MARKES international

TDTS

Thermal Desorption Technical Support

Note 39: Analysis of semi-volatile phosphorus pesticides using Mi™ thermal desorption systems - Demonstration of method validation using SecureTD™

Keywords:

'one shot', repeat analysis, phosphorus pesticides, split ratio, method validation

Introduction to SecureTD™- Re-collection for repeat analysis

During the process of thermal desorption (TD) organic analytes are extracted by heating the sample or sorbent bed in a stream of inert (carrier) gas. The desorbed compounds are then transferred to the analytical system in the carrier gas stream as a narrow, concentrated band of vapour. The process is readily automated and allows complete (100%) transfer of target analytes from the sample to the analytical system thus greatly enhancing sensitivity versus conventional solvent extraction methods. These advantages have made TD-GC (/MS) the method of choice for most environmental applications and other trace organic monitoring work. However, TD technique has historically been limited by its 'one shot' nature *i.e.* once a sample has been thermally desorbed it is completely used up and therefore lost.

SecureTD is a unique feature of Markes International Limited's thermal desorption systems which overcomes this 'one shot' limitation. It allows re-collection of a quantitative aliquot of sample for repeat analysis, sample archiving or third party analysis. An illustration of the sample flowpath within UNITY is shown in Fig 1. The short section of desorber flowpath connecting the main valve to the re-collection tube is a mirror image of that connecting the sample tube to the main valve during primary (tube) desorption. Quantitative, unbiased data, generated from a sample re-collected in this way thus shows unequivocally that sample is passing through the desorber flow path without adverse effects. Any impact/bias that the system was having on the sample would necessarily be accentuated by an extended run through the system (*i.e. en route* from the valve to the re-collection tube) and/or by a second pass through the system during repeat analysis. This means that SecureTD is also a convenient tool for the validation of TD methods and data.

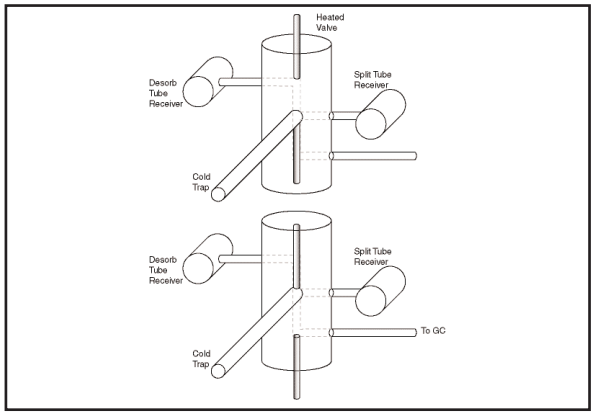

Figure 1: Schematic of the sample flowpath within UNITY

Sample

Two glass tubes (A and B) packed with Tenax TA™ were received pre-loaded with replicate 240 - 250 ng amounts of each of the following pesticides:

Dichlorvos	Etrimfos
Methacrifos	Pirimifos-Methyl
Diazinon	Fenitrothion
Phosphamidon	Malathion
Chlorpyrifos-Methyl	Chlorpyrifos

The tubes had been prepared from a liquid standard containing the pesticides in cyclohexane solvent, which was loaded onto the tubes in a stream of carrier gas.

Analytical conditions

UNITY TD conditions

Prepurge:	1 minute at ambient temperature (split on 22 ml/min and trap in line)
Sample tube Desorption:	280°C for 10 mins (no split)
Desorb flow:	25 ml/min
Flowpath:	200°C
Carrier gas pressure:	24 psi
Cold trap:	packed with quartz wool and Tenax TA™
Trapping temperature:	-15°C
Trap desorb:	300°C for 5 minutes. Maximum heating rate. (Split on. 22 ml/min flow)
Split ratio:	~10:1

GC conditions

GC:	Agilent 6890
Column:	Methylsilicone 30 m x 0.25 mm I.D. x 0.25 µm phase
Program:	Start 60° C (0.5 mins) up to 100°C (rate 40°C/min) to 200°C for 2 mins (rate 5°C/min)
Column flow:	~2 ml/min

Detection

Detector:	Agilent 5973MSD
AUX2 transfer line:	280°C
MS source:	230°C
MS quad:	150°C
SCAN mass range:	45 to 350 AMU
SIM:	2-12 mins: masses 109, 185, 208, 240 12-17.5 mins: masses 304, 179, 292, 277, 264, 127, 286,288 17.5 mins - end: masses 290, 276, 260, 277, 173, 158, 314, 197

Method and discussion

Sample tube A pre-loaded with the pesticide sample was analysed using the conditions shown and with the MS in SCAN mode. Figure 2 shows the Total Ion Chromatogram (TIC) SCAN result for this tube.

Tube B containing a replicate loading of pesticides, was then also desorbed using the same conditions but with the MS in SIM mode (see above for selected masses) (figure 3). During the desorption of tube B, all the split effluent was re-collected onto the desorbed/conditioned tube A. The re-collected analytes from tube B were then redesorbed in SCAN mode as above and the result shown in figure 4. A blank of Tenax tube A obtained by analysing it again, immediately after desorption of the re-collected analytes, is shown in figure 5. The complete lack of artifacts or carryover confirms complete desorption of all target compounds under the analytical conditions used. Comparison of both the original TIC SCAN of tube A and that of the re-collected analytes from tube B is shown in figure 6 on the same scale.

A comparison of peak areas obtained for each component from tube A and the repeat analysis of tube B is shown in Table 1. Note that as the split ratio used was ~10:1, peak areas for the re-collected sample B, should be approximately 10% lower than those obtained from the analysis of tube A. Minor discrepancies in the data are primarily due to the fact that the re-collected sample was from a second (supposedly replicate sample) tube B, not tube A itself. Also, the analytical conditions used were not optimised for the application, but were set as required by the third party laboratory concerned.

The presence of large quantities of solvent in the primary analysis of both tubes (see figure 2), and the fact that all the peaks were significantly overloaded, indicates that a higher overall split ratio and higher focusing temperature (+30°C to selectively eliminate the solvent) would be required for optimum quantitative performance.

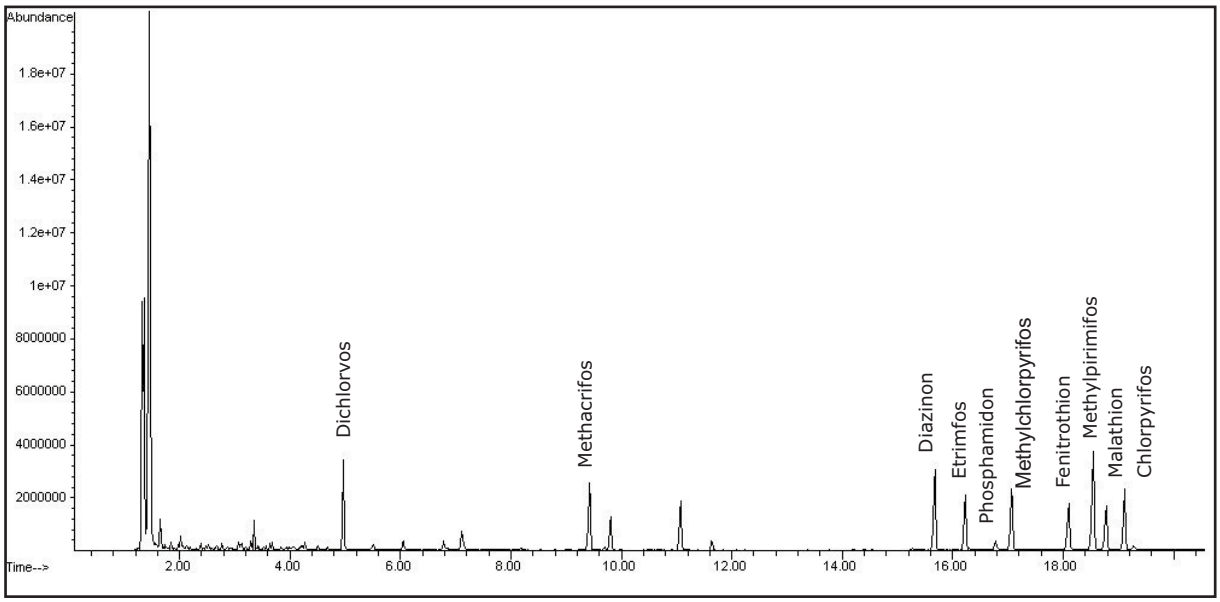

Figure 2: TIC SCAN chromatogram of tube A showing high solvent levels

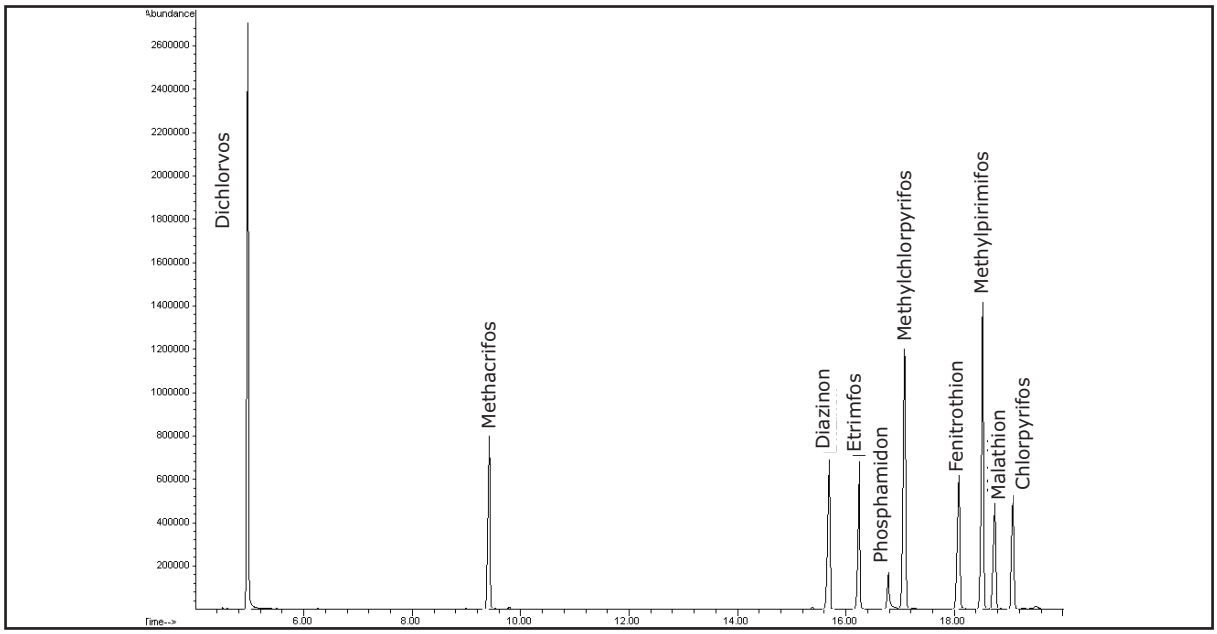

Figure 3: SIM Chromatogram generated from tube B

This said, the deviation of the actual result from re-collected Tube B to that predicted from the original data from Tube A is well within the normal uncertainty of air monitoring methods.

Summary

This work demonstrates the compatibility of Markes International desorption systems with respect to quantitative performance with reactive, semi-volatile compounds such as phosphorous pesticides. The system flowpath is short, narrow-bore, uniformly heated and constructed from inert compounds such as Silcosteel® tubing, quartz and fused silica, allowing the compounds to transfer quantitatively through the desorption system and into the GC analyser. The data also illustrate the utility of SecureTD™ as a tool for TD method validation.

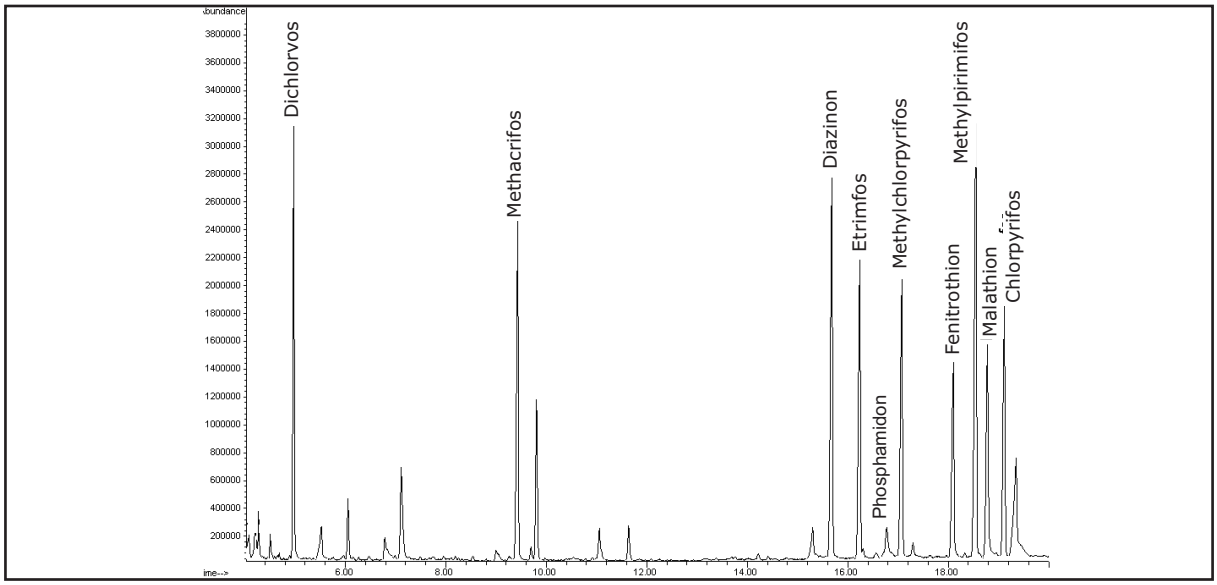

Figure 4: TIC SCAN chromatogram for analytes re-collected from tube B

Figure 5: Blank chromatogram generated by a second desorption of tube A immediately after it was used for analysis of the analytes re-collected from tube B

Trademarks

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

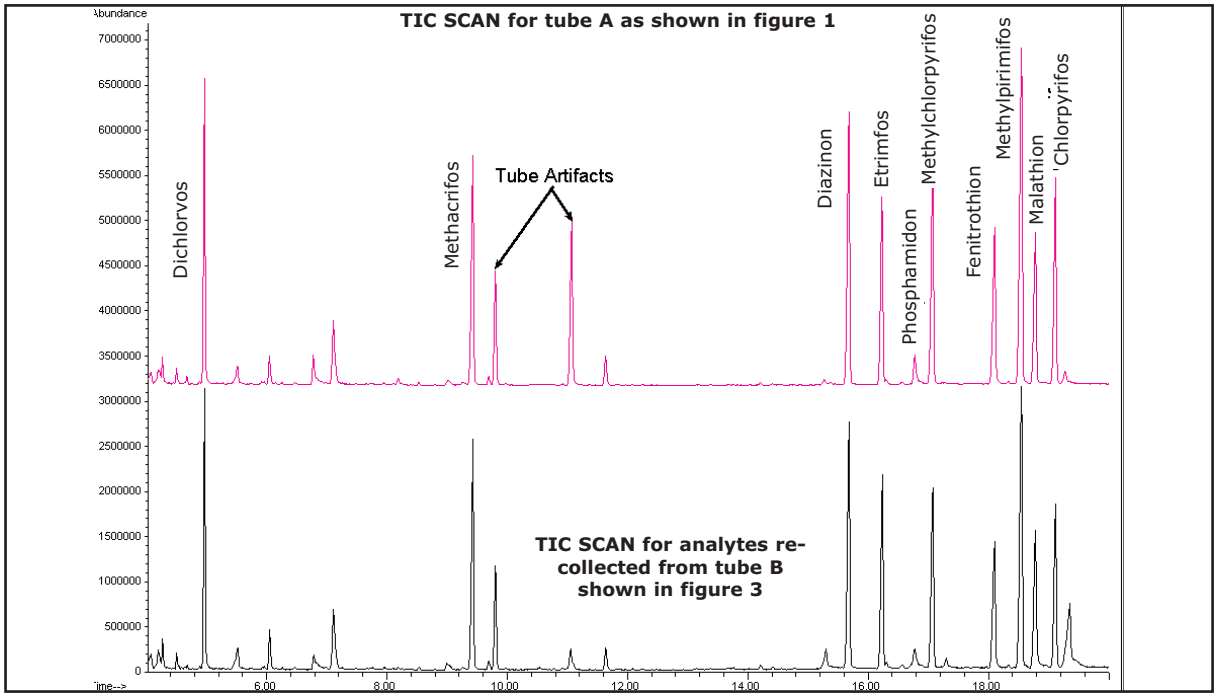

Figure 6: TIC SCAN from tube A compared with that of the recollected analytes from tube B

Compound	Peak area from tube A desorption (x 10^6)	Peak area from desorption of analytes re-collected from tube B (x 10^6)	% Difference (B to A)
Dichlorvos	59.117	54.478	-7.8
Methacrifos	65.581	60.508	-7.7
Diazinon	82.538	73.982	-10.4
Etrinfos	53.684	56.396	+5.1
Phosphamidon	10.878	10.531	-3.2
Chlorpyrifos-Methyl	64.865	56.114	-13.5
Fenitrothion	51.629	42.486	-17.7
Pirimifos-Methyl	113.887	92.305	-19.0
Malathion	47.905	47.735	-0.4
Chlorpyrifos	58.576	49.784	-15.0

Table 1: Comparison of peak areas for the two analyses