TDTS 44

The analysis of free-VX from sorbent tubes at low and sub-nanogram levels

Summary

This Application Note demonstrates measurement of free-VX (*i.e.* underivatised VX) at the sub-nanogram level using a standard non-passivated UltrA-UNITY™ automated thermal desorption system, in conjunction with GC/FPD. Calibration using 0.5–10 ng standards shows a linear response, with good stability from two datasets separated by a period of 2½ weeks.

Preliminary investigations of trace levels of free-VX (45 pg) were also carried out successfully.

Introduction

VX (S-[2-(Diisopropylamino)ethyl] *O*-ethyl methylphosphonothioate) is a particularly dangerous nerve agent. It is relatively high-boiling (b.p. 298°C) and vapour-phase concentrations under ambient conditions are extremely low.

In view of the extreme toxicity of this compound, limit levels are reviewed regularly. The current recommended occupational (workplace) limit (WL) level (based on an 8-hour exposure) is 0.01 µg/m^3, and the current recommended General Population Limit (GPL) level is 0.003 µg/m^3. On the basis of a 12-hour sample at 500 mL/min, the masses of VX that would be collected at these limit levels are 3.6 ng and 1.08 ng respectively.

The most sensitive monitoring methods for vapour-phase organics are invariably based on pumped sampling of air through a sorbent tube, allowing the target compounds to be concentrated from a large volume. This is then followed by two-stage thermal desorption (TD)–GC(MS) analysis (*i.e.* a standard 'DAAMS'-type procedure). However, the low vapour pressure and reactivity of VX have made it almost impossible to measure at low levels using conventional thermal desorption apparatus, without first derivatising it and/or undertaking extensive system passivation. Furthermore, neither of these approaches have proved to be completely satisfactory, with issues relating to system stability and incomplete recovery in both cases.

Figure 1: Markes' UltrA-UNITY system for automated thermal desorption.

Markes' UltrA-UNITY (Figure 1) is an automated TD platform with capacity for up to 100 tubes and incorporating an electrically-cooled focusing trap for optimum concentration enhancement. It is compliant with US EPA Method TO-17 for monitoring vapour-phase organic compounds in ambient air.

The system is compatible with glass, stainless steel or inert-coated stainless steel tubes, which are kept sealed on the autosampler both before and after desorption. The thermal desorber incorporates a stringent, no-flow ambient-temperature leak test of each sample prior to analysis, which helps ensure data quality and preserves the integrity of failed tubes.

The two key features of the standard UltrA-UNITY system that enable it to analyse free-VX are:

- A short uniformly-heated flow path constructed of inert materials
- A custom-packed, electrically-cooled focusing trap that desorbs in backflush mode at rates up to 100°C/s to release analytes in ~200 µL of vapour at flows down to 2–3 mL/min.

Experimental

Optimum analytical conditions were found to be:

TD:

Tubes:	Inert-coated stainless steel, packed with 200 mg Tenax® TA
Tube desorption:	300 °C for 8 min
Desorption flow:	80 mL/min; no split
Flow path:	200 °C
Focusing trap:	Chemical agent trap (U-T10CW)
Trapping temp.:	20 °C
Trap desorption:	300 °C for 3 min (no split)
Carrier gas:	He, 30 psi, EPC-controlled

GC/FPD:

Column:	30 m × 0.32 mm × 0.25 µm film HP-5
Oven:	60 °C (0 min), 20 °C/min to 250 °C (5 min)
Detector temp.:	250 °C
Detector gas flows:	H_2: 150 mL/min; Air: 110 mL/min; N_2: 55 mL/min

Results and discussion

1. Linearity and precision at low nanogram levels

Standard solutions of VX in methanol were introduced onto the sampling end of Tenax TA tubes in a 80 mL/min flow of pure helium using a Calibration Standard Loading Rig (CSLR™). The tubes were left connected to the rig for three minutes, thereby purging the bulk of the methanol solvent from the tube before analysis.

Calibration of VX was carried out with levels ranging from 0.5 ng to 10 ng. Replicate injections were carried out at each of the four levels. Repeat desorption of the highest (10 ng) standard showed <0.3% carryover, and excellent peak shape was obtained at all levels (Figures 2 and 3). At the 10 ng level, 10 replicate analyses gave an RSD of just over 4%.

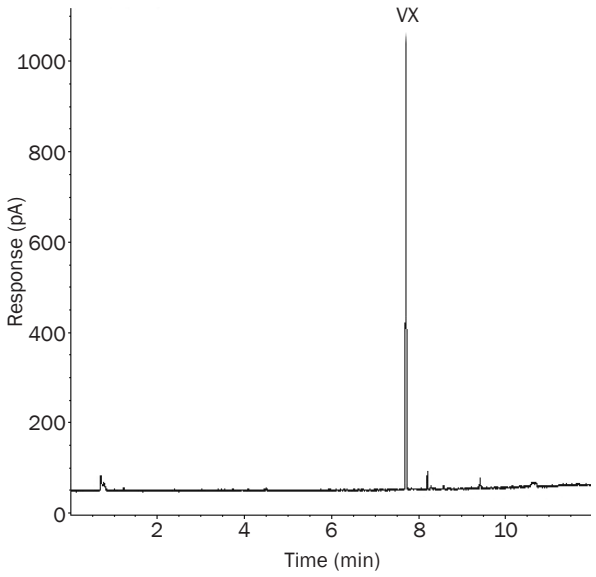


Figure 2: Entire chromatogram obtained from the splitless analysis of 0.5 ng VX.

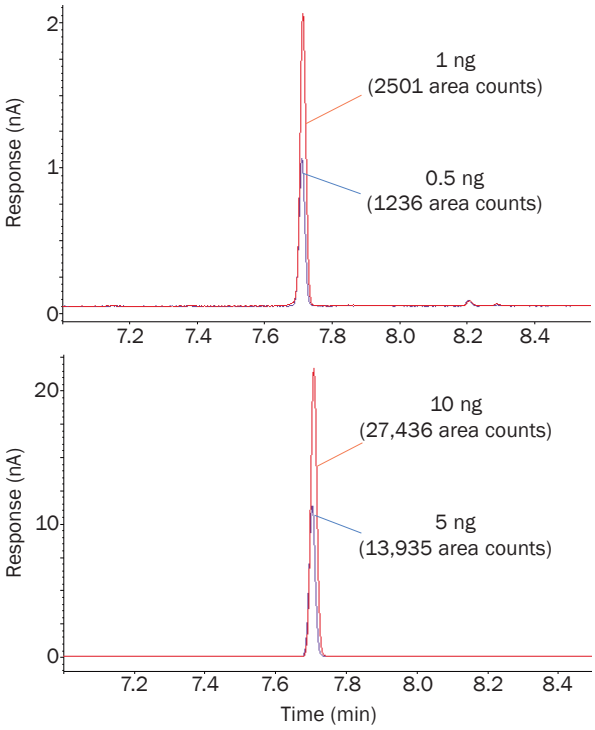
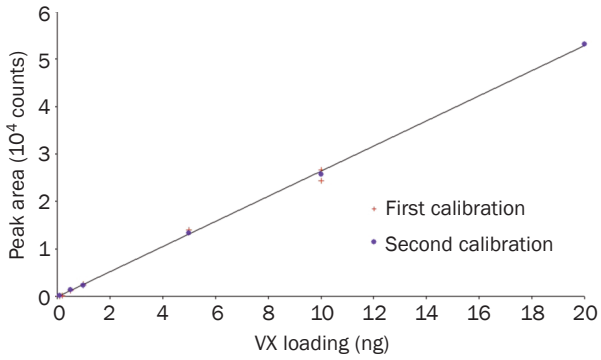


Figure 3: Expanded chromatograms for the analysis of free-VX at four levels, showing Gaussian peak shape in each case. The area count for the 10 ng sample is an average of 10 runs (RSD = 4.2%).

The calibration data show good linearity of response over this range (Figure 4), and replicates at 0.5, 1.0 and 5 ng show good agreement at each level.

To check data stability, the calibration was repeated 2½ weeks later at the 0.1, 0.5, 1, 5, 10 and 20 ng levels (Figure 4).



VX loading (ng)	Peak area	
	First calibration	Second calibration
0.1	–	102
0.5	1286; 1236	1381
1	2501; 2261	2274
5	13,935; 11,122	13,359
10	24,356; 26,685	24,749
20	–	53,155

Figure 4: Results from two calibrations of free-VX, performed 2½ weeks apart, presented in graphical and tabular form.

This second set of calibration data also extends the concentration range of the original data in both directions. The excellent stability demonstrated over this timeframe is a clear indication of system inertness and robustness.

The linearity of the calibration curve and good replicate precision obtained at levels down to 0.5 ng is encouraging, given that 0.5 ng of free-VX is the mass that would be collected from 12 hours' sampling at 500 mL/min at an atmospheric concentration of half the current GPL.

2. Trace-level analysis

Low levels (45 pg) of VX were analysed under the same conditions as previously, and the RSD and S/N ratio calculated. Early results gave peak area counts for five runs of 52.1, 52.55, 58.3, 54.2 and 58.7, with an RSD of 5.69%.

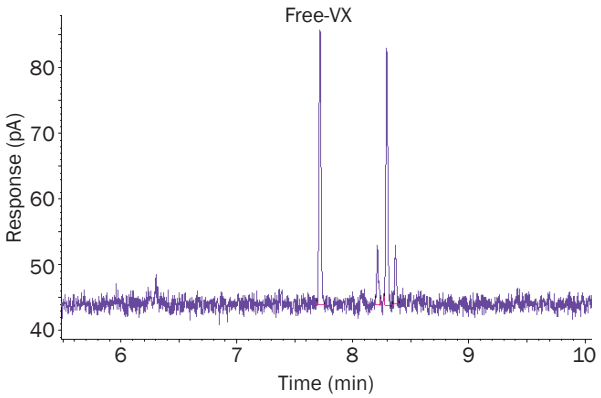


Figure 5: Analysis of 45 pg of free-VX.

Figure 5 shows a typical chromatogram of 45 pg of free-VX, and indicates a sharp, readily integrated peak, with a mean S/N ratio of 10:1. This represents the mass of free-VX that would be collected when monitoring at $^{1}/_{24}$th of the GPL.

3. Use of re-collection to assist system validation

A secondary series of tests were performed on 50 ng loadings of VX using similar analytical conditions to those outlined above but with a sample split ratio of 5:1 (20%) during secondary (trap) desorption.

In this part of the study, we used the SecureTD-Q™ feature of the UNITY thermal desorber – the ability to quantitatively re-collect the split portion of a sample onto an identical sorbent tube for repeat analysis. To validate this process, the peak areas obtained from a sequence of re-collections and repeat analyses of a single sample can be compared with that predicted from the split ratio. Any significant deviation between the actual and predicted responses would indicate that losses are occurring somewhere in the analytical system. On the other hand, a close match confirms that recovery of the analyte through the entire analytical system is good. If required, the SecureTD-Q feature can be fully automated to overcome the traditional one-shot limitation of thermal desorption.

The peak area obtained from the 50 ng sample of free-VX split with a ratio of 5:1 (see Table 1) was almost identical to that obtained from the 10 ng samples run earlier (see Figure 4). Data from the sequence of repeat analyses of this sample indicate ~90% recovery of VX through the analytical system.

	VX peak area	Proportion of expected recovery (%)
Original sample	23,869	–
First re-collection	16,617	87.0
Second re-collection	12,041	90.6
Third re-collection	886	92.2

Table 1: Results from sample re-collection and analysis (using a 5:1 split each time) from a single 50 ng sample of free-VX.

Acknowledgements

This work was carried out in collaboration with scientists from the Chemical Analysis & Detection Laboratory at DSTL, Porton Down, UK.

Trademarks

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

Version 5
December 2012