

Application of SecureTD[™] for Re-collection and Repeat Analysis of Desorbed Samples

Overcoming the one-shot limitation of thermal desorption

Technical Overview

Introduction

Thermal desorption (TD) has a number of very significant advantages versus conventional solvent extraction methods. These include:

- Increased sensitivity
 - Detection limits enhanced by a factor of 10^3 to 10^4 .
 - Higher sample recovery. A 95% or better desorption efficiency for all volatile organic compounds (VOCs), including polar compounds, vs. 30% to 80% for most solvent extraction methods.
- Cost savings
 - No manual sample preparation required, thus reducing time and cost per analysis.
 - Reusable TD tubes (100 to 200 times).
- No solvent required
 - No masking of peaks of interest by the solvent.
 - No introduction of artifacts/impurities from the solvent.
 - Improved laboratory working environment (with elimination of a health hazard). Carbon disulfide (CS_2), the most commonly used extraction solvent, is very toxic.
 - No solvent disposal costs or expensive air extraction equipment required.

However, once a sample has been thermally desorbed (that is, heated in a flow of carrier gas), no sample remains for repeat analysis. In contrast to this, CS₂ extracts from charcoal tubes can be injected many times, as long as they are kept refrigerated. In some cases this can be a significant consideration, overriding the many other advantages of TD. Markes International TD systems, including UNITY[™] (single tube thermal desorber) and ULTRA-UNITY[™] (100-tube automated thermal desorber), are the only thermal desorbers with SecureTD[™]. SecureTD is designed to overcome the one-shot limitation of conventional TD by using quantitative re-collection for repeat analysis.

SecureTD: Split Re-collection for Repeat Analysis

UNITY, The Markes International platform thermal desorber, was specifically designed to overcome the one-shot limitation of conventional analytical TD by harnessing the idea of split re-collection pioneered by Dr Jan Kristensson [1]. Using any of Markes International TD systems, samples may be split as they are transferred from the primary sample tube to the focusing trap and/or during subsequent transfer from the focusing trap to the analyzer. 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), 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.

TD offers such a large enhancement in sensitivity versus solvent extraction that it is invariably possible to redirect a portion of the sample for re-collection without compromising method detection limits. The short length of the UNITY flow path leading to the split re-collection tube is constructed of inert Silcosteel[™] tubing, heated 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 in between samples without interrupting gas flow to the analyzer. An automated ULTRA-UNITY system may use manual SecureTD for method development/validation or re-collection of critical samples. If automatic re-collection is required for every sample, then the SecureTD function may be automated using an AutoSecure™ system. See Figure 3.



Figure 3. AutoSecure system.

Laboratory Test of Re-collection Performance

The performance of SecureTD was tested with a high loading (~1 μ g) of toluene. To prepare the standard, 1 μ L 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 standard loading rig (C-CSLR).

Analytical conditions:

Tenax tube				
Tube desorb:	280 °C for 5 min			
Flow path:	120 °C			
Cold trap packed with Tenax and Carbopack				
Cold trap low:	−10 °C,			
Cold trap high:	300 °C for 2 min			
Helium carrier gas:	14 psi (giving a column flow of 1.5 mL/min)			
Desorb flow:	15 mL/min, Split flow: 40 mL/min giving a split ratio of 99:1			
GC column:	$30 \text{ m} \times 0.32 \text{ mm} \times 1 \text{ mm}$ film methyl silicone			

The sample was re-collected and re-analyzed four times.

Recovery data are presented in Table 1. Figure 4 shows a chromatogram from a recovered sample and a bar chart for the toluene recoveries over the four re-collection and reanalysis steps.

Table 1.	Analysis of Toluene Using Re-collection with		
	98.9 : 1 Split Ratio		

Analysis number	Area counts	Data point as a % of previous	Data point as % of original
1	643952		100.0
2	638144	99.1	99.1
3	630494	98.8	97.9
4	623338	98.9	96.8
5	616320	98.9	95.7



Figure 4. Chromatogram and bar chart of relative peak area % on subsequent "saved" samples.

SecureTD performance was also tested with a low concentration (approximately 170 ng/ μ L) benzene, toluene, o-xylene (BTX) solution. Two μ L of the solution was introduced onto a conditioned Tenax tube, as above, and analyzed under similar conditions - this time using a split ratio of 21:1. Six re-collection, repeat-analyses were carried out and showed good correlation between the expected and observed decay. See Figure 5.

SecureTD: Why Re-Collect?

There are a number of situations where re-collection of a portion of the sample is advantageous.

- Method development/validation
- Erroneous GC parameters, for example, co-elution, detector problems, premature completion of the GC run, etc.
- Incorrect split conditions, including 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, for example, re-collection from online/headspace samples



Figure 5. Re-collection and re-analyses of BTX solution.

Method Validation - Validation of Quantitative Recovery of High Boiling Compounds

A solution of the following phthalates (high boiling plasticizer compounds) was analyzed with re-collection:

DEPDiethyl phthalateDMPPDimethyl propyl phthalateDBPDibutyl phthalateDEHPDiethyl hexyl phthalateDOPDioctyl phthalateDNPDinonyl phthalate

Figure 6 shows how SecureTD re-collection was used to validate the quantitative recovery of high boiling compounds such as dioctyl and dinonyl phthalate. No bias was observed throughout the sequence of primary and repeat analyses. Blanks run between each of the repeat analyses demonstrated no carryover.



Figure 6. Re-collection of high boiling compounds.

Erroneous GC Parameters - Evaluation of Repeat Analysis for Labile, High Boiling Analytes

To test the repeat analysis capability for other demanding applications, a Tenax TA tube was loaded with low μ g levels of a series of labile, high boiling organic amines. See Table 2. The loaded tube was prepared in the South Wales laboratory of Solutia UK Ltd. using direct injection of a liquid standard. A blank tube was also analyzed. Split effluent from the sample was re-collected on a conditioned Tenax TA tube and re-analyzed. During the first analysis of the standard, the GC run finished prematurely, half-way through elution of 4A. Its relative concentration, however, was determined from analysis of the re-collected sample. Relevant chromatograms are shown in Figures 7 to 9. Analytical conditions were set as follows:

Tube desorb:	320 °C for 10 min			
Flowpath:	200 °C			
Cold trap packed with Tenax TA				
Cold trap low:	−10 °C,			
Cold trap high:	300 °C for 5 min			
Helium carrier gas at	15 psig giving a column flow of ~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			
GC column:	$30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \text{ mm}$ film methyl silicone			
GC oven:	50 °C for 2 min, 30 °C/min to 2 50 °C for 3.5 min, 15 °C/min to 2 80 °C for 0 min (run 1) or 1 min (subsequent analyses)			

Table 2. Repeat Analysis of Amines

		Peak area	Peak area
Compound name	Abbr	Run 1	Repeat analysis
Para-nitrochlorobenzene	PNCB	3225	3583
Formaninlide	FAN	4177	4352
N-isopropyl, N'-phenyl paraphenylenediamine	1PPD	4729	4950
4-Nitrodipheylamine	4N	3104	3274
4-Aminodiphenylamine	4A	4967*	5283

*Extrapolated from rpt analysis







Figure 8. Chromatogram of blank tube desorbed after liquid standard - showing no system carryover.



Figure 9. Chromatogram of re-collected split sample.

Troubleshooting

A solution of high molecular weight hydrocarbons (C28, C32, C36, and C40) was loaded onto preconditioned sorbent tubes packed with quartz wool and Tenax TA, then analyzed.

Each compound was nominally present at a similar concentration; however, the C36 and C40 peak 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 reanalyzed three times and no bias, that is, no loss of n-C36 or n-C40, was observed. This showed that higher boiling components were in fact at a lower concentration than the more volatile species, and it was later determined that the high boilers were dropping out of solution before they could be loaded onto the primary sorbent tube. See Figure 10.



Figure 10. Stacked chromatograms of successively re-collected high molecular weight hydrocarbons.

Summary

This work illustrates the significant benefits of SecureTD, both for overcoming the one-shot limitation of traditional TD, and as a powerful tool for method development and validation. This innovation should allow TD, with all its inherent advantages of cost, sensitivity, and safety, to be used for all relevant environmental health and safety applications.

Acknowledgement

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Reference

1. J. Kristensson, Thermal desorption: A multi-shot technique, Stockholm Sweden: University of Stockholm; 1987.

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