound of interest to pass through. This then makes it difficult to trap volatile species quantitatively *i.e.* forward flow desorption limits the analyte volatility range that can be analysed simultaneously even if liquid cryogen is used to reduce trapping temperatures below -100°C

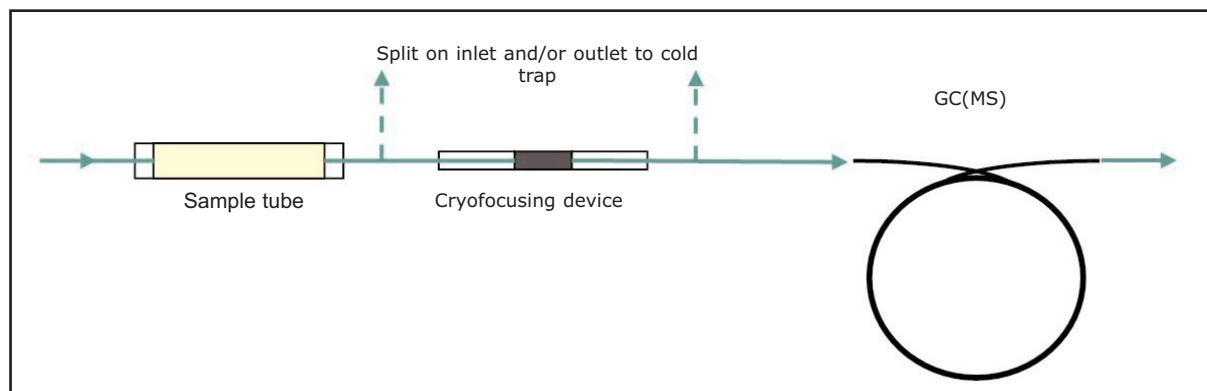
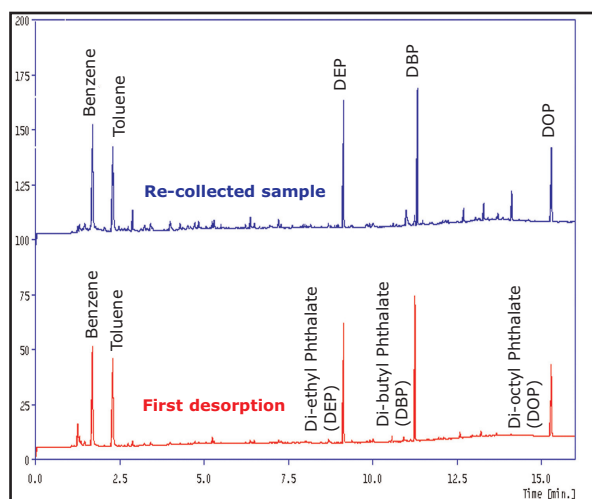


Figure 3: Systems without a main heated valve only offer forward flow desorption of the focusing trap, thus limiting the volatility range that can be analysed in a single run.

Validation of analyte recovery using SecureTD-Q™

Markes thermal desorption systems uniquely offer SecureTD-Q - quantitative re-collection for repeat analysis - for method development/validation as described in ASTM D6196. (See TDTS24 and Markes' brochure on validation.) SecureTD-Q was used to evaluate the performance of a Markes thermal desorption for simultaneous analysis of volatiles (benzene and toluene) in the presence of semi-volatile phthalates. (Figure 4).

The split portion of the original sample analysis was quantitatively re-collected and redesorbed. Poor recovery of one or more compounds would have been observed as bias in the analysis of the re-collected sample (see TDTS24 and ASTM D6196-03). The results show quantitative recovery of analytes across the volatility range.



Compound	Run 1	Repeat
Benzene	94.5	94
Toluene	90.4	95.9
DEP	60.7	64.5
DBP	72.1	69.8
DOP	60.2	60.7

Figure 4: The analysis of benzene, toluene, di-ethyl, di-butyl and di-octyl phthalates with subsequent analysis of re-collected sample. Peak area results for analysis and re-collection are shown

Similar results for an automated series of repeat analyses of a mix of higher and lower volatility phthalates using series 2 ULTRA 50:50™ with UNITY 2 are shown in figure 5. Again, full recovery is demonstrated across the volatility range.

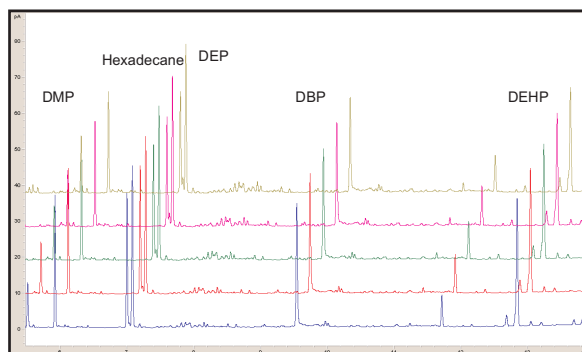


Figure 5: Primary and repeat analyses of phthalate standard, demonstrating quantitative recovery

Summary

Results show that the Markes TD technology, incorporating a main heated valve and backflush desorption of the cold trap facilitates simultaneous analysis of VOC and SVOC compounds - such as those of interest to materials emissions testing. Further that this capability can be validated using the SecureTD-Q quantitative re-collection for repeat analysis facility (see Markes brochure "Validation of Thermal Desorption featuring SecureTD-Q".)

Trademarks

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Applications were performed using the stated analytical conditions. Operation under different conditions, or with incompatible sample matrices, may impact the performance shown.