MARKES international

Application

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Application Note 063

Continuous monitoring of trace-level toxic chemicals in air

Summary

This Application Note discusses Markes' TT24-7™ instrument for continuous on-line and near-real-time sampling of airborne chemical warfare agents. Examples include the evaluation of performance for trace-level agents such as HD (mustard) and free-VX.

Introduction

Continuous sampling of air is essential in situations where the target compounds may pose an immediate and severe hazard to human health. Chemical warfare agents (CWAs) are key examples of such compounds, and demand 100% monitoring efficiency, both at both military installations (stockpile sites, agent incineration plants, *etc.*) and in key civilian areas – *i.e.* as a defence against potential terrorist attack.

Meeting this demand, Markes' transportable thermal desorption system, the TT24-7, enables continuous on-line sampling and pre-concentration of airborne chemical warfare agents. The enriched vapour sample is subsequently analysed using gas chromatography (GC), with or without mass spectrometry (MS), or with direct MS technology.

The TT24-7 (Figure 1) incorporates two, electrically-cooled large-capacity traps, which are sampled sequentially at high flow rates (~1 L/min), allowing adequate pre-concentration of trace-level agents in the shortest possible time, and thus providing near-real-time (NRT) analysis.

This Application Note describes an evaluation of the performance of the TT24-7 for trace-level agents such as HD and free-VX. 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.

Figure 1: Markes' TT24-7.

Background

Detection of chemical agents

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 workplace 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 GC or GC–MS cannot detect them with certainty. A means of pre-concentrating the air sample is therefore required prior to analysis, and the technique of choice is thermal desorption (TD).

Thermal desorption and air sampling

Thermal desorption primarily depends on the selective retention (adsorption) of volatile and semi-volatile organic chemicals (VOCs and SVOCs) as air or gas passes through a sorbent bed. The focused vapours are subsequently thermally desorbed and transferred to the analyser in 200–300 µL of carrier gas. Concentration enhancement factors above 10^6 are possible.

Air sampling can be achieved in two ways:

1. Pump large volumes of air (up to 1000 L) through metal or glass sample tubes (typically 89 mm long × 6.4 mm o.d.) containing suitable sorbents. Sampling typically takes 8–24 hours, and the sorbent tubes are then analysed off-line using TD–GC(–MS). In the US demilitarisation community, this process is typically referred to as DAAMS tube monitoring (Depot Air Analysis Monitoring Systems).
2. 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 and rapid on-line analysis. This mode of operation is an absolute requirement for CWA monitoring at military-stockpile sites or demilitarisation/destruction facilities, and can also be used for continuous monitoring of civilian locations.

Near-real-time monitoring

NRT monitoring of CWAs and other toxic chemicals offers early alert and compound identification in the event of a chemical incident. Organisations such as the Centers for Disease Control and Prevention (CDC)[2] in the USA have defined parameters for NRT monitoring, including completion of the

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entire sampling and analytical process within 15 minutes, plus continuous sampling of air with no 'blind spots'. This requires dual reciprocating sampling traps, so that sampling can continue on one channel, while the other is desorbed and analysed.

Markes' TT24-7 was developed to meet these requirements. Air is drawn into the system using either positive sample pressure or by a vacuum pump at rates of ~1 L/min for up to 10 minutes (controlled by an electronic mass flow controller). Sampling of each channel is followed by rapid desorption and analysis by GC, MS or GC–MS within 5 minutes.

Detecting free-VX

Whether on-line or off-line methods are used, one of the most difficult CWAs to monitor is the nerve agent VX, [2-(diisopropyl-amino)ethyl]-*O*-ethyl methylphosphonothioate ($C_{11}H_{26}NO_2PS$). It has a very low vapour pressure (0.00063 mmHg at 25°C), a 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 limits of detection (LODs) that would be unsafe to be exposed to.

Consequently, some monitoring methods involve derivatising VX to the more stable 'G' analogue before TD–GC(–MS) analysis. However, this process is often incomplete or inefficient, producing variable (non-quantitative) data, so it is of interest to develop methods that can monitor 'free' (underivatised) VX quantitatively.

Objectives

The main objectives of this study were:

- To evaluate the peformance of the TT24-7 with regard to stability, linearity and LODs.
- To check compatibility with free-VX.
- To test detection/quantitation limits.
- To monitor compliance with NRT requirements.

Operation of the TT24-7

The TT24-7 is a multi-functional, twin-trap TD 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.

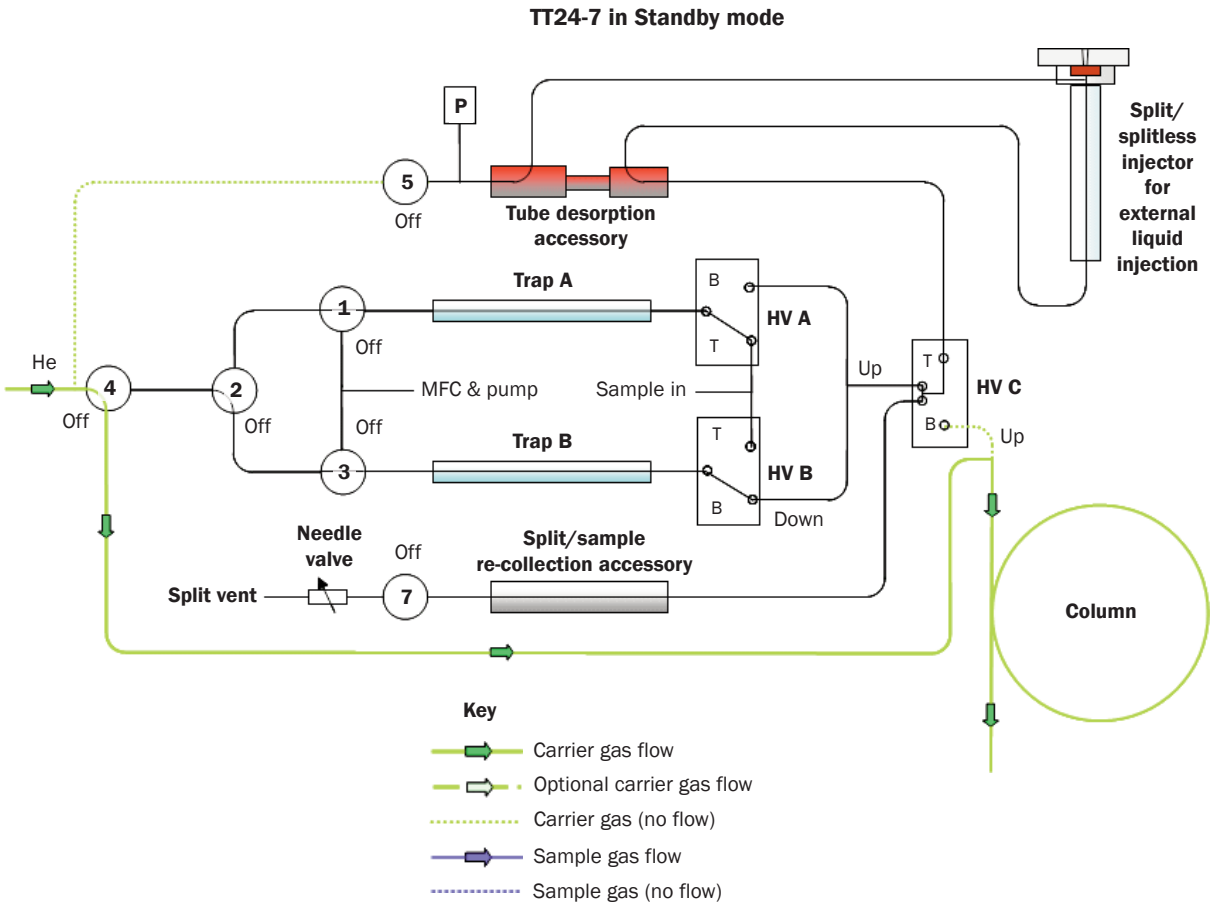

Figure 2: Flow path of the TT24-7, incorporating tube desorption accessory, split point (sample re-collection), and external (liquid) injector.

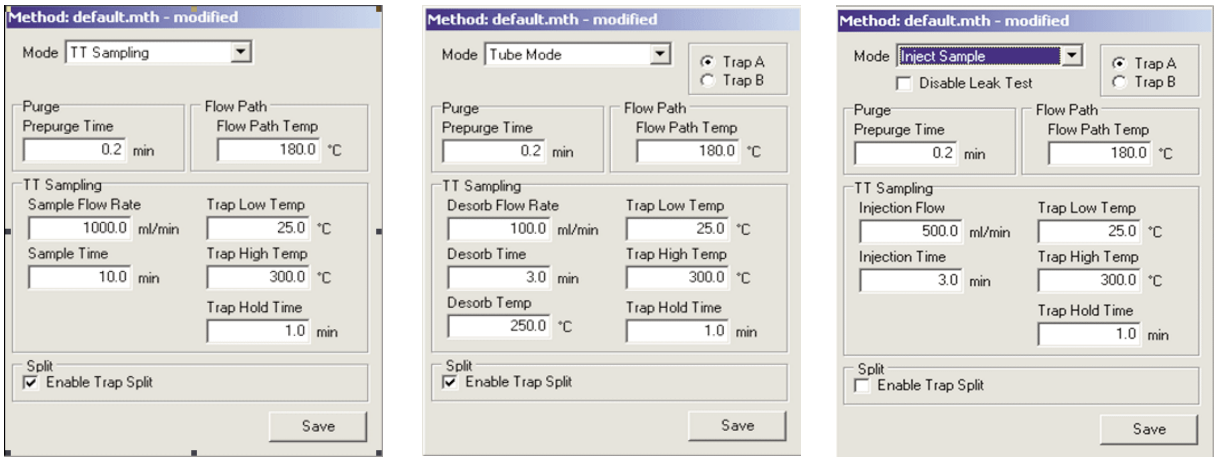

Figure 3: User interface of the TT24-7 for (left) on-line sampling, (middle) tube desorption, and (right) liquid injection.

The four main modes of TT24-7 operation are:

1. Platform product. Operates in continuous sampling mode, with a high sample flow rate (1 L/min) passing through each trap alternately (A, B, A...).
2. Platform product with tube desorption accessory. This enables desorption of a single tube onto either trap, thus simplifying calibration and validation of on-line sampling performance.
3. As for Mode 2, but with additional sample splitting and re-collection capability. This allows analysis of higher-concentration atmospheres, and facilitates validation of recovery by repeat analysis.
4. As for Mode 3, but with the addition of an external injection port for liquid standards. The liquid injector can 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 Figure 3.

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 the detector being a flame photometric detector in phosphorus mode (FPD) or a mass spectrometer (MS). Several agents, including VX, respond well to the selectivity and sensitivity of the FPD in phosphorus mode. Where additional identifying qualifiers are required, MS is the detector of choice, providing three-dimensional data and also the capacity to identify trace-level co-eluting compounds in complex matrices using spectral deconvolution.[3]

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, *e.g.* CWAs (see Application Note 036), pesticides, and toxic industrial chemicals.

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 (mustard) 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-VX.

The following experiments were performed to assess system performance:

A. Linearity and limit of detection (LOD) for HD

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.

B. On-line sampling of HD

On-line monitoring was evaluated by introducing a plug of HD vapour (i) directly to the inlet port of the TT24-7, and (ii) at the distal end of a 1 m 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. The 0.6 and 1.0 ng masses of HD overlap with the middle of the calibration curve generated in Experiment A, and allowed direct correlation of data from the three sampling techniques.

C. Linearity and sensitivity to free-VX at low-picogram levels

Solutions of free-VX were prepared in methanol and injected using Markes' Calibration Solution Loading Rig (CSLR™) 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.

D. NRT analysis of HD and free-VX

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. Solution of agents 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 of the traps of the TT24-7. 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 that would be retained if an atmosphere containing 0.25 times 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 × 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 so 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 = 1 × 10^{-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

A. Linearity and limit of detection (LOD) for HD

Figure 4 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. The signal-to-noise ratio is ~8:1, which translates into a limit of quantitation (LOQ) of ~0.1 ng.

B. On-line 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 5). 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 (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 min 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 sampling for ~5 min at 1 L/min.

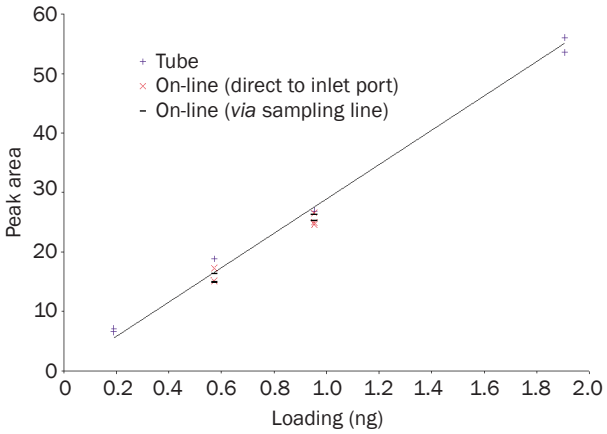

Figure 4: HD calibration curves (0.2–2.0 ng) for tube and on-line sampling.

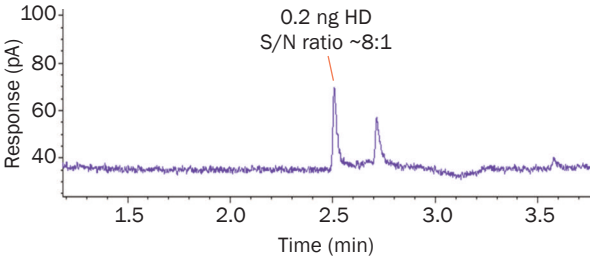

Figure 5: Chromatogram showing detection of 0.2 ng HD.

C. Linearity and sensitivity to free-VX at low-picogram levels

Figure 6 shows the VX calibration curve from 1.5 ng to 9 pg. Excellent linearity is observed, with a correlation coefficient of 0.999. Figure 7 shows an overlay of three consecutive analyses at the 9 pg level, with a mean peak area 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).

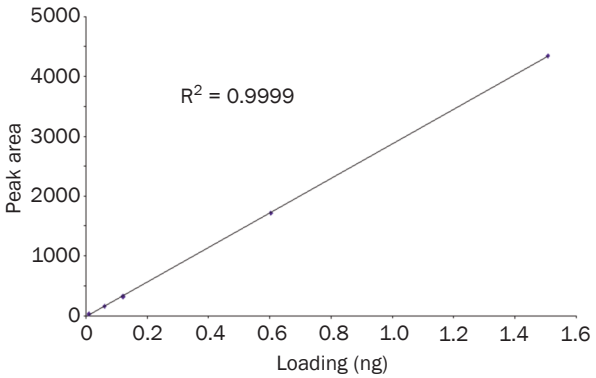

Figure 6: Free-VX calibration curve (9 pg to 1.5 ng).

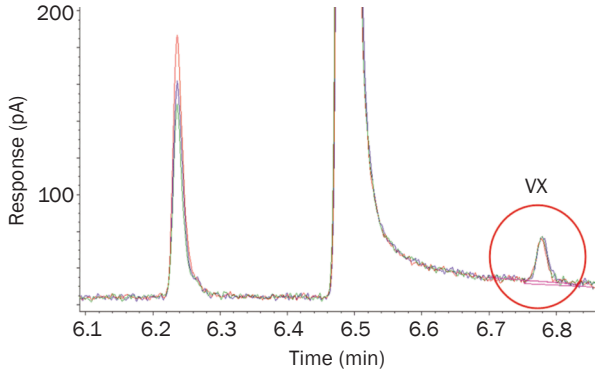

Figure 7: Overlay of three consecutive analyses of 9 pg VX.

D. NRT analysis of HD and free-VX

Figures 8 and 9 show preliminary data obtained using the liquid injection accessory. Figure 8 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 min. Furthermore, the HD peak elutes at 0.855 min under these conditions. Based on sampling a 10 L volume of air (*i.e.* 1 L/min for 10 min) 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 ratios. The peak height of VX at 0.25 × STEL is ~60 pA.

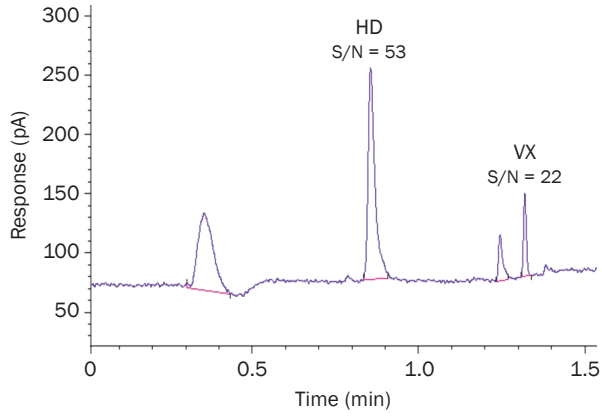

Figure 8: Chromatogram of 0.25 × STEL HD and VX.

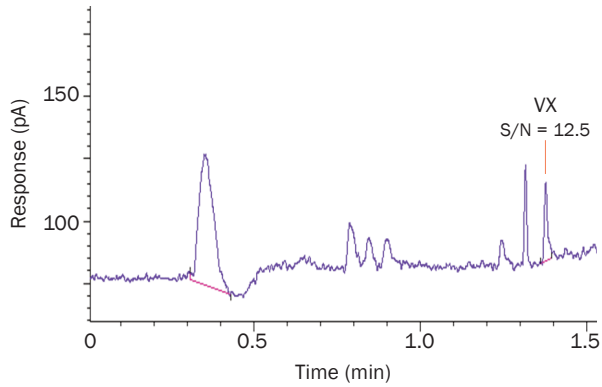

Figure 9: Chromatogram of 1 × WPL VX.

Figure 9 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 C.

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.

Conclusions

The ability to detect airborne CWAs at trace levels and in near-real-time is highly advantageous. It has obvious application at military installations such as stockpile bunkers or agent demilitarisation/destruction facilities. Moreover, given the continued threat of terrorist activity, the capacity to detect trace-level CWAs (and 'ordinary' toxic industrial chemicals) at key civilian locations remains of great importance.

The data shown here indicates the capacity of the TT24-7 to accommodate NRT monitoring for highly active agents at extremely low concentrations (sub-ppt), as is required for civil defence.

Addition of the accessories evaluated in this study also demonstrates the extension of the basic functionality of the TT24-7, highlighting it as a flexible multi-mode system and general-purpose CWA analytical platform.

References

1. US Army Chemical Materials Agency (www.cma.army.mil).
2. Centers for Disease Control and Prevention (www.cdc.gov).
3. G.M. Roberts, Proceedings of the 2004 Scientific Conference on Chemical and Biological Defense Research, November 2004, Hunt Valley, Maryland.

Trademarks

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

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