Thermal Desorption Technical Support

Note 63: Using the TT24-7 with Twin Electrically-Cooled Focusing Traps for Continuous Monitoring of Trace Level Toxic Chemicals (e.g. Chemical Warfare Agents) in Air

Keywords

airborne exposure limit (AEL), general population limit (GPL), preconcentration, demilitarisation, free-VX

Summary

A new (transportable) thermal desorption system (TT24-7) has been developed by Markes International Ltd, which enables continuous online sampling and pre-concentration of airborne chemical warfare agents. The enriched vapour sample is subsequently analysed using gas chromatography (GC), GC with mass spectrometry (GC/MS), or direct MS technology. Continuous sampling is essential where target compounds are extremely toxic. Chemical warfare agents (CWA) are key examples of such compounds and require 100% monitoring efficiency at both military installations (stockpile sites, agent incineration plants, *etc.*) and in key civilian areas *i.e.* as a defence against potential terrorist attack.

The TT24-7 incorporates two, electrically-cooled (Peltier) large-capacity traps which are sampled sequentially at high flow rate (~1 L/min), allowing adequate preconcentration of trace-level agent in the shortest possible time (*i.e.* providing near real-time (NRT) analysis).

This application note describes an evaluation of TT24-7 performance for trace level agents, such as HD and free (underivitised) VX. Both off-line and near real-time operation is discussed. Linear FPD calibration curves ranging from 15 ng to 10 pg for VX and from 2 ng to 0.2 ng for HD are presented.

Introduction

The toxicity of airborne nerve agents is extremely high, even at very low concentrations. The current US airborne exposure limit (AEL)[1] (also referred to as the work place limit (WPL) value) for VX is 0.001 µg.m^{-3} (~0.1 ppt) and the general population limit (GPL) is 0.0006 µg.m^{-3}. These concentrations are so low that conventional analytical systems such as gas chromatography (GC), or GC combined with mass spectroscopy (GC/MS) cannot detect them with certainty. A means of pre-concentrating the air sample is

Figure 1: TT24-7

therefore required prior to analysis, and the technique of choice is thermal desorption (TD)[2]. Adsorption/thermal desorption primarily depends on the selective retention (adsorption) of volatile and semi-volatile organic chemicals as air or gas passes through a sorbent bed. The focused vapours are subsequently thermally desorbed and transferred to the analyser in a 200-300 µL 'plug' of carrier gas. Concentration enhancement factors above 10^6 are possible.

Air sampling can be achieved in two ways. Option one is to pump large volumes of air (up to 1000 L) through metal or glass sample tubes (typically 89 mm long x 6.4 mm O.D.) containing suitable sorbents. Sampling typically takes 8 to 24 hours and the sorbent tubes are then analysed off-line using thermal desorption with GC(/MS). This is typically referred to in the US demilitarization community as DAAMS tube monitoring (Depot Air Analysis Monitoring Systems). Option two is to draw smaller volumes of air (typically 5-10 L), over a much shorter time period (~10 minutes) directly into a focusing trap within the thermal desorber and analyse in near real-time (NRT). NRT monitoring of extremely toxic compounds such as the G or V type nerve agents, requires continuous sampling with no time 'blind' spots and rapid online analysis. This mode of operation is an absolute requirement for CW monitoring at military-stockpile sites or demilitarization/destruction facilities and can also be used for continuous monitoring of civilian locations in case of terrorist attack.

NRT monitoring of chemical warfare agents and other toxic chemicals offers early alert and compound identification in the event of a chemical incident. Organisations, such as the Centre for Disease Control (CDC)[3] in the USA, have defined parameters for 'NRT' monitoring including completion of the entire sampling and analytical process within 15 minutes, plus continuous sampling of air with no 'blind' spots. This requires dual reciprocating sampling traps such that sampling can continue on one channel, while the other is desorbed and analysed. The new TT24-7 has been developed by Markes International to meet these requirements. Air is drawn into the system using either positive sample pressure or by vacuum pump at electronic mass flow controlled rates of ~1 L/min for up to 10 minutes. Sampling of each channel is followed by rapid desorption and fast GC, MS or GC/MS analysis (*i.e.* <5 minutes).

Whether on- or offline methods are used, one of the most difficult chemical warfare agents to monitor is the nerve agent VX (Ethyl S-2-diisopropyl aminoethylmethyl phosphonthioate), $C_{11}H_{26}NO_2PS$). It has a very low vapour pressure (0.00063 mm Hg @ 25°C), high boiling point (298°C), and it reacts very readily with any active sites in the sample flow path. This can result in low recovery, poor chromatographic peak shape and ultimately limits of detection (LODs) which are unsafe for human exposure. Consequently, current monitoring methods involve derivatising VX to the more stable 'G' analogue before TD-GC(/MS) analysis.

The main objectives of this study were:

- to evaluate the TT24-7 performance (stability, linearity and LODs)
- to check compatibility with free- (underivitised) VX
- to test detection/quantitation limits
- to monitor compliance with NRT requirements

System description

The TT24-7 is a multi-functional, twin-trap thermal desorption system capable of several modes of operation. These modes are configured by the addition of one or more optional accessory kits to the main platform product. Figure 2 shows a schematic of a fully configured TT24-7.

The four main modes of TT24-7 operation are:

1. Platform product. Operates in continuous sampling mode (24hrs/7days), with high sample flow rate (1 L/min) passing through each trap in turn - channel A, channel B, channel A, *etc*.
2. Platform plus tube desorption accessory. This enables desorption of a single tube onto either trap thus simplifying calibration and validation of online sampling performance

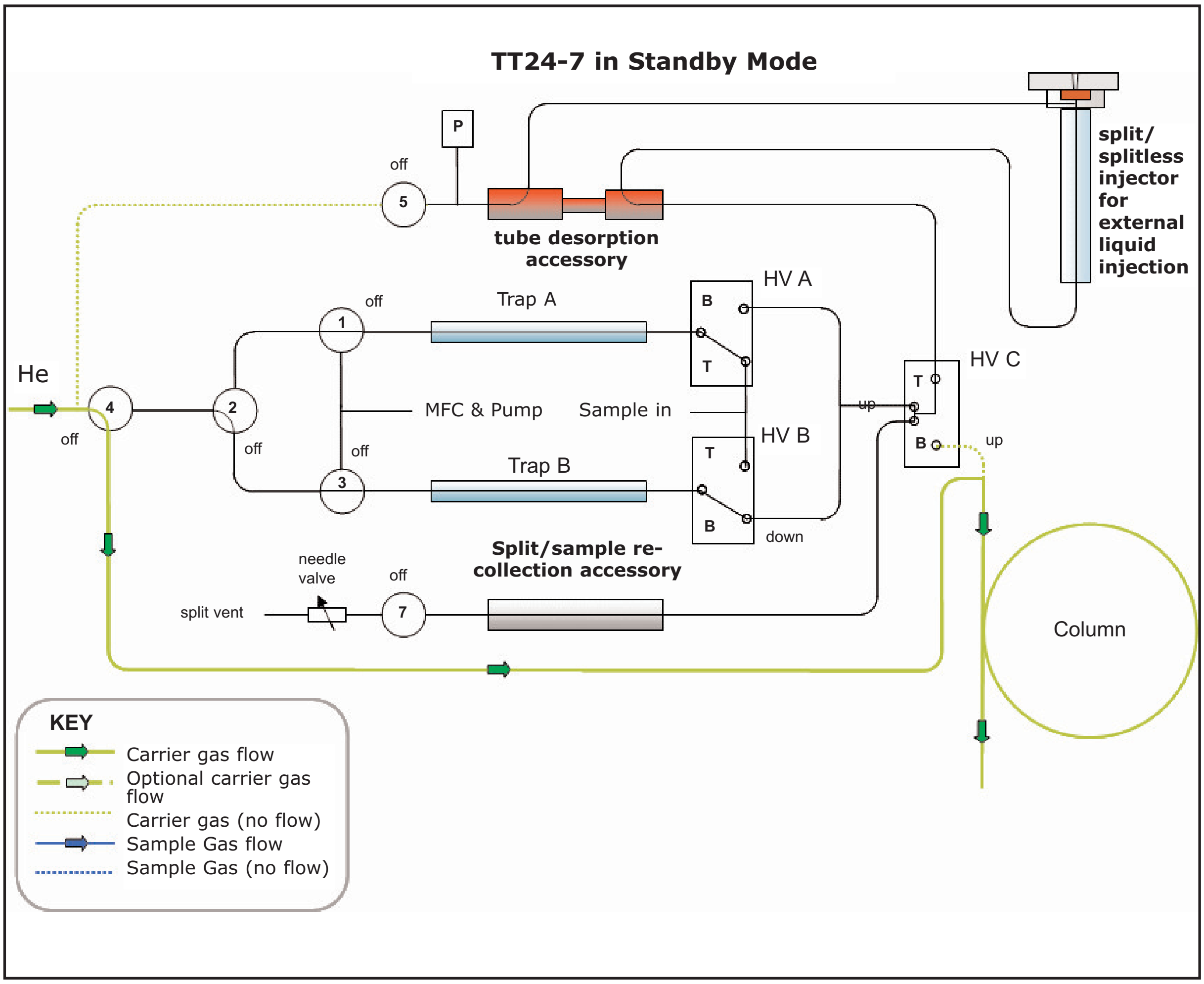


Figure 2: TT24-7 incorporating tube desorption accessory, split point (sample re-collection), and external (liquid) injector

3. As (2) but with additional split/sample-re-collection capability. This allows analysis of higher concentration atmospheres and facilitates validation of recovery by repeat analysis.

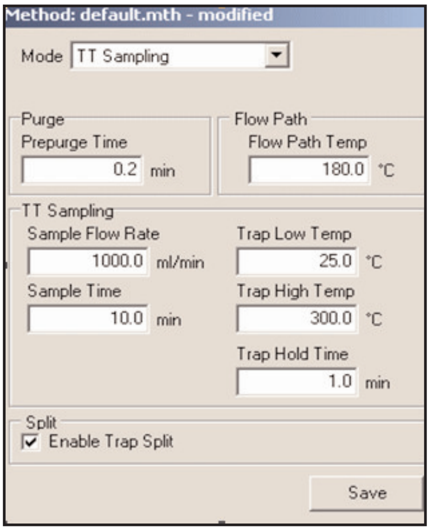
4. As (3) but with the addition of an external injection port for liquid standards. The liquid injector may be automated. Interchange between tube desorption and liquid injection is simple, but they cannot operate simultaneously.

The operating mode is selected using TT24-7 control software and examples of the user interface are shown in Figures 3, 4 and 5.

Notice that in tube desorption and liquid injection mode, the operator has to choose whether to sample onto trap A or B. This provides a mechanism for validating the performance of each trap independently and checking equivalence. As the TT24-7 software is a standard windows based application, remote system access is available, enabling distance monitoring of either military or civilian monitoring locations.

Experimental

Analysis was carried out using gas chromatography (6890N, Agilent Technologies) with flame photometric detector in phosphorous mode (FPD) or mass spectrometer (MS) detector. Several agents, including VX, respond well using the selectivity and sensitivity of the FPD in phosphorus mode. Where additional identifying qualifiers are required; MS is the detector of choice, providing 3 dimensional data, and also the capacity to identify small co-eluting compounds in complex matrices using spectral deconvolution[4].


Method: default.mth - modified

Mode: TT Sampling

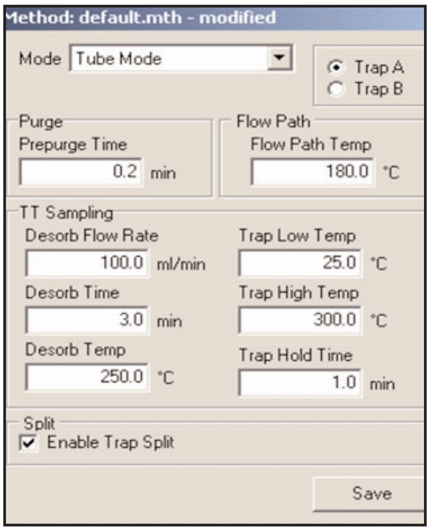
Purge
Prepurge Time: 0.2 min

Flow Path
Flow Path Temp: 180.0 °C

TT Sampling
Sample Flow Rate: 1000.0 ml/min
Sample Time: 10.0 min
Trap Low Temp: 25.0 °C
Trap High Temp: 300.0 °C
Trap Hold Time: 1.0 min

Split
☑ Enable Trap Split

Figure 3: Online sampling


Method: default.mth - modified

Mode: Tube Mode
● Trap A
○ Trap B

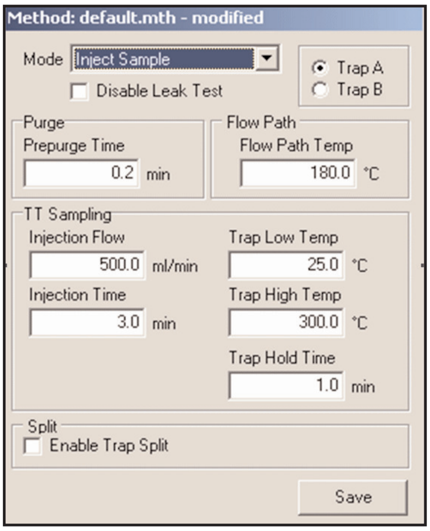
Purge
Prepurge Time: 0.2 min

Flow Path
Flow Path Temp: 180.0 °C

TT Sampling
Desorb Flow Rate: 100.0 ml/min
Desorb Time: 3.0 min
Desorb Temp: 250.0 °C
Trap Low Temp: 25.0 °C
Trap High Temp: 300.0 °C
Trap Hold Time: 1.0 min

Split
☑ Enable Trap Split

Figure 4: Tube Desorption


Method: default.mth - modified

Mode: Inject Sample
☐ Disable Leak Test
● Trap A
○ Trap B

Purge
Prepurge Time: 0.2 min

Flow Path
Flow Path Temp: 180.0 °C

TT Sampling
Injection Flow: 500.0 ml/min
Injection Time: 3.0 min
Trap Low Temp: 25.0 °C
Trap High Temp: 300.0 °C
Trap Hold Time: 1.0 min

Split
☐ Enable Trap Split

Figure 5: Liquid injection

To enhance retention time control and reproducibility, back pressure-regulated electronic pneumatic control (EPC) was fully integrated into the TT24-7 system. EPC offers several significant advantages. It stabilises retention times, independent of desorber status/parameter settings, and thus allows for the development of a retention time locked (RTL) database of key target compounds *i.e.* CW agents (See TDTS 36), pesticides and toxic industrial chemicals, *etc.*

To assess system performance, a fully configured TT24-7 was interfaced to a 6890N GC and tested in various modes of operation. Initially the blistering agent HD was analysed using both the tube accessory and on-line sampling techniques. This was followed by the analysis of HD using external liquid injection. Finally, the system was challenged with free-(underivitised) VX. [Note that the traditional process of derivitising VX to the 'G' analogue is often incomplete/inefficient, producing variable (non-quantitative) data.]

The following experiments were performed to assess system performance:

1. Linearity and limit of detection (LOD) for HD using the tube desorption accessory

Solutions of HD were prepared in methanol and injected into an inert-coated tube packed with quartz wool and Tenax TA ready for desorption using the TT24-7 tube desorption accessory. A calibration curve was prepared for masses ranging from 2 ng to 0.2 ng. Linearity and quantitation limits were determined and the data used for comparison with that obtained when sampling HD vapours into the trap on-line *i.e.* using a heated sample inlet line.

2. Online sampling of HD

On-line monitoring was evaluated by introducing a plug of HD vapour a) directly to the inlet port of the TT24-7 and b) at the distal end of a 1m heated sampling line. The vapours were introduced at two levels (0.6 ng and 1.0 ng of HD respectively) in a pumped (vacuum) air flow of 800 ml/min. The flow was regulated using the internal mass flow controller of the TT24-7. 0.6 and 1.0 ng masses of HD overlap with the middle of the calibration curve generated in (1) (above), and allowed direct correlation of data from the three sampling techniques.

3. Linearity and sensitivity to free-VX at low pg levels using sorbent tubes

Solutions of free VX were prepared in methanol and injected using a calibration loading rig into an inert-coated tube packed with quartz wool and Tenax TA. The tube was then desorbed using the TT24-7 tube accessory. A multi level calibration of VX was performed, with levels ranging from 9 pg to 1.5 ng. Three replicate injections were carried out at the lower level to assess reproducibility.

4. NRT analysis of HD and free VX using the external liquid injection accessory

TD and GC parameters were optimised to achieve elution of GB, HD and VX within a 2 minute time window to ensure compliance with NRT cycle time limits. Agent solutions in hexane were injected (splitless) into the hot split/splitless inlet of the GC. They were then vaporised and swept by the helium carrier gas onto one or other of the internal TT24-7 traps (A or B). Note that the inlet and all stainless steel connecting tubing were coated with deactivating material to ensure an inert flow path. The masses of HD and VX introduced to the system were matched to the masses which would be retained if an atmosphere containing 0.25 x the US short term airborne exposure limit (STEL) of each agent was sampled at 1 L/min for a 10 minute period. [Note that 0.25 x STEL equates to 0.0000025 mg/m^3 for VX, and 0.00075 mg/m^3 for HD and the masses introduced were therefore 25 pg and 7.5 ng for VX and HD respectively]. Signal to noise ratios were calculated at these concentration levels.

An additional lower-level standard was prepared such that tubes could be spiked with 10 pg of VX *i.e.* the mass that would be collected from a 10 L volume of air containing VX at the workplace limit level (WPL (also called AEL) = 1x10^{-6} mg/m^3). Peak heights from analysis of the WPL-level standard were compared to those obtained from the 0.25 STEL-level standard.

Results

1. Linearity and LOQ analysis for HD using the tube desorption accessory

Figure 6 shows the multi level calibration curve for HD for concentrations ranging from 0.2 ng to 2 ng. Good linearity (correlation value 0.9948) is observed. Figure 7 shows the chromatographic response at the lowest level. Signal to noise is ~ 8:1, which translates into a Limit Of Quantitation (LOQ) of ~ 0.1 ng.

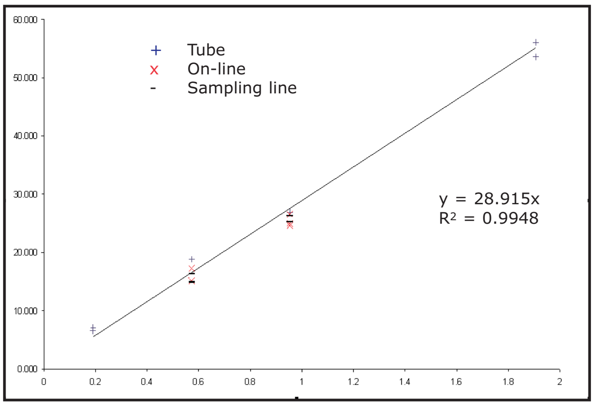


Figure 6: 0.2 to 2.0 ng HD calibration curves for both tube and on-line sampling

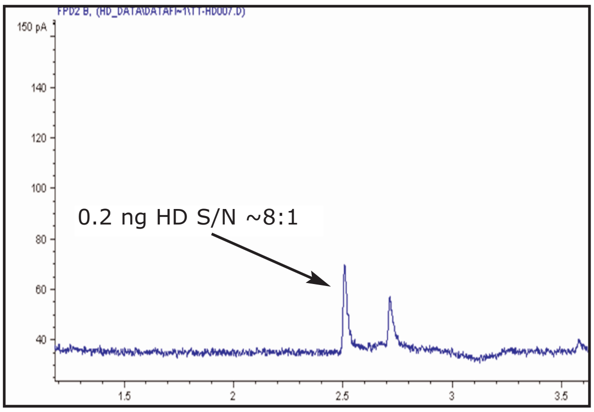


Figure 7: Chromatogram showing 0.2 ng HD

2. Online sampling of HD

Data for the 0.6 and 1.0 ng masses of HD sampled on-line, both at the sample inlet and at the distal end of a 1 m heated sampling line, correlated well with that obtained using tube desorption (Figure 6). This indicates excellent recovery of HD through the heated sample inlet line. The US WPL value for HD (TWA 8 h) is

0.0004 mg/m^3 *i.e.* 0.4 ng/L.

The observed LOQ from these experiments is ~ 0.1 ng. Therefore, if the sampling flow rate entering the TT24-7 was controlled at 1 L/min, a sampling time below 1 minute would be adequate to detect HD at lower levels than the WPL. The US general population limit (GPL) value for HD (TWA 12 h) is 0.02 ng/L. Detection at this level would require ~5 minutes sampling at 1 L/min.

3. Linearity and sensitivity to free-VX at low pg levels using sorbent tubes

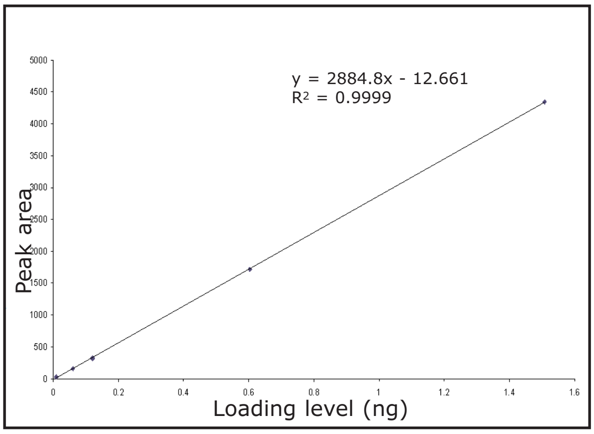


Figure 8: Calibration curve for free VX from 9 pg to 1.5 ng

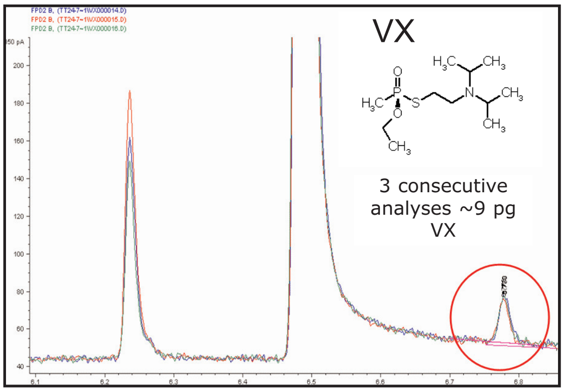


Figure 9: VX overlay of 3 separate analyses at 9.0 pg

Figure 8 shows the VX calibration curve from 1.5 ng to 9 pg. Excellent linearity is observed with a coefficient of 0.999. Figure 9 shows the chromatographic overlay of 3 consecutive analyses at the 9 pg level, with a mean peak area value of ~22.0. For reference, 9 pg is equivalent to <1 parts per quadrillion in 1000 L of air (0.000009 µg/m^3) or <0.1 ppt in 10 L of air (0.0009 µg/m^3).

NRT analysis of HD and free VX using the external liquid injection accessory

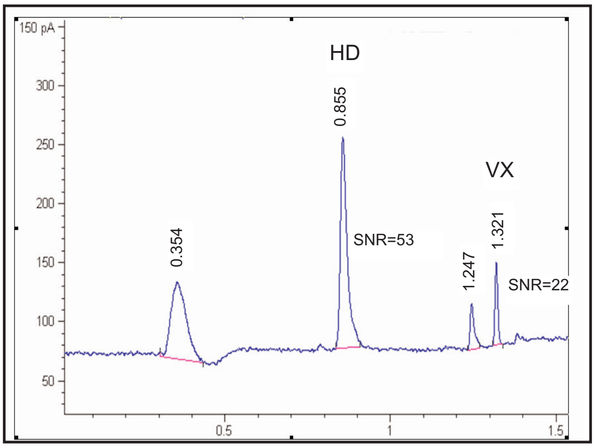


Figure 10: Chromatograms of 0.25 STEL HD and VX

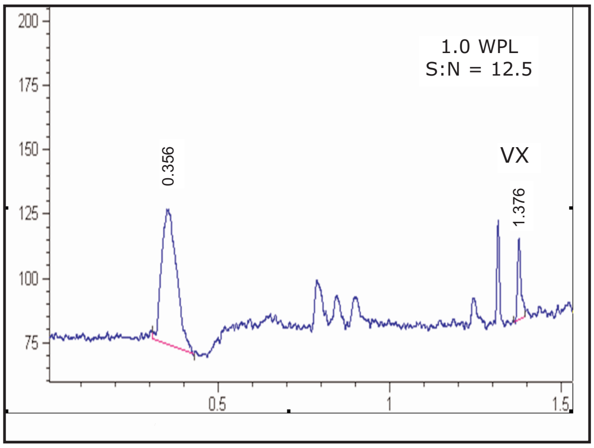


Figure 11: Chromatogram of 1 WPL VX

Figures 10 and 11 show preliminary data obtained using the liquid injection accessory. Figure 10 shows the NRT chromatographic response of 0.25 STEL for both free VX and HD. The chromatogram shows excellent peak shape for VX, with a very short retention time of only 1.321 minutes. Furthermore the HD peak elutes at 0.855 minutes under these conditions. Based on sampling a 10 L volume of air (*i.e.* 1 L/min for 10 mins) at 0.25 STEL, the mass of VX collected is 25 pg (*i.e.* 2.5 pg/L).

Both compounds have excellent signal to noise (S/N) ratio. The peak height of VX at 0.25 STEL is ~60 pa.

Figure 11 shows the response to 10 pg of free VX - equivalent to sampling 10 L of air at 1 WPL (1 pg/L). The peak height is ~ 28 pa, a factor of 2.14 less than that of the 0.25 STEL value. This is very close to linear. The peak area for 10 pg VX *via* liquid injection was 26.0. This compares well with the peak area of 22.0 obtained from the tube desorption of 9 pg VX in experiment 3.

Although this is preliminary data, this is a good indication of efficient recovery of VX through the injection port and through the entire flow path of the TT24-7.

Implications

The ability to detect airborne chemical warfare agents at trace levels and in near real-time is highly advantageous. It has obvious application at military installations such as stockpile bunkers or agent demilitarization/destruction facilities. However, given the current threat of terrorist activity, the capacity to detect trace levels of CW agents (and more conventional toxic industrial chemicals) at key civilian locations, has become very topical. Data shown here indicate the capacity of the TT24-7 to accommodate NRT monitoring for highly active agents at extremely low concentration levels (sub-ppt) as is required for civil defence.

Addition of the accessories evaluated in this study has also been shown to extend the basic functionality of the TT24-7 - allowing it to become a flexible multi mode system and general purpose CW analytical platform.

References

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