Sampling and analysis of chemical weapons: Improving identification, throughput and reliability.

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Introduction

The acute toxicity of airborne chemical warfare agents (CWAs) requires sampling and detection systems that can identify trace levels of these compounds, potentially in complex matrices. This is a requirement both at military installations, and more recently for pre-emptive monitoring at key civilian locations. Online and offline methods based on pre-concentration technology, coupled with Gas Chromatography - Mass Spectrometry or other specific detectors have been developed and refined over the years. Recent advances in analytical hardware and software have enabled improved identification of compounds, increase workflow/throughput capabilities and greater flexibility in sampling methods. Many CWAs and their respective simulants are sticky and/or reactive species that present a significant analytical challenge, especially at sub-ng and pg levels. Relevant configurations include on-line systems (generating semi-continuous near-real-time measurement) and off-line laboratory-based installations. Both may be deployed in conventional or mobile laboratories. The most widely used sampling options include pumped monitoring onto sorbent tubes and round-the-clock in-line air monitoring and analysis.

Sampling and Analysis

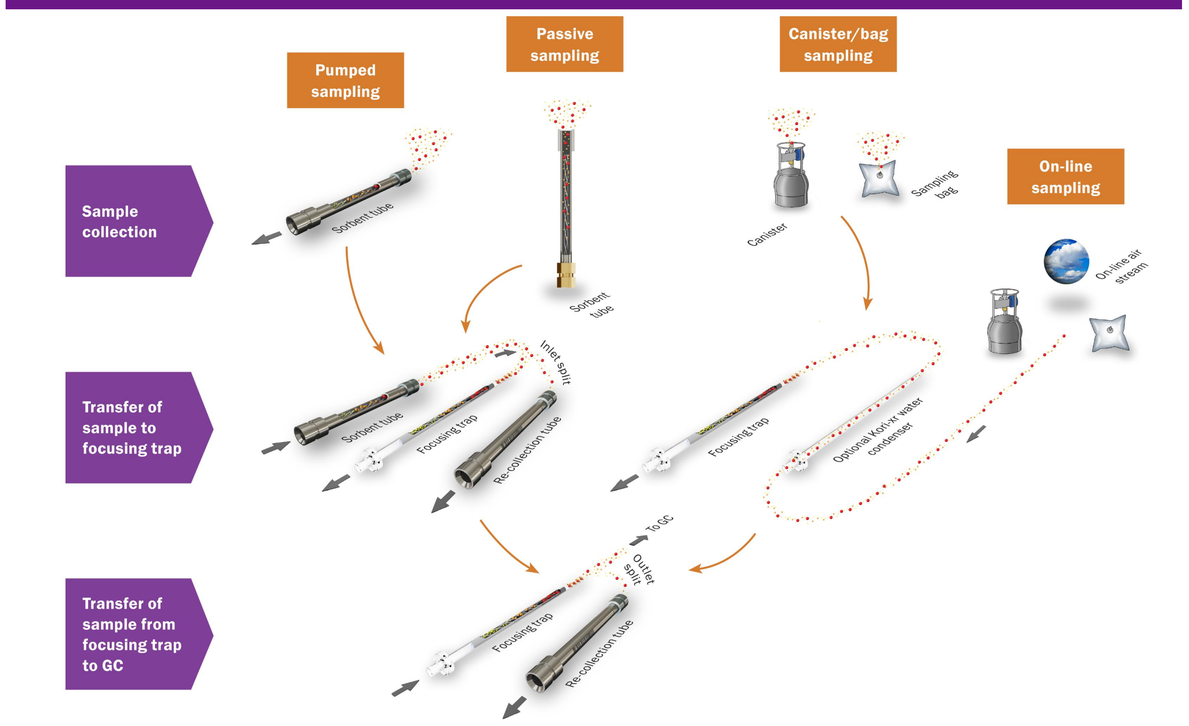

Figure 1: Various sampling techniques coupled with pre-concentration for trace analysis by GC-MS/dFPD.

Analysis of Chemical Warfare Agent simulants

Proof of performance

Simulants are used to mimic real CWAs:

- Dimethyl methyl phosphonate (DMMP) = Sarin, Soman and Tabun
- Triethyl Phosphate (TEP) = Sarin, Soman and Tabun
- Methyl Salicylate (MS) = Mustard gas
- 2-Chloroethyl phenyl sulphide (CEPS) = Mustard gas
- Malathion = VX

Stock standard was produced with the compounds above in methanol for a serial dilution to the following levels: 0.1, 0.5, 1, 5, 10, 25, 50 and 100 ng/µl. 1µl of each level was spiked onto the sorbent tubes for analysis and splitless analysis for ultimate sensitivity.

Linearity Calibrations were performed over eight levels between 100 pg and 100 ng using 1-µL injections of the standard solutions. Note that while low ng and pg levels are more representative of the levels collected during air monitoring, 100-ng levels are seen in some important chamber tests. The linearities for all five compounds were excellent across this extended dynamic range with R^2 values ≥0.9991 (Figure 2).

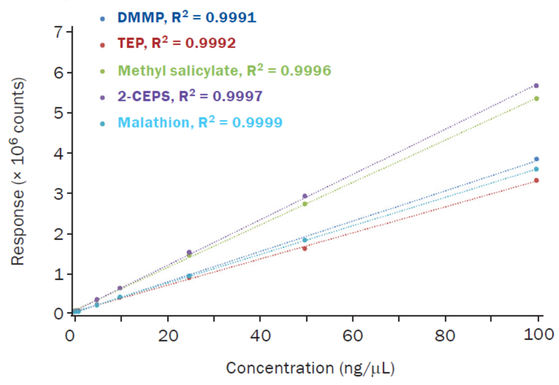

Figure 2: Excellent linearities were obtained for the target compounds for a range of 0.1–100 ng.

Carryover in the tube and system was assessed by loading tubes with a 100-ng standard and desorbing them twice shows a maximum carryover of 1.5% even at these extremely high levels (Figure 3).

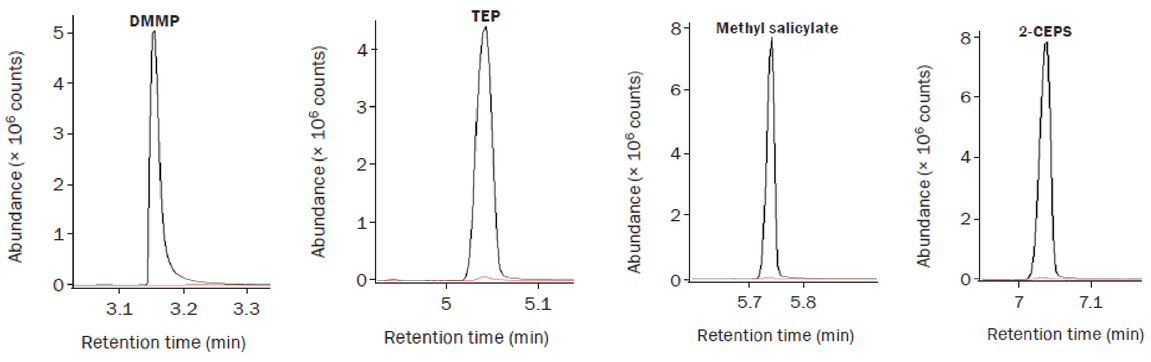

Figure 3: Original desorption of 100-ng/µL standards (black) overlayed with the subsequent re-desorption (red).

Reproducibility was tested at low and high concentrations to verify method parameters. The relative standard deviation (%) can be seen in Table 1 for 5, 50 and 100 ng/µL. Values for all compounds at all levels are at or below 5%.

Table 1: The reproducibility of target simulants at three different concentration levels.

RSD (%)	5 ng/µL (n = 10)	50 ng/µL (n = 7)	100 ng/µL (n = 10)
Dimethyl methylphosphonate (DMMP)	3.21	4.30	2.46
Triethyl phosphate (TEP)	2.97	2.81	2.41
Methyl salicylate	2.72	1.73	1.31
2-Chloroethyl phenyl sulfide (2-CEPS)	4.04	1.82	1.76
Malathion	5.02	2.06	1.71

Improving detection limits – reaching trace levels more easily

The very high toxicity of chemical agents means detection is required at extremely low, *e.g.* picogram levels, necessitating the concentration of large volumes of air using pumped sorbent tubes before analysis. Calculations were performed to determine the limit of quantitation (LOQ, calculated using a signal-to-noise ratio of 10) and limit of detection (LOD, calculated by using a signal-to-noise ratio of 3) from the linearity data (Table 2). Markes' TD systems now offer users the option to 'stack' the desorptions of two or more samples on the same focusing trap. This is useful, for example, where air volumes are limited by sampling time or analyte breakthrough and it requires multiple samples to be collected in parallel at the monitoring location.

Compound	LOQ (ng)	LOD (ng)
Dimethyl methylphosphonate (DMMP)	0.207	0.062
Triethyl phosphate (TEP)	0.159	0.048
Methyl salicylate	0.066	0.020
2-Chloroethyl phenyl sulfide (2-CEPS)	0.068	0.020
Malathion	0.147	0.044

Table 2: Target compounds and their respective limits of quantitation (LOQ) and limits of detection (LOD).

Internal standard reduce analytical uncertainty by identifying variability between injections that may otherwise have gone unnoticed, for example variable detector response. Gas-phase internal standard to be automatically introduced to the sampling end of sorbent tubes at two different stages of air monitoring operation to help improve precision:

- Pre-loading sorbent tubes prior to transport and sampling.
- Immediately before tube desorption as part of the automated analytical process.

Analysis of Chemical Warfare Agents

Markes' Thermal Desorption system's performance was evaluated using live agents. For this part of the study, a UNITY–ULTRA-xr system for standard (3.5-inch) tubes was connected to a GC–MS/dual FPD instrument configured for both S and P modes for simultaneous full characterisation of agents with variable splits for higher sensitivity to specified detectors. A mixed 10-ng standard of live agents was spiked onto an inert-coated sorbent tube that had been used to sample air.

The total ion chromatogram (TIC) shows significant interferences and illustrates the difficulty in identifying trace chemical warfare agents in real samples. The merge extracted ion profiles (EIC masses 86, 99, 106, 114, 127 and 133 m/z) identify multiple agents including sarin (4.9 minutes), soman (8.4 minutes), tabun (9.76 minutes), mustard gas (10.71 minutes), VX (18.8 minutes) and Russian VX (19.05 minutes) and demonstrate the excellent performance of TD systems for live agent analysis. Although 10 ng is a relatively high level for the analysis of CWAs, subsequent re-desorption of the same sorbent tube showed no carryover for all compounds except VX, which is notoriously sticky. However, carryover for VX was below 0.25%, even with 70% of the sample sent to the FPD for higher sensitivity (Figure 4).

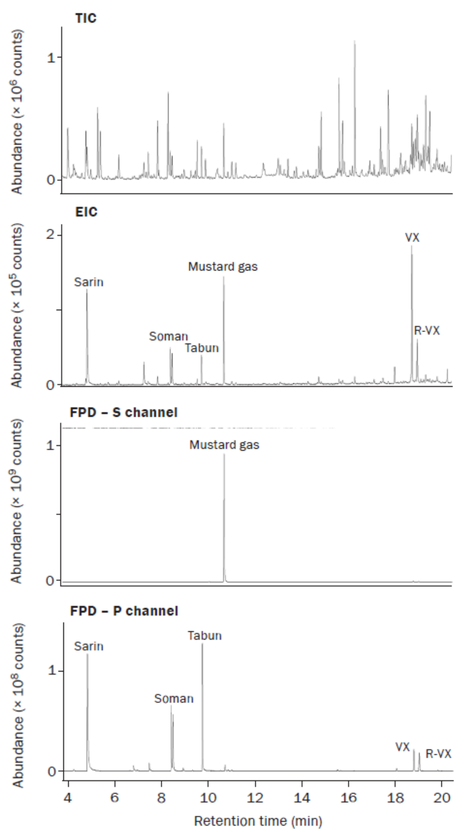

Figure 4: TIC (top) of a 10-ng mixed agent standard on a tube with interferences from the atmospheric sample. Trace 2 shows the merged EIC for target compounds. Trace 3 shows mustard gas (HD) in the S channel of the FPD and Trace 4 (bottom) shows the P channel for the remaining agents (sarin, soman, tabun, VX and Russian VX). Analysis performed using a TD–GC–MS/dFPD with a 70:30 split to the MS.

Real-world air monitoring of agents requires detection at picogram levels to protect the public and military personnel. Analysis of a 10-pg standard of live agent showed no response for the target compounds using the mass spectrometer in full scan, but good response and peak shape with the FPD channels as shown in Figure 5. VX and Russian VX can be seen in the inset and show an excellent response and peak shape for a 10-pg standard. The analysis was again carried out splitless on the TD system but did include capillary flow splitting technology to divide the sample between the mass spectrometer and flame photometric detector, meaning only ~6 pg of each analyte reached the selective detector for measurement.

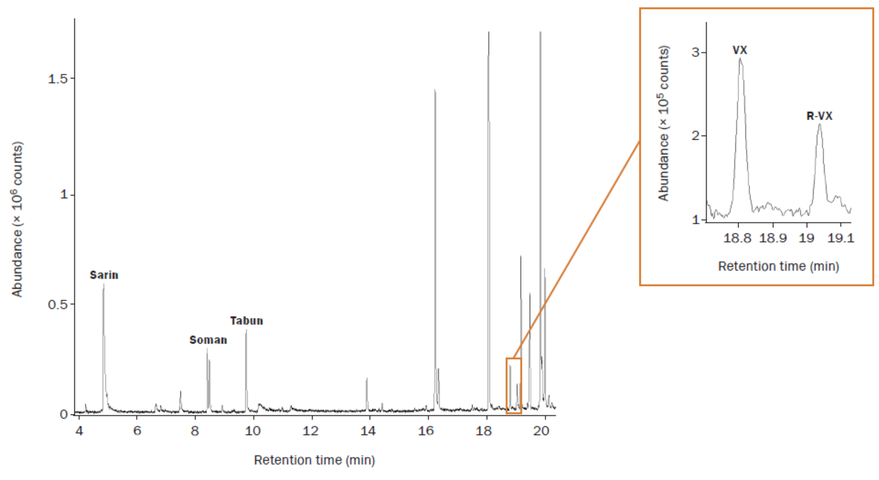

Figure 5: (Left) Analysis of an air sample with an FPD P channel showing sarin, soman, tabun, VX and Russian VX at the 10-pg level on the tube. (Right) Inset image shows a close-up of VX and Russian VX identified.

Conclusions

Key aspects of TD technology, which facilitate analysis of such challenging compounds, include:

- The short, inert and uniformly-heated flow path, including proprietary heated TD valve.
- The exceptional performance of the focusing trap with low thermal mass and heating rates of 100°C/s, delivering fast GC injection and optimum sensitivity (narrow peaks) even with low or zero split flows.
- The proprietary heated valve, which enables analytes to enter and leave the trap from the same end (backflush operation), allowing the highest-boiling, stickiest compounds to be trapped and released from the front of the trap – quickly and easily. This allows target compounds over a wide volatility range to be analysed simultaneously and ensures good recovery and peak shape.
- Selection of hydrophobic sorbents and precise control of trapping temperatures allow any atmospheric humidity (water) to be purged out of the system before analysis.

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