TDTS 53

Quantitative recovery and method validation of high-boiling SVOCs using TD–GC/MS

Summary

This Application Note demonstrates the excellent performance of UNITY™ 2 and TD-100™ thermal desorbers for the analysis of semi-volatile organic chemicals (SVOCs) from standard solutions by thermal desorption (TD)–GC/MS. It also demonstrates the application and benefit of sample re-collection and analysis (SecureTD-Q™ technology) for simple validation of analyte recovery.

Background to the UNITY 2 and TD-100

Markes' **UNITY 2** thermal desorber has been designed to provide a universal platform compatible with a wide range of applications, including quantitative recovery of semi-volatile compounds up to n-$C_{40/44}$.

For the analysis of multiple samples, the **TD-100**, which incorporates the UNITY 2 and an autosampler in a single module, allows automated sampling and (optional) re-collection of up to 100 samples over the same range of applications.

Figure 1: Markes' UNITY 2 (left) and TD-100 (right) thermal desorbers.

The short, uniformly-heated flow path in both instruments is narrow-bore and is constructed entirely of inert materials, while the patented PTFE valve is embedded in a heated aluminium block to eliminate cold-spots. The flow path is designed to optimise linear gas velocity and ensure efficient transfer of semi-volatiles through the system at practical/moderate gas flow rates both during desorption and optional re-collection.

An optimised combination of quartz packings at the inlet/outlet end of the focusing ('cold') trap, backed up by graphitised carbon black sorbents, facilitates quantitative retention and release of compounds over a wide volatility range. The highest-boiling compounds (*e.g.* 5- and 6-ring PAHs, hydrocarbons above n-C_{36}) are trapped on the low-surface-area quartz beads right at the very front of the trap, and are readily released when the trap is backflushed onto the GC column during secondary (trap) desorption.

UNITY 2 and TD-100 are uniquely versatile TD platforms. The sorbent-packed focusing trap can be filled with up to four different sorbents, ensuring quantitative retention and recovery of compounds over a wide boiling range in a single analysis, *e.g.* n-C_6 to n-C_{40} (see Application Note TDTS 64). The same TD flow path can also be operated at low temperatures, allowing compatibility with thermally labile species such as thiols, CS gas and amines.

Experimental

(a) Hydrocarbon analysis

UNITY 2:

Desorption temp.:	350°C
Desorption time:	10 min
Sorbent tube:	Quartz wool–graphitised carbon black
Trap low:	0°C
Trap high:	370°C
Trap hold:	5 min
Trap:	Quartz–graphitised carbon black
Trap flow during primary desorption:	40 mL/min
Split flow during primary desorption:	0 mL/min
Split flow during secondary desorption:	30 mL/min
Column flow:	3–4 mL/min
Flow path temp.:	210°C

(b) Phthalate analysis

UNITY 2:

Desorption temp.:	350°C
Desorb time:	10 min
Sorbent tube:	Quartz wool–graphitised carbon black
Trap low:	0°C
Trap high:	370°C
Trap hold:	5 min
Trap:	Quartz–graphitised carbon black
Trap flow during primary desorption:	50 mL/min
Split flow during primary desorption:	0 mL/min
Split flow during secondary desorption:	20 mL/min
Column flow:	3 mL/min
Flow path temp.:	210°C

TD-100:
Desorption temp.: 320 °C
Desorb time: 10 min
Sorbent tube: Quartz wool–graphitised carbon black
Trap low: –10 °C
Trap high: 320 °C
Trap hold: 10 min
Trap: Quartz–graphitised carbon black
Trap flow during primary desorption: 50 mL/min
Split flow during primary desorption: 0 mL/min
Split flow during secondary desorption: 50 mL/min
Column flow: 1.2 mL/min
Flow path temp.: 200 °C

(c) PAH analysis

UNITY 2:
Desorption temp.: 350 °C
Desorption time: 10 min
Sorbent tube: Quartz wool–graphitised carbon black
Trap low: 0 °C
Trap high: 370 °C
Trap hold: 5 min
Trap: Quartz–graphitised carbon black
Trap flow during primary desorption: 50 mL/min
Split flow during primary desorption: 0 mL/min
Split flow during secondary desorption: 30 mL/min
Column flow: 3 mL/min
Flow path temp.: 210 °C

TD-100:
Desorption temp.: 300 °C
Desorption time: 12 min
Sorbent tube: Quartz wool–Tenax® TA
Trap low: 30 °C
Trap high: 400 °C
Trap hold: 10 min
Trap: Quartz–graphitised carbon black
Trap flow during primary desorption: 50 mL/min
Split flow during primary desorption: 0 mL/min
Split flow during secondary desorption: 50 mL/min
Column flow: 3 mL/min
Flow path temp.: 210 °C

(d) PCB analysis

UNITY 2:
Desorption temp.: 350 °C
Desorption time: 10 min
Sorbent tube: Quartz wool–graphitised carbon black
Trap low: 0 °C
Trap high: 370 °C
Trap hold: 5 min
Trap: Quartz–graphitised carbon black
Trap flow during primary desorption: 50 mL/min
Split flow during primary desorption: 0 mL/min
Split flow during secondary desorption: 25 mL/min
Column flow: 4 mL/min
Flow path temp.: 210 °C

Results and discussion

To demonstrate the application range of Markes' thermal desorption technology, UNITY 2 and/or TD-100 instruments were used to analyse standard samples of high-boiling hydrocarbons, high-boiling phthalates, polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs).

(a) High-boiling hydrocarbons

2 µL of a liquid standard mixture of hydrocarbons (n-C_6 to n-C_{44}, concentration: 500 ng total hydrocarbon per µL) was injected into a TD tube packed with quartz wool and graphitised carbon black sorbent, and analysed using a standard UNITY 2. The boiling point range of this mixture was ~65 °C to >550 °C. Carryover was evaluated by re-desorbing the sample tube after it had been analysed (Figure 2). Note that the hydrocarbons were not present in equal concentrations (nominal percent concentrations are presented in Table A1 (see Appendix)).

Recovery was tested using Markes' patented SecureTD-Q™ facility. SecureTD-Q was pioneered by Markes in the late 1990s, and allows the split effluent, from both primary (tube) desorption and secondary (trap) desorption, to be re-collected onto a conditioned sorbent tube and used for repeat analysis and method/data validation (see UNITY 2 brochure). Re-collected analytes have, by definition, passed through all the main components of the TD flow path before reaching the conditioned re-collection tube. Therefore, when the re-collection tube is subsequently analysed, any component loss will show up in the repeat data analysis as a deviation from the amount predicted by the split ratio and/or in low recovery relative to other compounds in the standard.

The results from primary and repeat analyses of the least volatile compounds in the standard are shown in Figure 3, together with the amounts expected (calculated from mixture composition details supplied with the standard).

Excellent recoveries (>95%) were observed across the hydrocarbon range, including n-C_{44}, under the conditions specified.

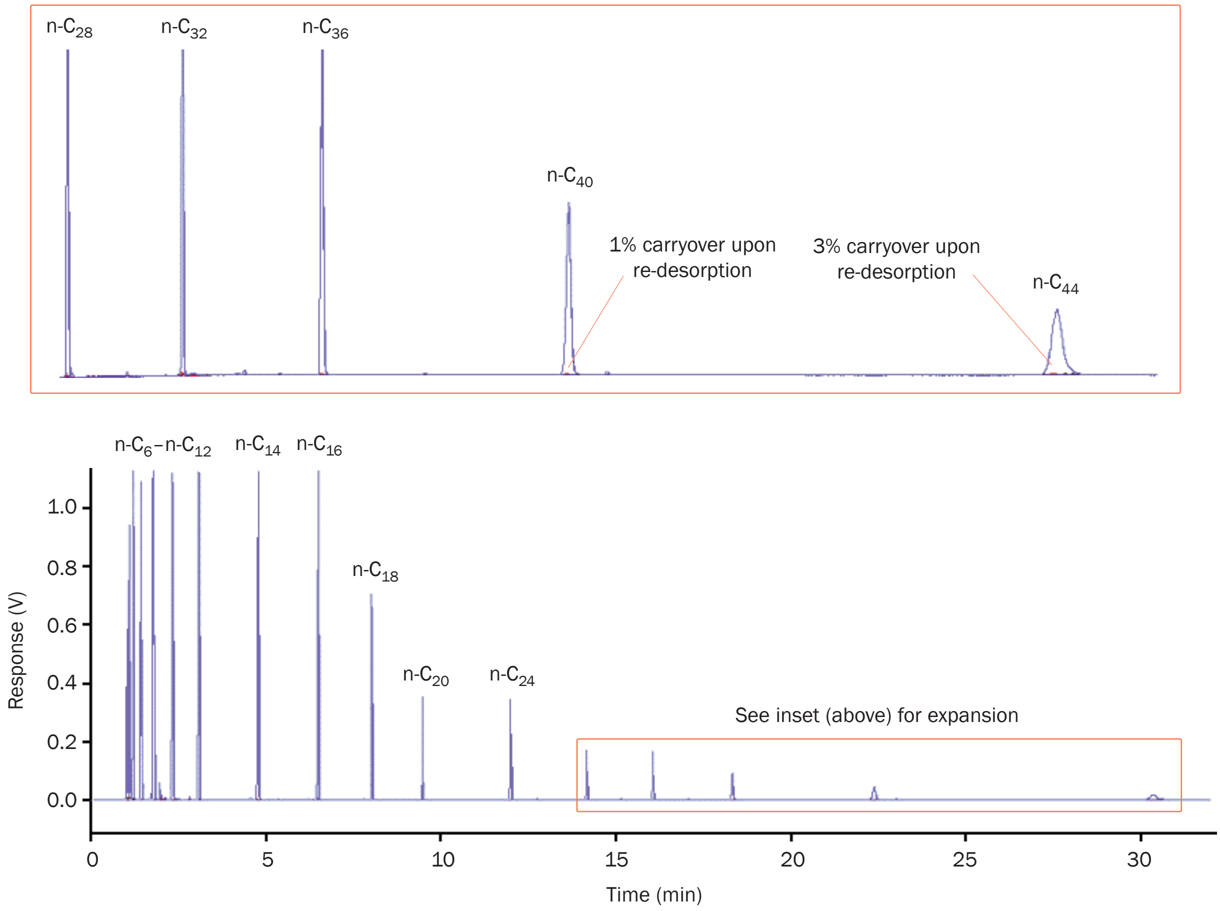

Figure 2: Analysis of 2 µL of a 500 ng/µL n-C$_6$ to n-C$_{44}$ hydrocarbon standard using UNITY 2 (blue trace), and re-desorption of the same tube (red trace) to determine carryover.

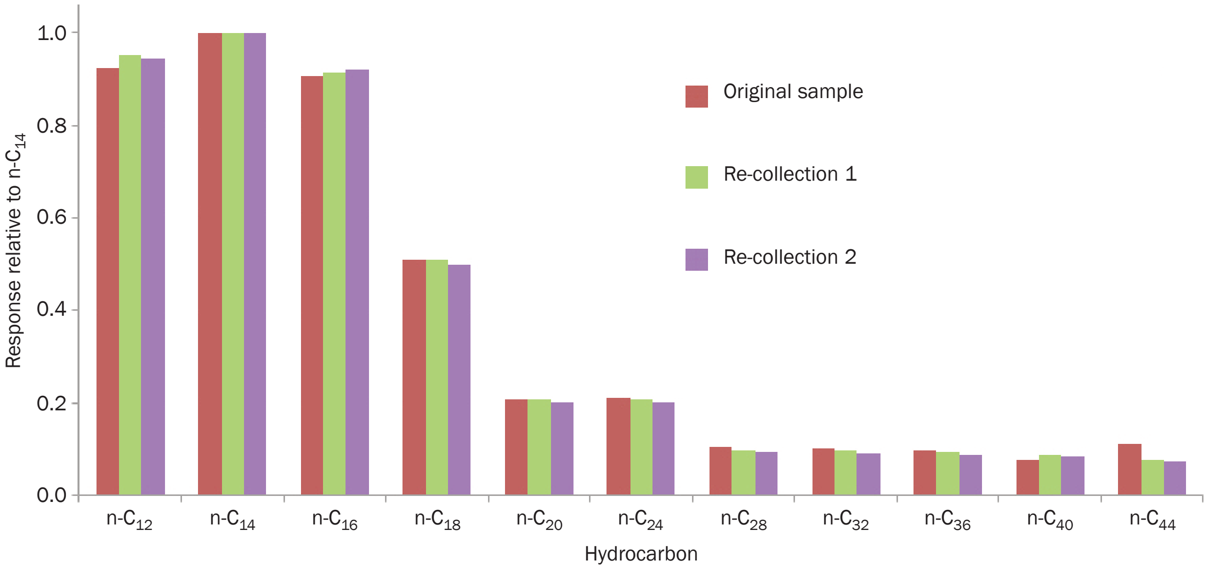

Figure 3: Recovery of a hydrocarbon standard using UNITY 2, demonstrated for the lower-volatility compounds.

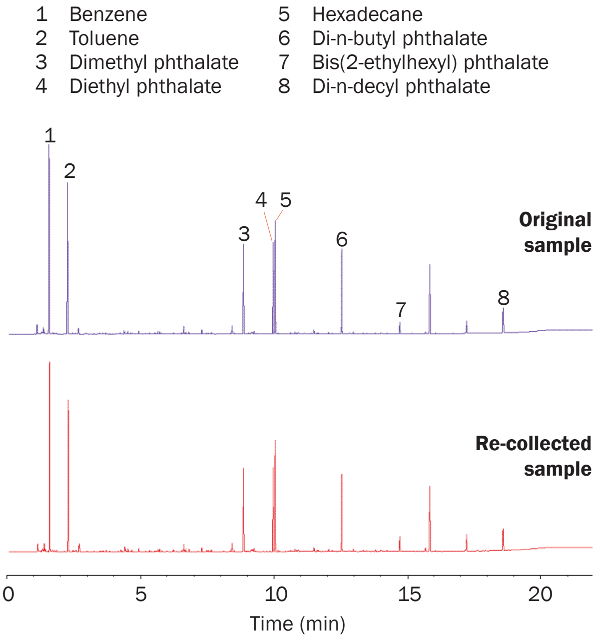

Figure 4: Primary and repeat analyses of a phthalate standard using UNITY 2, demonstrating quantitative recovery.

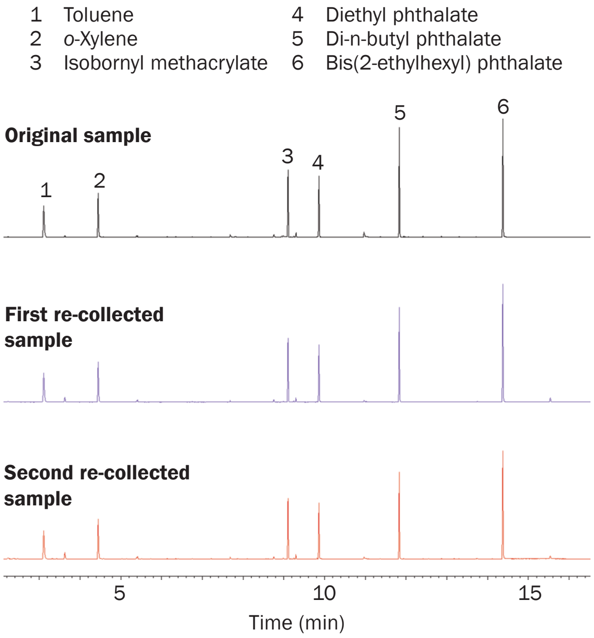

Figure 5: Primary and repeat analyses of a phthalate standard using TD-100, demonstrating quantitative recovery.

(b) High-boiling phthalates

Compounds such as di-n-butyl phthalate (b.p. ~340°C), bis(2-ethylhexyl) phthalate (b.p. ~385°C), di-n-nonyl phthalate (b.p. ~415°C) and di-n-decyl phthalate (b.p. ~450°C) are widely used in industry as plasticisers. Concern over their environmental fate and potential human health effects has led to an increased demand for them to be measured, both in the environment and in emissions from construction products and other materials used indoors. For example, di-n-butyl phthalate, bis(2-ethylhexyl) phthalate, diisobutyl phthalate and benzyl n-butyl phthalate are all listed by the European Commission as SVHCs (substances of very high concern) on the REACH authorisation list[1].

Their polarity and long-chain hydrocarbon tails make phthalates 'sticky' as well as high-boiling. However, UNITY 2 and TD-100 achieve quantitative recovery across the range, as demonstrated in Figures 4 and 5.

(c) Polycyclic aromatic hydrocarbons (PAHs)

PAHs are another group of environmentally significant semi-volatiles. Benzo[a]pyrene (a 5-ring PAH) in particular is recognised as a human carcinogen and a priority environmental pollutant. Anthracene (a 3-ring PAH) is also classed as a substance of very high concern under REACH, together with several associated preparations.

Primary and repeat analysis of a standard containing the higher-boiling 4- to 6-ring PAHs using UNITY 2 with GC/MS (Figure 6) shows quantitative recovery of these high-boiling and sticky compounds through the system.

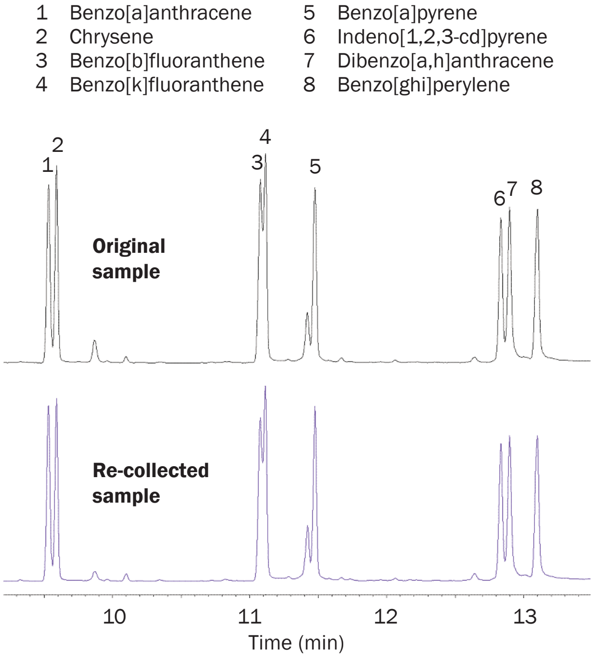

Figure 6: Primary and repeat analyses of a PAH standard using UNITY 2, demonstrating quantitative recovery.

This performance is confirmed by linearity tests on the same group of compounds using UNITY 2 (Figure 7) and TD-100 (Figure 8).

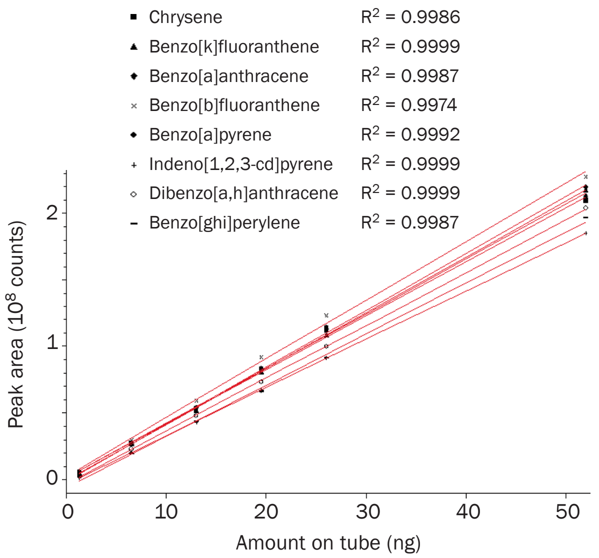

Figure 7: Linearity of compounds from the PAH standard using UNITY 2.

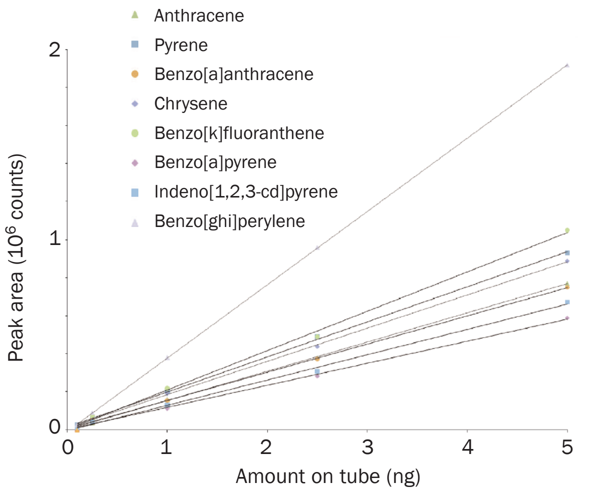

Figure 8: Linearity of compounds from the PAH standard using TD-100.

(d) Polychlorinated biphenyls (PCBs)

PCBs enter the environment *via* contaminated dielectric liquids in capacitors and transformers, various thermal processes and disposal of some electronic components. They are considered persistent and bio-accumulative, leading to increased environmental concern.

Primary and repeat analysis of the PCB standard (Aroclor 1260) was again used to demonstrate quantitative recovery of these high-boiling compounds with Markes' thermal desorption systems (Figure 9).

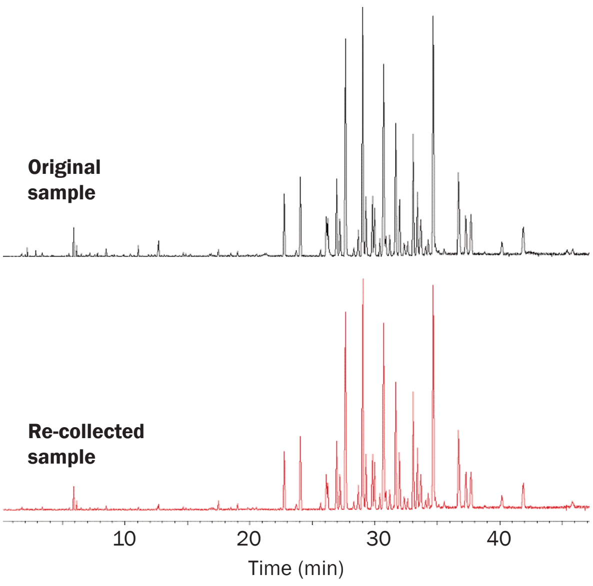

Figure 9: Primary and repeat analyses of a PCB standard (Arochlor) using UNITY 2, demonstrating quantitative recovery.

Conclusions

In this Application Note, we have demonstrated quantitative recovery of high-boiling compounds such as bis(2-ethylhexyl) phthalate and di-n-decyl phthalate, 5- and 6-ring PAHs, PCBs and n-C_{44} hydrocarbons from standard solutions using Markes' standard UNITY 2 and TD-100 thermal desorbers. No operator intervention (for example, changing the flow path or valve) is required for these applications. These systems have also been shown to allow analysis of volatile and semi-volatile compounds in the same run.

This study has also demonstrated the benefits of Markes' unique SecureTD-Q facility for validating compound recovery through the analytical system. More information on this aspect can be found in Application Note TDTS 24 and in the brochures for the UNITY 2 and TD-100 instruments.

It is important to note, however, that in real-world air monitoring applications, SVOCs are commonly split between the vapour and adsorbed/particulate phases. Thermal desorption is primarily used as a tool for analysis of retained vapours. The composition of particulates is usually unknown and may include active and sorptive materials such as soot. Therefore, while recovery should remain high for trapped SVOCs (provided suitable (weak) sorbents were selected for the sampling tube), desorption efficiency from samples which include particulate material will be dependent on the specific nature of the particle matrix and may be compromised.

For more advice on how to minimise particle ingress and selectively sample only the airborne vapour fraction, Markes technical specialists are pleased to offer advice – please contact us at enquiries@markes.com.

References

1. REACH: EC Directive 1907/2006: Registration, Evaluation, Authorisation and restriction of CHemicals

Trademarks

SecureTD-Q™, TD-100™ and UNITY™ are trademarks of Markes International Ltd, UK.

Tenax® is a registered trademark of Buchem B.V., The Netherlands.

Appendix

Hydrocarbon	Proportion of hydrocarbon mixture (weight%)
n-C_6	7.5
n-C_7	5.7
n-C_8	7.5
n-C_9	11.4
n-C_{10}	11.4
n-C_{11}	11.3
n-C_{12}	11.3
n-C_{14}	11.1
n-C_{16}	9.4
n-C_{18}	4.7
n-C_{20}	1.9
n-C_{24}	1.9
n-C_{28}	0.9
n-C_{32}	0.9
n-C_{36}	0.9
n-C_{40}	0.9
n-C_{44}	0.9

Table A1: Composition of the standard hydrocarbon mix.

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