TDTS 24

Overcoming the ‘one-shot’ limitation of thermal desorption by the re-collection of desorbed samples

Summary

In this Application Note, we demonstrate how sample splitting and re-collection (SecureTD™ technology) can overcome the ‘one-shot’ limitation of thermal desorption, providing a powerful tool for method development and validation.

Introduction

The advantages of thermal desorption

Thermal desorption has a number of significant advantages compared to conventional solvent-extraction methods. Most notably, these include:

- Sensitivity
  - Detection limits enhanced by a factor of 10^3–10^4
  - Reliable: 95% or better desorption efficiencies for all VOCs, including polar compounds, compared to 30–80% for most solvent-extraction methods.
- Cost-saving
  - No manual sample preparation, thus reducing the time and cost of each analysis
  - Re-usable tubes: Thermal desorption tubes can be re-used 100–200 times.
- No solvent required
  - No masking of peaks of interest by the solvent
  - No introduction of artefacts/impurities from the solvent
  - Improved laboratory working environment
  - Eliminates a health hazard: CS_2, the most commonly used extraction solvent, is very toxic
  - No solvent disposal costs or expensive air extraction equipment.

The ‘one-shot’ limitation of thermal desorption

Despite these advantages, thermal desorption systems have historically had a significant drawback. This is the so-called ‘one-shot’ limitation – once a sample has been thermally desorbed (heated in a flow of carrier gas), no sample remains for repeat analysis.

In contrast, CS_2 extracts from charcoal tubes can be injected many times, as long as they are kept refrigerated. In some cases has been a significant consideration, over-riding the advantages of thermal desorption.

To address this, Markes UNITY™ and ULTRA–UNITY™ thermal desorption systems have been designed to overcome the one-shot limitation by allowing quantitative re-collection of desorbed samples (SecureTD™ technology).

SecureTD: Split re-collection for repeat analysis

Using any of Markes’ TD systems, samples can be split as they are transferred from the primary sample tube to the focusing (cold) trap, and/or during subsequent transfer from the focusing trap to the analyser. The split flow is directed to either a tube filled with charcoal, to scrub the effluent stream, or to a conditioned sorbent tube for sample re-collection. The same conditioned sorbent tube is used to collect the flow, whether splitting on the inlet to the trap (primary desorption), the outlet to the trap (secondary desorption), or both (see Figures 1 and 2).

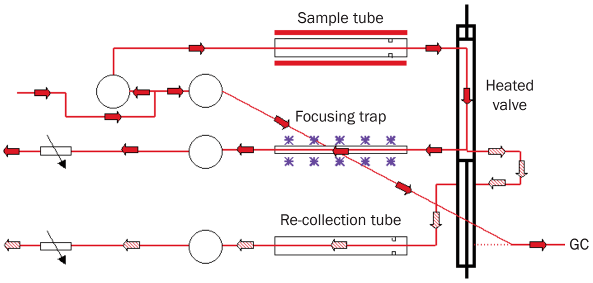

Figure 1: Re-collection during primary (tube) desorption.

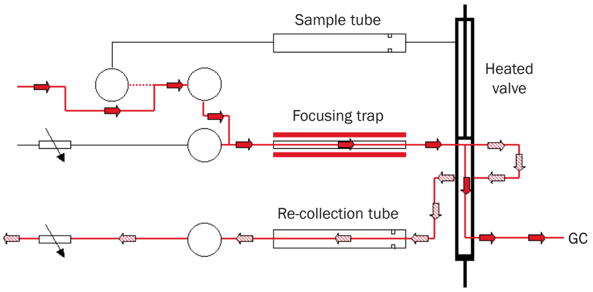

Figure 2: Re-collection during secondary (trap) desorption.

Thermal desorption offers such a large enhancement in sensitivity compared to solvent extraction that it is always possible to redirect a portion of the sample for re-collection without compromising method detection limits. The short length of UNITY flowpath leading to the split re-collection tube is constructed of heated, inert-coated stainless steel tubing to prevent analyte condensation or degradation. A steep temperature gradient inside the re-collection tube ensures quantitative trapping of target analytes over the relatively short re-collection period without condensation or breakthrough. UNITY control software allows exchange of the split re-collection tube inbetween samples without interrupting gas flow to the analyser.

With the automated ULTRA–UNITY system, manual SecureTD can be used for method development/validation or re-collection of critical samples. Alternatively, if automatic re-collection is required for every sample, then the SecureTD function can be automated.

SecureTD: Why re-collect?

There are a number of situations where re-collection of a sample portion would be advantageous:

- Method development/validation
- Erroneous GC parameters: co-elution, detector problems, premature completion of the GC run *etc.*
- Incorrect split conditions – too little or too much sample passed onto column
- Identification of unknowns
- Troubleshooting
- Sample archiving – for critical one-off samples or samples taken for regulatory compliance
- Unique samples, *e.g.* re-collection from on-line/headspace samples.

Test of re-collection performance

The performance of Markes' re-collection technology was tested with a high loading (~1 µg) of toluene. To prepare the standard, 1 µL of a 0.1% (v/v) toluene standard in methanol was introduced to a conditioned Tenax TA tube in stream of pure nitrogen via the Calibration Standard Loading Rig (CSLR).

Analytical conditions

TD:

Sorbent tube:	Packed with Tenax
Focusing trap:	Packed with Tenax and Carbopack B
Carrier gas:	Helium at 14 psi
Column flow:	1.5 mL/min
Desorb flow:	15 mL/min; split flow: 40 mL/min, giving a split ratio of 99 : 1

GC:

Column:	30 m × 0.32 mm × 1 µm film methyl silicone
Tube desorb:	280 °C for 5 min
Focusing trap high:	300 °C for 2 min
Focusing trap low:	–10 °C
Flowpath:	120 °C

The sample was re-collected and analysed four times. Data is presented in Table 1 and in Figure 3.

Analysis	Area counts	Data point (% of previous)	Data point (% of original)
1	643952	–	100
2	638144	99.1	99.1
3	630494	98.8	97.9
4	623338	98.9	96.8
5	616320	98.9	95.7

Table 1: Toluene analysis using re-collection with a 98.9 : 1.1 split ratio.

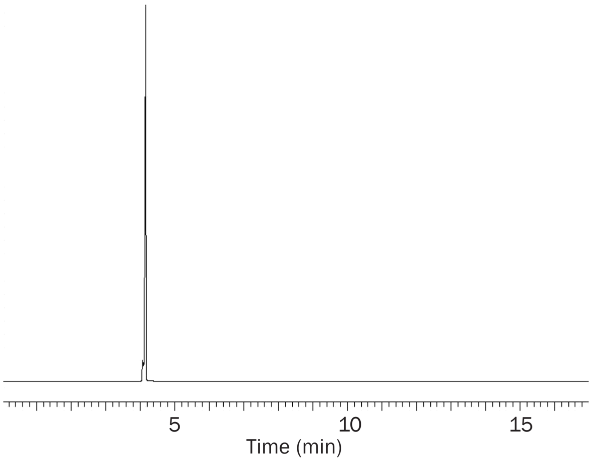

Figure 3: Chromatogram showing analysis of a high loading of toluene.

SecureTD performance was also tested with a low concentration (approximately 170 ng/µL) of a solution of benzene, toluene and *o*-xylene (BTX). 2 µL of the solution was introduced onto a conditioned Tenax tube, as above, and analysed under similar conditions, this time using a split ratio of 21:1. Six re-collections and repeat analyses were carried out, with good correlation being obtained between expected and observed decay (Figure 4).

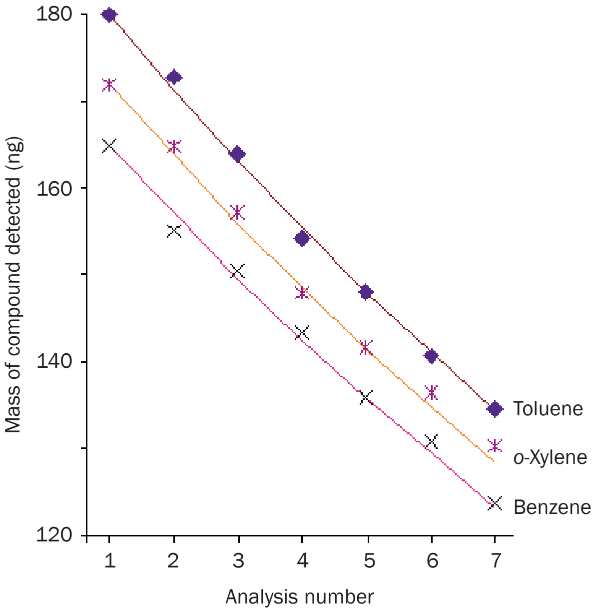

Figure 4: Re-collection and analysis of a BTX solution. The lines indicate the expected decay; points indicate actual data.

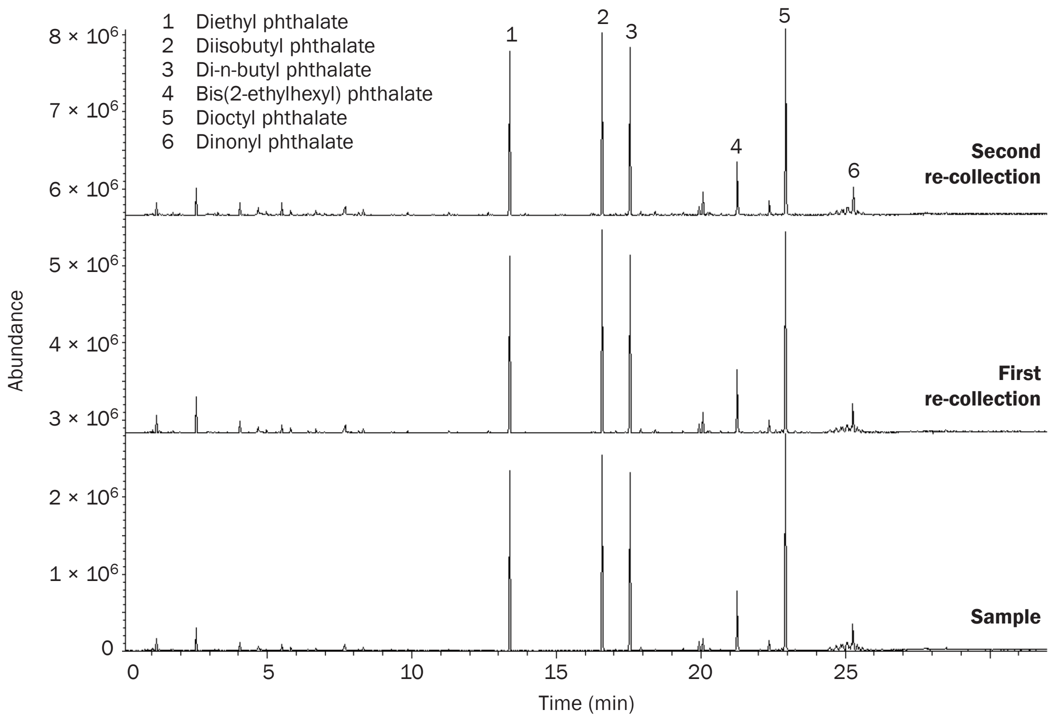

Figure 5: Re-collection of high-boiling compounds.

Application 1: Method validation

A standard solution of six phthalates (high boiling plasticisers) was injected and analysed, with two subsequent re-collection–analysis cycles.

Figure 5 shows how re-collection can be used to validate the quantitative recovery of high-boiling compounds such as dioctyl phthalate and dinonyl phthalate. No bias was observed throughout the sequence of primary and repeat analyses. Blanks run between each of the repeat analyses demonstrate no carryover.

Application 2: Checking for erroneous GC parameters

To test the repeat analysis capability for other demanding applications, a Tenax TA tube was loaded with low-microgram levels of a series of labile, high-boiling organic amines and nitro-compounds by direct injection of a liquid standard. A blank tube was also analysed. Split effluent from the sample was recollected on a conditioned Tenax TA tube and re-analysed. During the first analysis of the standard, the GC run finished prematurely, halfway through elution of 4-aminodiphenylamine, one of five key components. Its relative concentration was determined from analysis of the re-collected sample. Relevant chromatograms are shown in Figure 6.

Analytical conditions

TD:

Focusing trap:	Packed with Tenax TA
Carrier gas:	Helium at 15 psig
Column flow:	~1.5 mL/min
Desorb flow:	15 mL/min; split flow (inlet and outlet): 47 mL/min, giving an overall split ratio of ~130:1

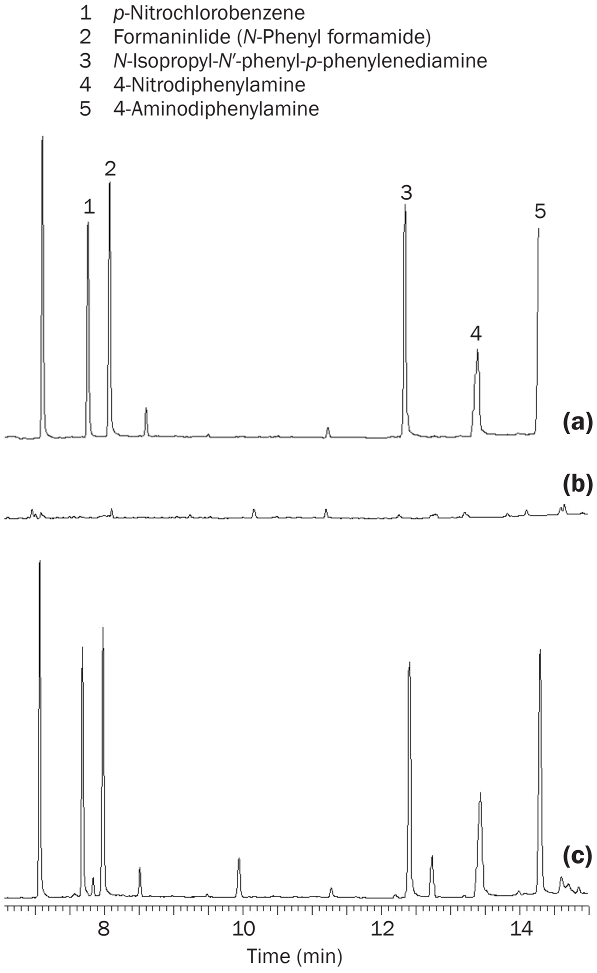

Figure 6: Analysis of a liquid standard containing a series of labile, high-boiling amines and nitro-compounds. (a) First desorption; (b) Subsequent run of blank tube; (c) Subsequent run of re-collected split sample.

GC:

Column:	30 m × 0.25 mm × 0.25 µm film methyl silicone
Tube desorb:	320 °C for 10 min
Flowpath:	200 °C
Focusing trap high:	300 °C for 5 min
Focusing trap low:	–10 °C
GC oven:	50 °C for 2 min, 30 °C/min to 250 °C for 3.5 min, 15 °C/min to 280 °C for 0 min (run 1) or 1 min (subsequent analyses)

Application 3: Troubleshooting

A solution of high molecular weight hydrocarbons (C_{28}, C_{32}, C_{36} and C_{40}), was loaded onto pre-conditioned sorbent tubes packed with quartz wool and Tenax TA. Each compound was nominally present at a similar concentration. However, the C_{36} and C_{40} peaks in particular were much smaller than expected. It was unclear at first whether this was an instrumentation problem, or an issue with the sample solution. The sample was re-collected and re-analysed three times, and no bias (*i.e.* no loss of n-C_{36} or n-C_{40}) was observed. This showed higher-boiling components were at a lower concentration than the more volatile species. It was later found that the high boilers were dropping out of solution before they could be loaded onto the primary sorbent tube.

Summary

This work illustrates the significant benefits of re-collection technology, both for overcoming the one-shot limitation of traditional thermal desorption, and as a powerful tool for method development and validation.

This innovation allows thermal desorption, with all its inherent advantages of cost, sensitivity and safety, to be used for a wide range of environmental health & safety applications.

Acknowledgement

Application 2 was carried out in collaboration with Solutia UK Ltd and Flexsys Ltd. We gratefully acknowledge their contribution to the work.

Trademarks

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Version 5
July 2012