Detection and Measurement of Chemical Warfare Agents

Technical Overview

Homeland Security

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Abstract

The need for effective methods for the detection and measurement of chemical warfare agents (CWA) has increased in recent years. Current stockpiles need to be monitored to ensure their safe containment. The remediation of sites containing abandoned CWAs requires analysis in support of safe removal and destruction of agents. More recently, counterterrorism efforts have underscored the need for methods to accurately detect and measure CWAs. This technical note describes systems available from Agilent Technologies to meet these needs.

Introduction

The methods used for detection of CWAs are dependant upon the specific circumstances in which they are encountered. If the situation is one where the identity of the agents involved is unknown, then the method must first be capable of providing unequivocal identification of the agent(s) present. This could be the case when an abandoned stockpile of CWAs is discovered or when a terrorist incident takes place. After the identities of the agents are confirmed, a map of their concentrations in the immediate area must be determined. This information is used to establish perimeters around a site to ensure public safety and to identify appropriate precautionary measures for entering the site. In the case of routine monitoring or in support of cleanup and remediation activities, methods optimized for the detection of specific agents can be used.

Indentification of CWAs

Table 1 lists most of the chemicals that have been used for military purposes. Abandoned chemical weapons stockpiles would be expected to contain materials on this list. The list also reflects most of the compounds currently in military stockpiles around the world. The list does not, however, include similar materials that may be constructed by illegitimate means. Clandestine production of chemical agents could use reactants of somewhat different structure to avoid the attention of enforcement agencies. Sometimes referred to as a “designer agents,” these materials also pose a risk.

Detection methods for CWAs should be capable of positive identification of the types of compounds in Table 1, as well as the identification of designer agents. Of particular concern are the G and V series nerve agents because of their extreme toxicity. Mustard (H and HD) is a concern because of the quantities produced. Gas chromatography interfaced to mass spectrometry (GC/MS) is well-suited to this task. Figure 1 shows a diagram of a GC/MS system configured for the detection and identification of CWAs.

Table 1. Compounds Used as CWAs

Name	Military designation	CAS number	Chemical name
Nerve			
Cyclohexyl sarin (GF)	GF	329-99-7	Cyclohexyl methylphosphonofluoridate
GE	GE	1189-87-3	Phosphonofluoridic acid, ethyl-, 1-methylethyl ester
Sarin (GB)	GB	107-44-8	Phosphonofluoridic acid, methyl-, 1-methylethyl ester
Soman (GD)	GD	96-64-0	Phosphonofluoridic acid, methyl-, 1,2,2-trimethylpropyl ester
Tabun (GA)	GA	77-81-6	Phosphoramidocyanidic acid, dimethyl-, ethyl ester
VE	VE	1189-87-3	Phosphonofluoridic acid, ethyl-, 1-methylethyl ester
Amiton	VG	78-53-5	Phosphorothioic acid, S-[2-(diethylamino)ethyl] O,O-diethyl ester
GV also GP	GV	141102-74-1	Phosphoramidofluoridic acid, dimethyl-, 2-(dimethylamino)ethyl ester
VM	VM	21770-86-5	Phosphonothioic acid, methyl-, S-[2-(diethylamino)ethyl] O-ethyl ester
VX	VX	50782-69-9	Phosphonothioic acid, methyl-, S-[2-[bis(1-methylethyl)amino]ethyl] O-ethyl ester
Blister agents/vesicants			
Distilled mustard (HD)	HD	505-60-2	Bis(2-chloroethyl) sulfide
Mustard gas (H)	H	505-60-2	Bis(2-chloroethyl) sulfide
Nitrogen mustard (HN-1)	HN-1	538-07-08	Bis(2-chloroethyl)ethylamine
Nitrogen mustard (HN-2)	HN-2	51-75-2	Bis(2-chloroethyl)methylamine
Nitrogen mustard (HN-3)	HN-3	555-77-1	Tris(2-chloroethyl)amine
Phosgene oxime (CX)	CX	1794-86-1	
2-Chloroethyl ethyl sulfide	T	693-07-2	
Sesqui mustard (Q)	Q	3563-36-8	1,2-Bis(2-chloroethylthio)ethane
Ethyldichloroarsine	ED	598-14-1	
Lewisite	L-1	541-25-3	2-Chlorovinyldichloroarsine
Lewisite2	L-2	40334-69-8	Bis(2-chlorovinyl)chloroarsine
Lewisite3	L-3	40334-70-1	Arsine, tris(2-chloroethenyl)-
Methyldichloroarsine	MD	593-89-5	Arsonous dichloride, methyl-
Mustard/Lewisite	HL		
Phenyldichloroarsine	PD	696-28-6	Arsonous dichloride, phenyl-
Blood agents			
Arsine	SA	7784-42-1	
Cyanogen chloride	CK	506-77-4	
Hydrogen cyanide	AC	74-90-8	
Vomiting agents			
Adamsite	DM	578-94-9	(10-Chloro-5,10-dihydrophenarsazine)
Diphenylchloroarsine	DA	712-48-1	
Diphenylcyanoarsine	DC	23525-22-6	

Table 1. Compounds Used as CWAs (continued)

Name	Military designation	CAS number	Chemical name
Choking/Lung/Pulmonary agents			
Ammonia		7664-41-7	
Chlorine	CL	7782-50-5	
Hydrogen chloride		7647-01-0	
Phosgene	CG	75-44-5	
Diphosgene	DP	503-38-8	Trichloroacetyl chloride
Nitric oxide	NO	10102-43-9	
Perflurorisobutylene (PHIB)	PFIB	382218	1,1,3,3,3-Pentafluoro-2-(trifluoromethyl)-1-propene
Red phosphorous	RP	7723-14-0	
Sulfur trioxide-chlorosulfonic acid	FS		(Smoke mixture)
Sulfur trioxide		7446-11-9	
Chlorosulfonic acid		7790-94-5	
Titanium tetrachloride	FM	7550-45-0	
Zinc oxide	HC	1314-13-2	
Incapacitating agents			
Agent 15 (thought to be similar to BZ)			
3-Quinuclidinyl benzilate	BZ	6581-06-2	3-Quinuclidinyl benzilate
Δ-9-THC		33086-25-8	Δ-9-Tetrahydrocannabinol
China white		79704-88-4	alpha-Methylfentanyl
Fentanyl		437-38-7	Propanamide, N-phenyl-N-[1-(2-phenylethyl)-4-piperidinyl]-
LSD		50-37-3	D-Lysergic acid N,N-diethylamide
Phenothiazine		92-84-2	Phenothiazine
Thorazine		50-53-3	Chlorpromazine
Riot control/Tear			
Bromobenzylcyanide	CA	16532-79-9	4-Bromophenylacetonitrile
Chloroacetophenone	CN	532-27-4	
Chloropicrin	PS	76-06-2	
CNB	CNB		10% CN, 45% Benzene, 45% Carbon tetrachloride
CNC	CNC		30% CN in Chloroform
CNS	CNS		23% CN, 38% Chloropicrin, 38.4% Chloroform
Dibenz-(b,f)-1,4-oxazepine	CR	257-07-8	
O-chlorobenzylidene malononitrile	CS	2698-41-1	CS1, CS2, CSX all have CS as agent

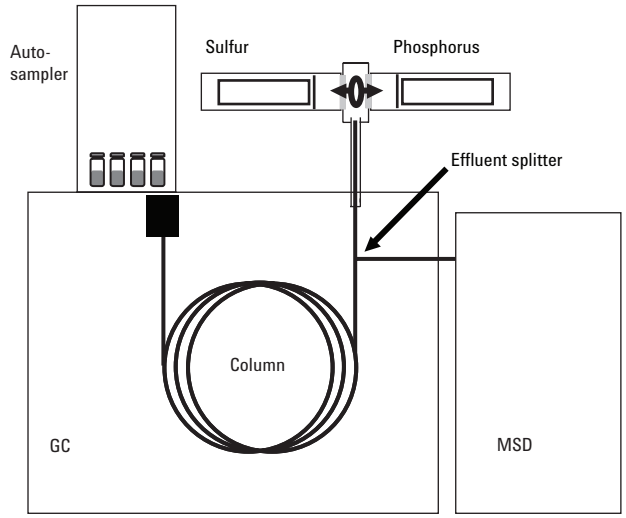

Figure 1. GC/MS system used for identification and measurement of CWAs. All aspects of data acquisition, data analysis, and report generation are automated and are controlled by Agilent GC/MS ChemStation software run on a PC (not shown).

Liquid samples or extracts of soil, wipes, swabs, etc. are sealed into sample vials and placed in the autosampler. A small volume (usually 1 µL) is injected into the GC (air samples are handled differently, as described below). The sample components are vaporized in a stream of helium carrier gas and swept through the column. They are physically separated in the column and emerge at different retention times. The effluent from the column is split between the two detectors, a dual flame photometric detector (FPD) and the Mass Selective Detector (MSD). Data can be acquired from both detectors simultaneously.

The dual-channel FPD is a rugged, highly selective detector that responds only to sulfur containing compounds on one channel and to phosphorus containing compounds on the other. This detector is particularly useful in monitoring for HD, which contains sulfur. It is also ideally suited for the detection of both conventional and designer nerve agents, most of which contain phosphorus. Sample peaks exiting the column are burned in a small hydrogen/air flame. Molecular emission spectra corresponding to sulfur are measured with an optical filter that passes light of 393 nm wavelength to a photomultiplier tube to measure the intensity. Phosphorus is measured at 525 nm. The response of phosphorus is directly proportional to the amount present. The sulfur signal is proportional to the square of the amount present (that is, doubling the amount of sulfur causes the signal size to quadruple).

Mass selective detection is a powerful technique for compound measurement, identification, and confirmation. The technique is sensitive, selective, and is able to identify complete unknowns. Sample peaks exiting the GC column are introduced into a vacuum chamber where the sample molecules are impacted by 70 EV electrons. The impact of the electrons fragments the sample molecules into ions. The ions produced are accelerated through a quadrupole mass filter where they are sorted according to their mass-to-charge ratio. The abundance of ions at each mass over a given range (usually 40–500 amu) is measured with an electron multiplier detector. The plot of abundance vs. mass of the fragments is called a mass spectrum. Each compound has a unique spectrum that serves as a fingerprint for that compound. This is the basis for compound identification. The abundance of ions measured in a spectrum is directly proportional to the amount of compound present. This is the basis of quantitative measurements.

Target Compound Analysis

For a predetermined list of compounds, target compound analysis basically asks the question “Is this specific compound present, and if so, how much?”

The steps involved in target compound analysis for CWAs are:

1. The instrument is calibrated by running standards containing known quantities of agents to be analyzed. The chromatographic retention time (RT), FPD response factor(s), response factor of the largest MS ion (target ion), and the ratios of up to three qualifier ions to the target ion are recorded for each analyte and entered into ChemStation software.
2. Samples are run under the same instrument conditions as the standards. At each RT for an agent, chromatograms for the target and qualifier ions are extracted and integrated. A quality factor based on how well the ion ratios match those of the standards is calculated. If the quality factor is sufficiently high, then the presence of the compound is assumed.
3. The amount of detected compound is calculated from the response at the target ion

compared to that of the standard. If the agent contains phosphorus and/or sulfur, the amount present can be calculated from the FPD response factors as well to serve as a cross check.

4. If a compound that would result in serious consequences (evacuations, etc.) is detected, the complete mass spectrum at the RT of that compound is examined to see if it clearly matches that of the agent. The use of RT, ion ratios, element content, and spectral matching ensures accuracy in compound identifications.

Table 2. Chromatographic Conditions

Column	15 m x 0.25 mm id x 0.25 µm film thickness HP-5MS
Inlet	Splitless mode, 250 °C; 1 µL liquid injection
Carrier gas	15.5 psi helium (constant pressure mode
Oven program	40 °C (0.4 min); 10 °C/min to 280 °C; hold 4 min
FPD	250 °C; H2 70 mL/min, Air 100 mL/min, N2 60 mL/min
MSD	Scan Mode, interface 250 °C

Figure 2 shows the chromatograms of a test mixture of 1000 ppm diesel fuel and 10 ppm each of several sulfur and phosphorus compounds in isooctane. Chromatographic conditions are given in Table 2. The sulfur and phosphorus compounds are used to simulate CWAs and the diesel fuel to simulate chemical interferences that might be present in real samples. The chromatogram labeled MS TIC represents the sum of all ions measured in each scan plotted versus time to serve as a general GC detector.

Target ion analysis for the test sample in Figure 2 works well at identifying all 12 compounds at the 10 ppm level. Even the presence of 1000 ppm diesel fuel in the sample does not interfere. For all compounds detected, the complete spectrum could be matched against that of the 143,000 compounds contained within the NIST02 compound library with high match factors. For all but the first two compounds, the spectrum taken at the apex of the peak in the TIC searched with high match factors. Because of overlapping interferences from the diesel fuel, it was necessary to subtract baseline spectra

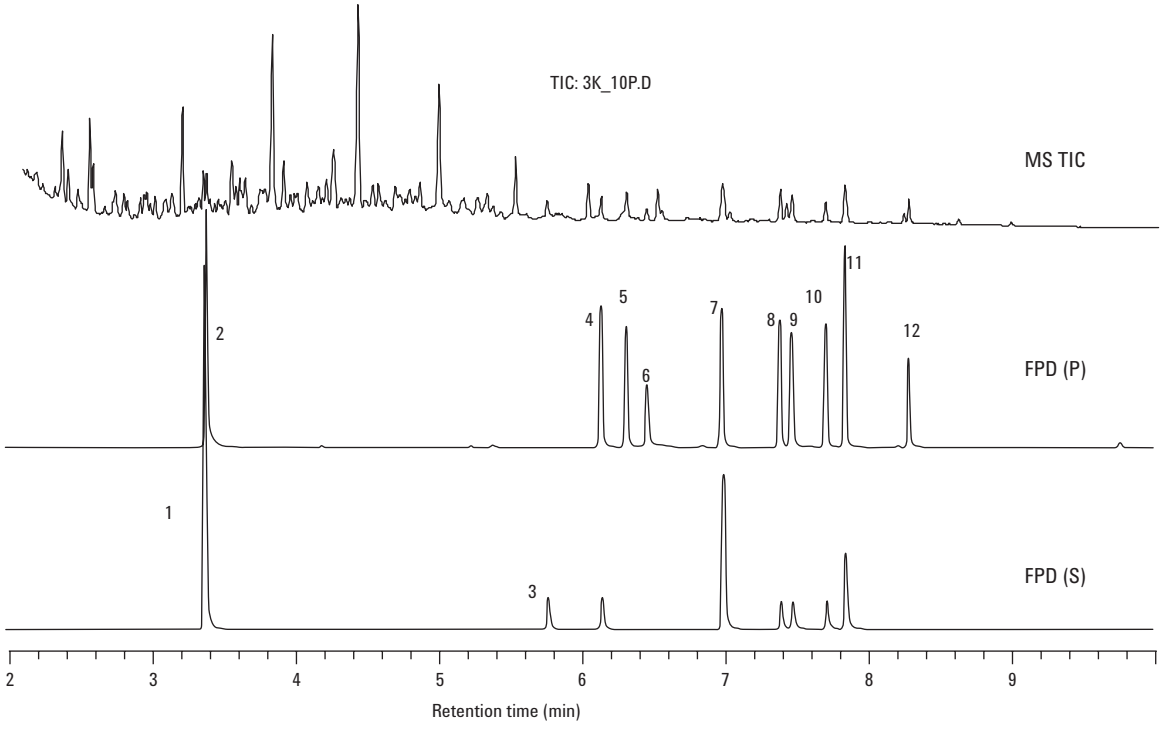

Figure 2. Chromatograms from a test mixture used to simulate CWAs. Peak identifications: (1) Di-t-butyl disulfide (2) Triethyl phosphate (3) 1-Dodecanethiol (4) Thionazin (5) Tributyl phosphate (6) Dicrotophos (7) Fonofos (8) Dichlofenthion (9) Chlorpyrifos methyl (10) Fenitrothion (11) Aspon (12) Crotoxyphos. Compounds are at 10 ppm each in isooctane. Diesel fuel added at 1000 ppm to simulate interferences.

immediately before and after the peak to obtain high match qualities for di-t-butyl disulfide and triethyl phosphate.

Figure 3 shows the baseline subtracted spectrum obtained for the triethyl phosphate peak.

A second sample of 1000 ppm diesel fuel and the 12 compounds at 1 ppm each was analyzed. With the exception of triethyl phosphate and 1-dodecanethiol, all compounds were identified with target compound analysis and confirmed by element detection. Inspection of the 1-dodecanethiol spectrum after background subtraction showed the target ion was clear, but with some interferences on the qualifiers. Given the RT match, target ion presence, and sulfur response, the compound was clearly identified.

Triethyl phosphate was less conclusive. The FPD signal clearly indicated a phosphorus compound at the correct RT, but the spectral interferences from the diesel fuel were too great to confirm the compound. In this situation, spectral deconvolution software can be used to reduce the interferences.

Automatic Mass Spectral Deconvolution and Identification Software (AMDIS)

AMDIS is provided with the Agilent GC/MS ChemStation when purchased with the NIST02 Mass Spectral Library. AMDIS was developed by the National Institute of Standards and Technology (NIST) to automatically detect chemicals in violation of the Chemical Weapons Convention. It identifies target compounds at low concentration levels in complex matrices and is used to minimize false positive identifications.

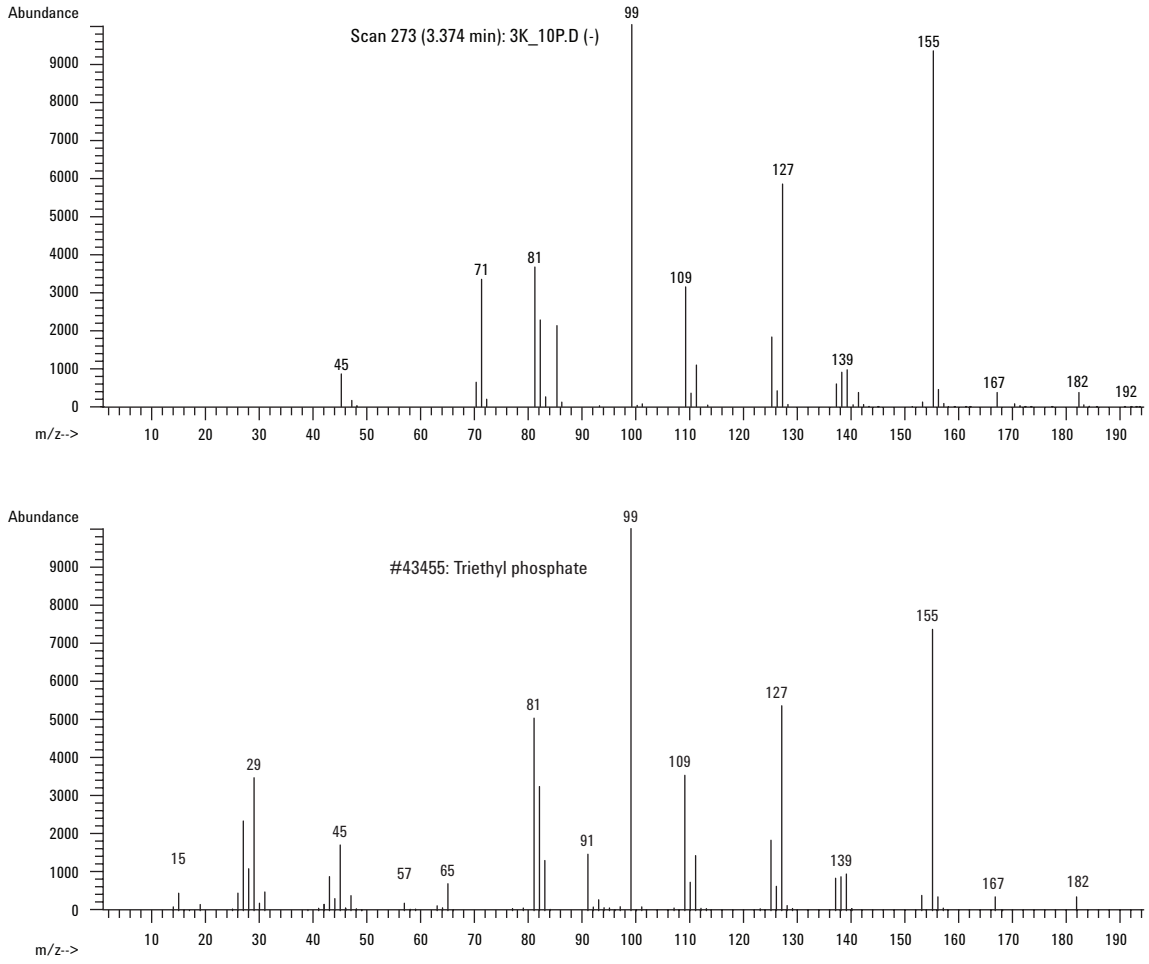

Figure 3. Baseline subtracted spectrum obtained for the triethyl phosphate peak (top) and NIST02 library spectrum (bottom).

AMDIS processes the GC/MS data file in the following steps:

1. The noise in the data is defined so that it can be compensated for. Signal-to-noise (S/N) ratio is used in all deconvolutions.
2. Scan skew is removed by mathematical correction.
3. The true peak maximum (RT) is calculated to nearest 1/10th of scan time.
4. Full spectrum deconvolution is done using all ions in spectrum. The algorithm finds ions whose abundances have the same time profile and generates corrected spectra (called components) for each chromatographic peak maximum found. These spectra have had the interfering spectra from overlapping peaks subtracted out.

The degree to which interferences are removed from the spectrum of a compound is dependent upon the relative amounts of compound and interference present, the degree of chromatographic overlap, and the number of common ions between the compound and the interference.

After processing, the "cleaned" component spectra can be used in multiple ways. Target compound analysis based on the full spectrum (instead of four ions) can be performed where each component spectrum is compared to a target library without using RT. If a component spectrum matches a target to a quality factor above a defined threshold, it is declared a hit. RT match can subsequently be used as a qualifier. The component spectra of unknown compounds not in the target library can be searched against the NIST02 main library for identification.

Figure 4 shows the result of AMDIS deconvolution on the spectrum of triethyl phosphate from the 1-ppm sample with 1000 ppm diesel interference.

Note that while the deconvolution did not remove the interferences completely, it did significantly reduce them. When the deconvolved spectrum was searched against an AMDIS target library created for these 12 compounds, the match quality was 42 (out of 100). The match was found at a time within 1.8 s of target RT. Thus, while the match quality is lower than desired, the fact that it fell at the correct RT for triethyl phosphate, taken with the phosphorus response on the FPD, confirms its presence.

Identification of Nontarget Compounds

Compounds that are not on the target list, such as designer agents, can also be identified with this system. If a suspect peak appears in the FPD chromatogram or TIC, the corresponding MS scan can be searched against the NIST 143,000 compound library. The same techniques described above can be used for obtaining a clean spectrum of the unknown. In the unlikely event the spectrum fails to match anything in the library, interpretation of the spectrum can be performed. This requires an analyst with experience in this procedure, however.

2-D GC for Analysis in High Matrix Samples

For samples containing high levels of an interfering matrix, Agilent offers an alternative system to the one described previously which incorporates a two dimensional GC (2-D GC) accessory [1]. The 2-D GC provides a much higher degree of chromatographic resolution which can be used to isolate agent peaks from interferences. Figure 5 shows the diagram of such a system.

Column 1 is the same type as used in the first system and is typically a 15 or 30 m × 0.25 mm id × 0.25 µm film thickness HP-5MS. It is connected to a single channel FPD (FPD1) through a Deans switch. Column 2 is a more polar column (for example DB-17MS) and is connected from the Deans switch to a second FPD (FPD2) and an MSD via an effluent splitter. Both FPDs are fitted with the same filters. Phosphorus filters are used for nerve agents and sulfur filters for mustard. Filters can be changed in less than 2 min. Typical chromatographic conditions are given in Table 3.

The system can be run in two different modes. The first mode is element driven and the second is similar to that described in Figure 1.

Element Driven Mode

In the element driven mode, samples are screened on column 1 and FPD1 for the presence of phosphorus compounds, for example. If no phosphorus peaks are detected, the analysis is complete. If a suspect phosphorus peak is detected, the sample is re-analyzed. The Deans switch is time-programmed to direct the flow from column 1 onto column 2 just before the suspect peak exits column 1 and back again just after peak elution. Since column 2 has a stationary phase of different polarity, the suspect

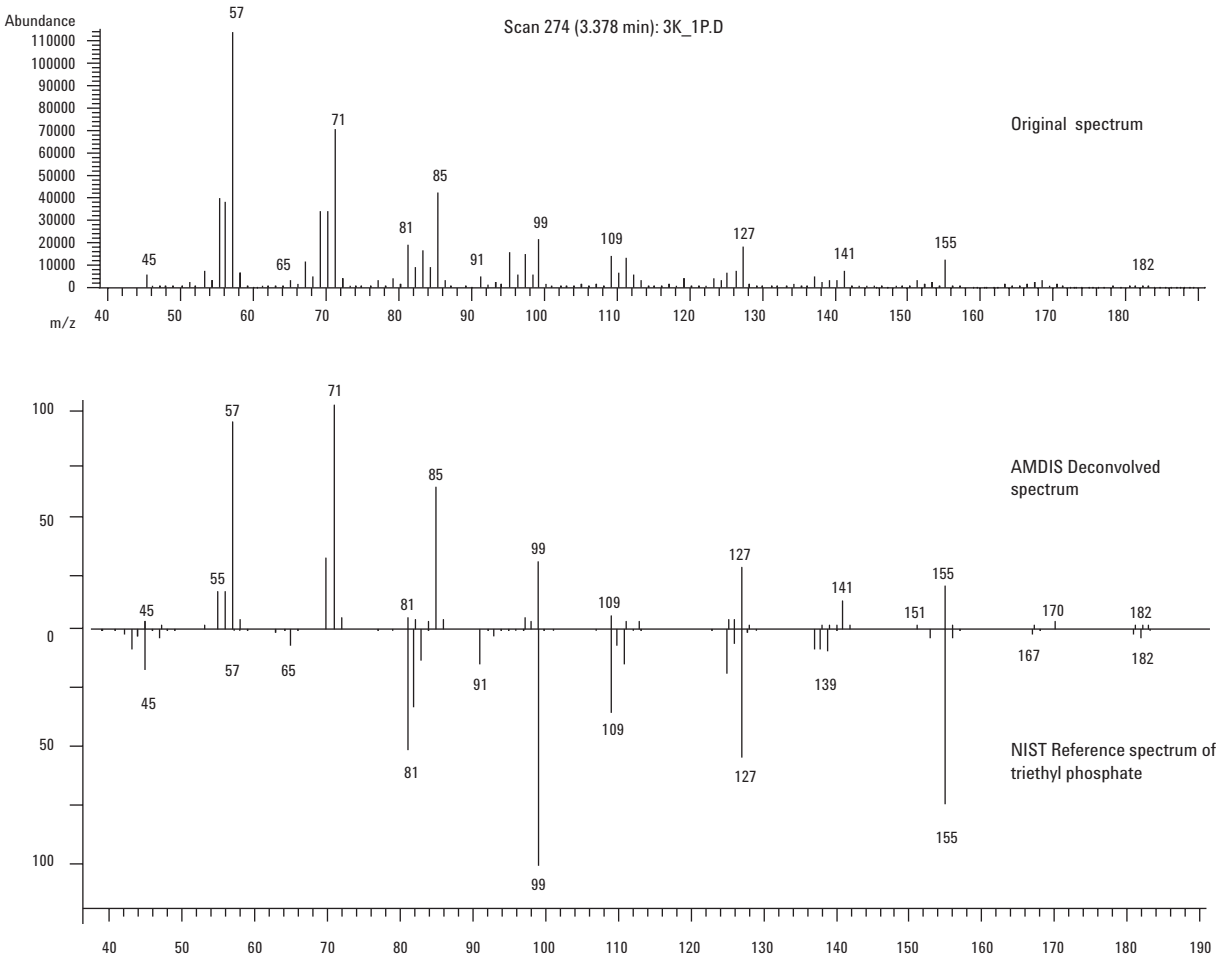

Figure 4. Original spectrum of triethyl phosphate from the 1-ppm sample with 1000-ppm diesel interference (top) AMDIS deconvolved spectrum (middle) and NIST library spectrum (bottom).

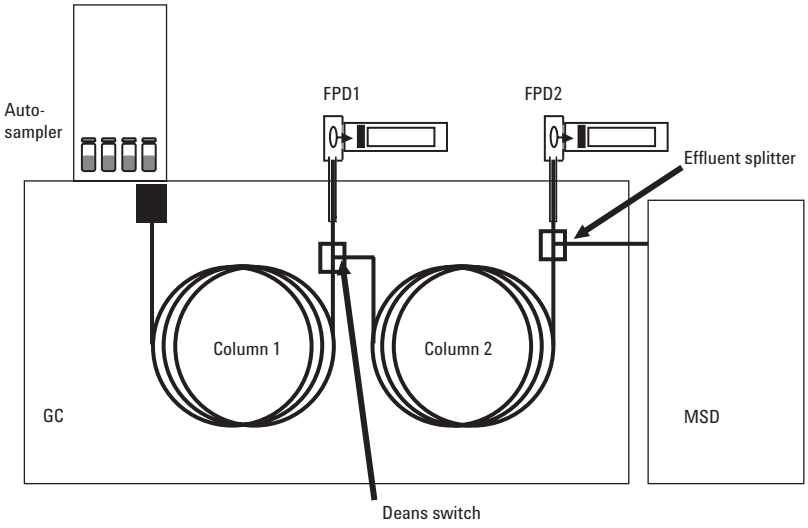

Figure 5. The 2-D GC system for analysis of high matrix samples.

Table 3. Chromatographic Conditions

Inlet	Splitless mode, 250 °C; 1 µL liquid injection
Column 1	15 m x 0.25 mm id x 0.25 µm film thickness HP-5MS
Carrier gas 1	30.3 psi helium (constant pressure mode)
Column 2	15 m x 0.32 mm id x 0.25 µm film thickness DB-17MS
Deans pressure	18.0 psi helium (constant pressure mode)
Oven program	40 °C (0.4 min); 10 °C/min to 280 °C; hold 4 min
FPD1 and 2	250 °C, H2 70 mL/min, Air 100 mL/min, N2 60 mL/min
MSD	Scan Mode, interface 250 °C

phosphorus peak will separate from those interfering compounds that co-eluted with it on column 1.

The top chromatogram in Figure 6 shows the analysis of 1 ppm each of the same compounds in Figure 2, but now with 5000 ppm diesel fuel. This fivefold increase in interference does not affect the phosphorus chromatogram of FPD1. The lower part of Figure 6 shows the chromatograms from FPD2 and the MSD for a run cutting the thionazin time range of column 1.

Note that thionazin is more polar than the interferences and is almost completely separated from them. Even at this high level of interference, the

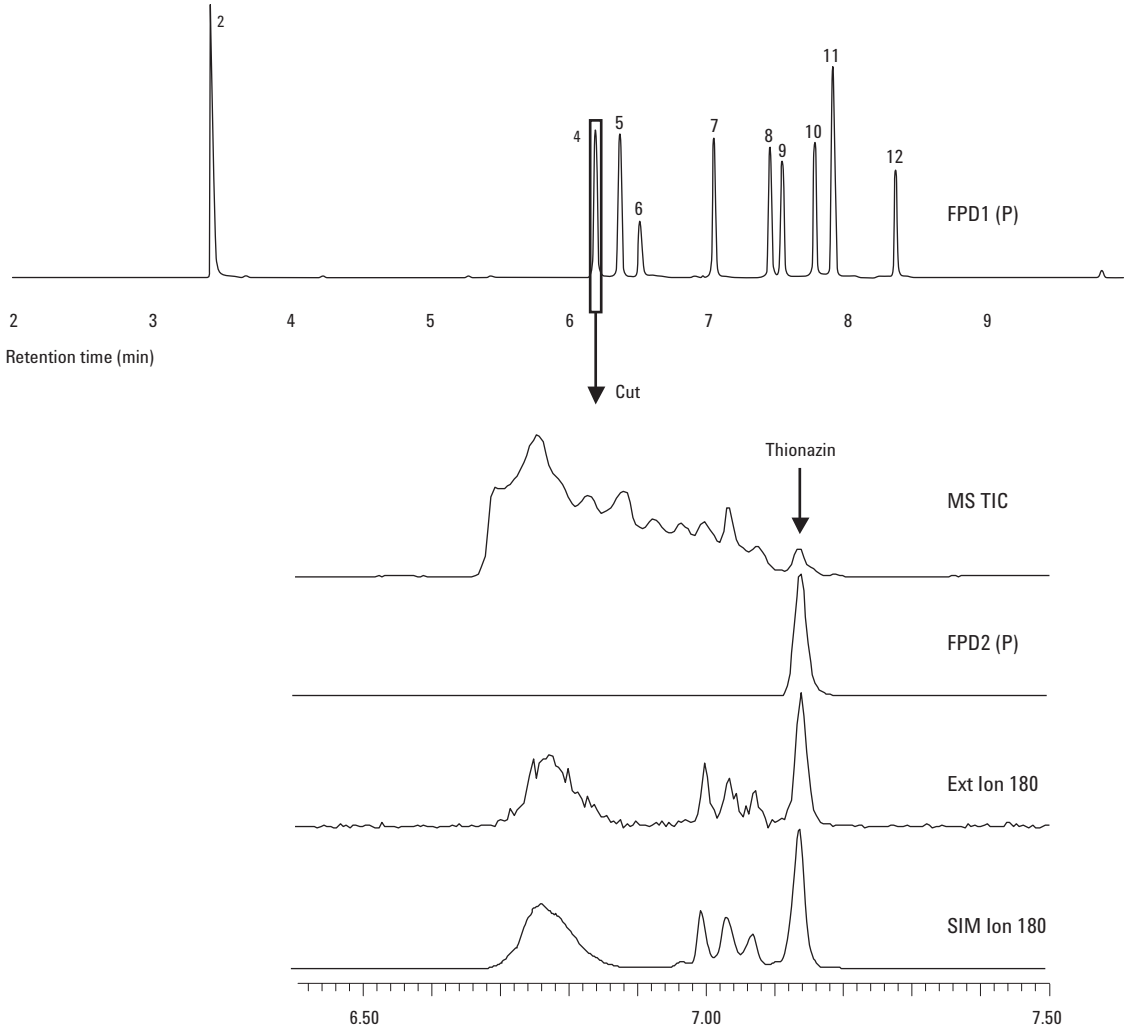

Figure 6. Top: Screening chromatogram on FPD1 of 1 ppm each of compounds from Figure 2. Bottom: MSD and FPD chromatograms from cutting 6.15-6.23 min (Thionazin) onto column 2. The MS TIC and extracted ion 180 amu chromatograms are collected in scan mode and the SIM 180 is collected in single ion monitoring mode.

separation is such that target compound analysis and spectral matching can be used directly to confirm the compound. Also, since the compound is separated from the interferences at the target ion, the analysis can be run in SIM mode at 180 amu. SIM mode at the target ion produced S/N ratios of between 300 and 1000 for the compounds when cut. The FPD phosphorus mode S/N was between 100 and 500. This suggests that for the phosphorus containing agents, detection with target ion confirmation could be done at ppb levels. The degree of separation in Figure 6 is typical of the results for most of the other test compounds as well.

Figure 7 shows the results of cutting the triethyl phosphate peak. Triethyl phosphate, as in the previous example, co-elutes with numerous diesel components on column 1. The 2-D GC improves the resolution significantly. With the higher matrix present in this sample, the compound was still identified by phosphorus FPD response at the correct RT and confirmed by target analysis with the MSD. Since the triethyl phosphate peak is completely separated from all interferences on the second column, spectral confirmation is greatly simplified. Searching the apex spectrum without baseline subtraction yielded a 99% match quality.

The chromatographic method used here is a tradeoff between analysis time and resolution. If particularly high matrix samples are encountered, using slower temperature program rates and/or longer columns can increase the chromatographic resolution of the method further. Hence, an advantage of the Agilent GC/MS is an inherent flexibility that allows the operator to adapt operating conditions to meet unforeseen needs. One is not locked into any predetermined and/or limited set of target compounds.

Cut All Mode

The second approach that can be used with the 2-D configuration shown in Figure 5 is to set the Deans switch to cut the effluent from column 1 onto column 2 all the time. This allows the MSD and FPD2 to be used in a similar fashion to the system described in Figure 1. Note that the 2-D system in this mode will have only a single channel FPD instead of two, the RTs will be longer because of transiting 2 columns, and the relative elution order will be somewhat different because the sample peaks now pass through 2 columns of different polarity.

Figure 8 shows the separation in the cut all mode. The MS and FPD data were collected simultaneously in one run and the sulfur in a subsequent run after changing the FPD filter.

The systems described thus far are powerful tools to identify and confirm the identity of previously unidentified CWAs. They can also be used for routine quantitative analysis as well, for example, in routine monitoring or during the cleanup phase of an incident.

Optimized Methods for Routine Monitoring

For those situations where the identities of the agents involved are known and the matrix interferences characterized, systems can be configured for routine monitoring. Figure 9 shows the diagram of a system configured for the analysis of CWAs in air samples.

Air samples (typically 5 L) are drawn through one of the sample collection tubes in the thermal desorption (TD) unit. Agents are trapped in the tube and after the entire sample has passed, the trap is heated briefly with a flow of GC carrier gas to remove water from the trap. After drying, the tube is heated to a higher temperature where the agents are thermally desorbed. The vaporized agents are recondensed in a focusing trap. The focusing trap

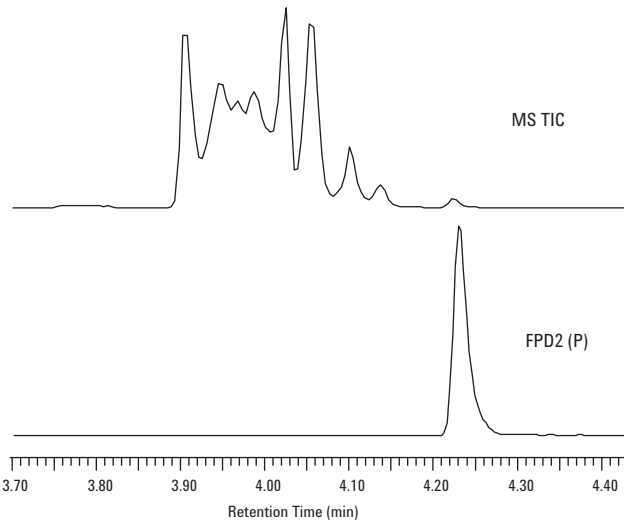

Figure 7. The 2-D GC analysis of triethyl phosphate, cut time 3.36-3.60. TIC (top) and FPD2 (bottom) signals from column 2.

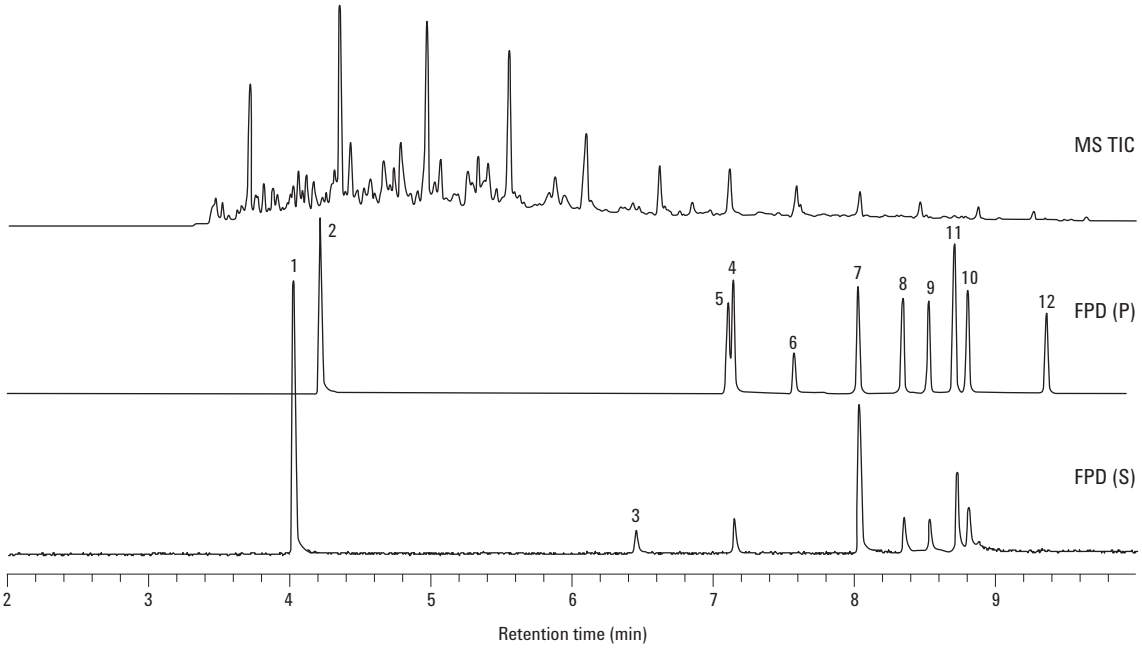

Figure 8. Cut all mode of 2-D configuration. Sample and peak number identifications same as Figure 2.

is smaller and can be heated very rapidly to produce a sharp peak. The agents are then rapidly desorbed from the focusing trap and directed into the GC, where they are split between two columns of differing polarity. The columns are each connected to single channel FPDs.

For mustard and the nerve agents, the FPDs are usually fitted with the phosphorus filter. Sulfur emission is attenuated with the phosphorus filter, but high levels will be detected. Since the required detection levels (DLs) for mustard are significantly higher than for the nerve agents, both the phosphorus and sulfur compounds can be detected at the desired levels simultaneously. The reason for using two columns in parallel is for confirmation purposes. For the agent to be declared present, it must appear at the correct RT on both columns and with the correct ratio of peak areas.

The TD system in Figure 9 contains two parallel trapping channels. This allows one channel to be trapping the next sample while the other is being desorbed and analyzed. This maximizes the sample throughput.

The Agilent GC ChemStation, which aquires the data, calculates the results, and prints the report, controls the entire system. If desired, the system can be programmed to trigger an alarm when detected agent concentrations exceed preset threshold values.

The analysis time and minimum detectable levels achievable with this system depend on the specific agent(s) to be detected and the types and amounts of interferences present.

Figure 10 shows example chromatograms for sarin (GB), soman (GD), and mustard (HD). Because of the large concentration gain with TD and the sensitivity of the FPDs, the agents can be measured to below the TWA levels for each compound. The analysis time is typically 10 min or less (depending on the matrix).

Retention Time Locking (RTL)

One of the most important parameters in the identification of compounds by GC is RT. RTs in GC vary from column-to-column and instrument-to-instrument due to the sum of small variations in column dimensions, oven temperature, inlet pressure and outlet pressure, etc. Agilent ChemStations have proprietary software available called retention time locking (RTL), which greatly reduces these RT variations [2,3]. RTL can be used to match RTs between any 6800 Series GC or GC/MS system located anywhere in the world.

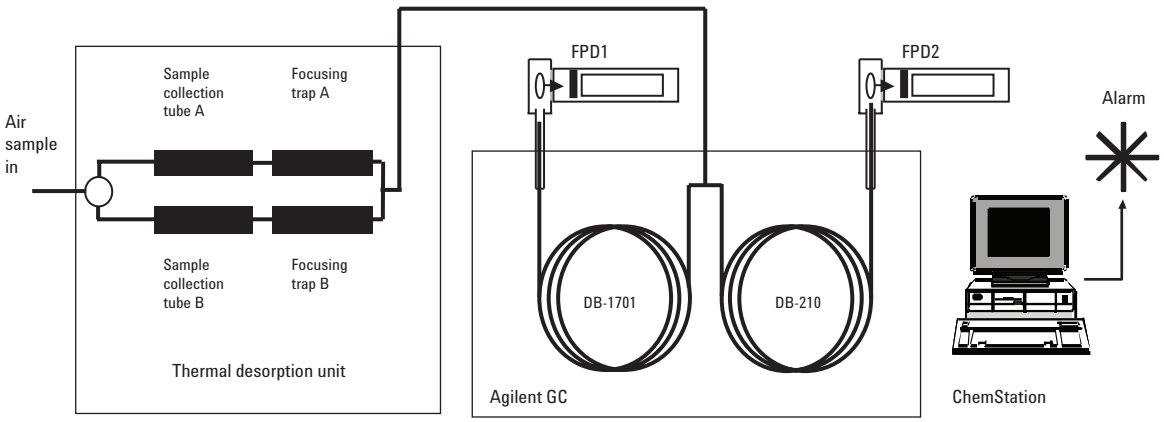

Figure 9. System for the routine monitoring of agents in air.

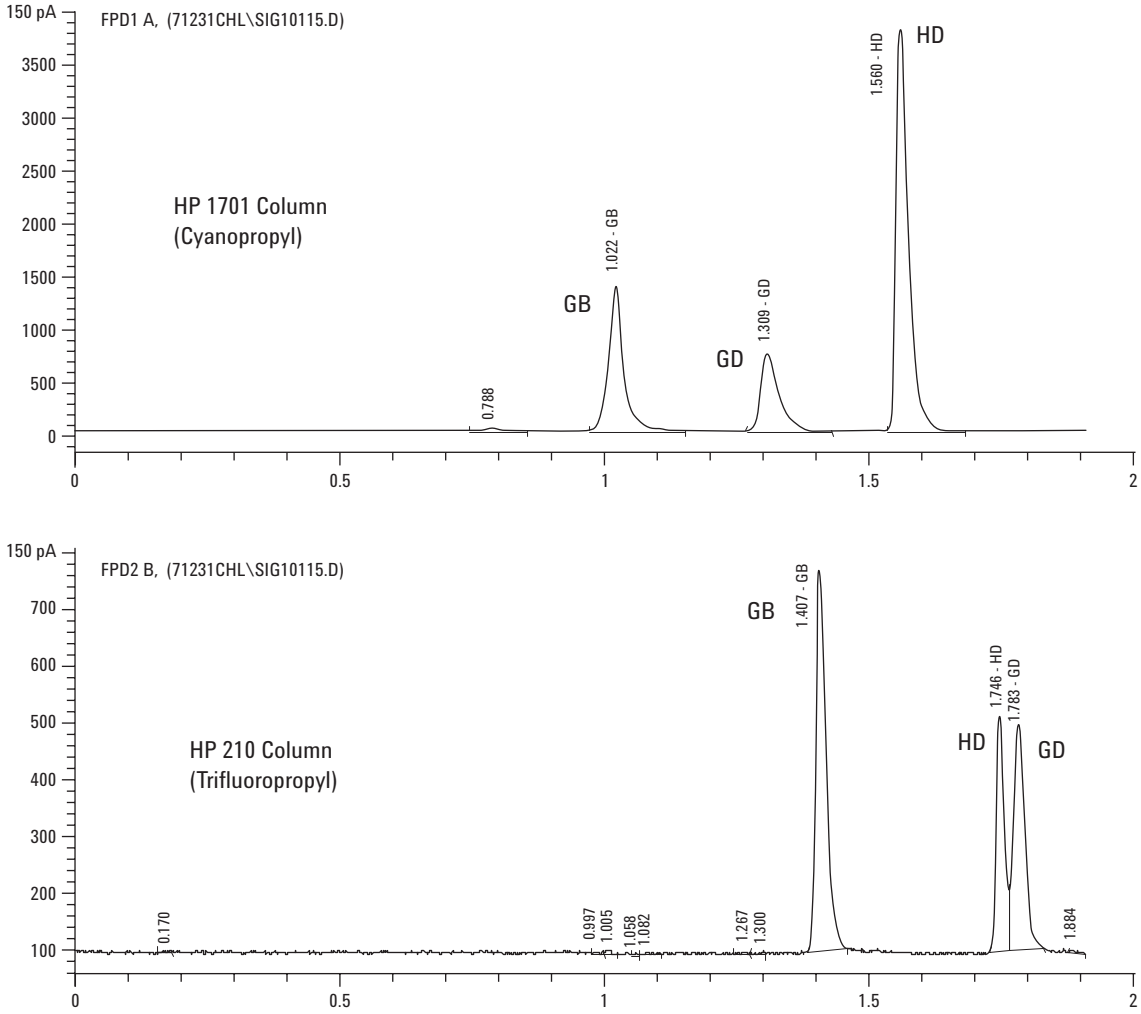

Figure 10. Chromatograms of sarin (GB), soman (GD), and mustard (HD) with TD GC system shown in Figure 9.

This capability makes instrument setup, method transfer, data analysis, data sharing, and data interpretation easier and more accurate. With RTL, RTs can typically be matched to within 0.030 min. This is particularly useful in the analysis of CWAs. Since CWAs are tightly controlled, standards may not always be immediately available to laboratories that encounter them. RTL allows methods developed with standards to be transferred to laboratories without standards and still obtain the same RTs. This permits recognition of peaks based on RT even though no standard is available. The concentration of a CWA whose identity is confirmed by MS and/or FPD can be estimated from the response factor of other similar non-CWA compounds, like pesticides. While quantitation with direct standardization is clearly the most accurate approach, this surrogate calibration can at least give a useful preliminary estimate.

Figure 11 shows the FPD phosphorus chromatograms of the test mix run in three very different configurations but having matched RTs via RTL. The top chromatogram is from the system in Figure 2, using a column outlet splitter. The middle chromatogram is the same GC and column, but now with the column outlet connected to the Deans switch in a 2-D configuration. The bottom chromatogram is from a different GC in a different location and the column is actually a 30-m version of 15-m column used in the other chromatograms. Even with these disparate configurations, the RTs are well matched.

Summary

The combination of precise GC RTs, element information, and mass spectral data offers a comprehensive solution to the task of detecting and identifying CWAs. The complimentary nature of these techniques provides corroborating information to support agent identifications.

The splitter configuration is useful for those applications where the levels of interferences are not extreme. The simultaneous sulfur, phosphorus, and mass spectral detection combined with precise RTs constitute a powerful screening and analysis tool for CWAs.

For applications where agents at very low levels need to be identified in high levels of interferences, the 2-D GC approach offers significant advantages. The ability to resolve the agents from

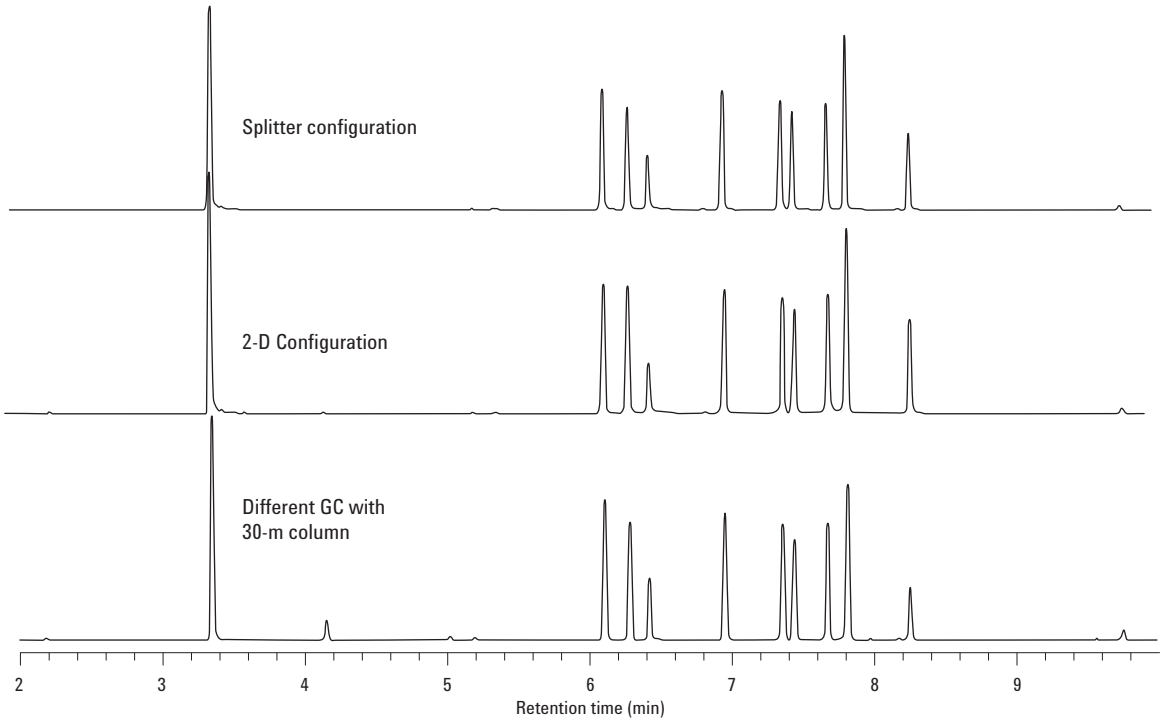

Figure 11. RTL allows matching of RTs beween different systems and/or configurations running the same method.

interferences provides both easier identity confirmations and lower DLs for target analysis. This configuration is especially useful for nerve and designer agents.

Configuring a GC with two FPDs and a TD sampling device provides an optimized package for routine monitoring of airborn levels of CWAs. The use of precise RTs, element selective detection, and dual column confirmation provides a reliable and cost effective means of measuring CWAs down to very low levels.

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