Screening for Hazardous Chemicals in Homeland Security and Environmental Samples Using a GC/MS/ECD/FPD with a 731 Compound DRS Database

Application Note

Homeland Security, Environmental

Authors

Bruce Quimby
Mike Szelewski
Agilent Technologies, Inc.
2850 Centerville Road
Wilmington, DE 19808
UASA

Abstract

Response to homeland security or environmental incidents involving hazardous chemicals requires first, the rapid and accurate identification of the chemical agent(s) involved and second, the quantitative measurement of that agent in large numbers of samples to aid in managing the response. Given the unknown nature of the analytes and the complexity of matrices that could be encountered, developing analytical methods for this analysis is challenging. The approach described in this work uses a gas chromatography/mass spectrometry (GC/MS) system with a micro-fluidic splitter added to the end of the column. The splitter divides the column effluent between the MS and either a dual-wavelength flame photometric detector (DFPD) or a micro electron-capture detector (μECD) and a single-wavelength FPD. This approach allows the simultaneous collection of MS and two channels of selective GC detector data from a single injection. This multisignal configuration provides: full-scan MS data for library searching, selective ion monitoring (SIM) data for trace analysis, μECD and FPD data for excellent selectivity and sensitivity in complex matrices. The systems use retention time locking (RTL) to produce retention times (RTs) that precisely match those in a 731 compound database of hazardous chemicals. Deconvolution Reporting Software (DRS) is used to provide fast and accurate interpretation of the MS data, especially in samples with high matrix contamination. The combination of selective GC detectors, SIM/Scan, and deconvolution makes a very powerful hazardous chemical analysis system that shows significant progress toward the above goals.

Introduction

In recent years, there has been increasing concern over the release of hazardous chemicals through either accidental or intentional acts. Both the homeland security and environmental communities recognize the need for preparing analytical laboratories that can respond quickly to such incidents. The terms toxic industrial chemicals/toxic industrial materials (TIC/TIM) are used in homeland security to refer to hazardous chemicals, while the environmental community uses different terminology like hazardous materials. In either case, the challenge is to develop laboratory methods with the capability of identifying any hazardous chemical(s) involved in an incident and to be able to measure its concentration in collected samples.

There are several significant challenges to face when developing methods for this analysis. The methods must able to:

- Rapidly and accurately identify the specific toxic agents involved
- Measure concentration correctly at high levels of agent at the epicenter (high dynamic range)
- Measure concentration correctly at low levels of agent at perimeters and during decontamination (low detection limits)

- Be highly selective over matrix interferences (wood smoke, fuels, burning tires, etc.) to minimize both false positives and false negatives
- Indentify as many toxic agents as possible
- Handle large numbers of samples

It is clear that there is no single analytical technique that can be used for detecting all possible hazardous chemicals. However, one technique that is widely applicable for the identification and measurement of broad classes of hazardous chemicals is GC/MS. GC/MS is widely used in laboratories worldwide for the analysis of thousands of different chemicals.

GC/MS methods are typically developed to analyze between 10 and 100 individual compounds. A target compound is deemed to be present if the target ion and two or three qualifier ions, with specific abundance ratios, fall within a defined RT window. The identity of the target may be further confirmed by comparison of the scan at the apex of the peak with a library reference spectrum.

Matrix interferences are usually minimized by optimizing a combination of the sample preparation, GC, and MS parameters. Since most methods only deal with at most a few matrix types, the ions chosen for identification purposes can be selected such that they are minimized in the matrix. With the limited number of targets addressed by the method, recalibration of response factors, RTs, and qualifier ion abundance ratios can be accomplished with the injection of a few calibration mixtures.

General screening methods for very large numbers of targets in widely varying and complex matrices offer a new set of challenges for the method developer. When screening for hundreds of targets, several factors must be addressed:

- Use of sample preparation to reduce matrix interferences is now significantly limited because rigorous cleanup steps may unintentionally remove targets. This reduced level of cleanup can result in significantly higher levels of matrix interferences to contend with.
- Recalibration of response factors, RTs, and qualifier abundance ratios is difficult or impossible because of the large number of targets.
- The methods may be deployed in laboratories without access to standards for all of the targets.
- The time required for data review of hundreds of targets in complex matrices can become unmanageably large.
- Even with a very large database of targets, it is possible that hazardous chemicals not in the target list could be present in a sample.

Recently, several techniques have become available to help address the above set of challenges. RTL produces RTs that precisely match from instrument-to-instrument and to those in a database [1]. This eliminates the need for recalibration of the individual RTs and timed events. The introduction of reliable and inert microfluidic splitters allows for the simultaneous collection of mass spectral data and, for example, phosphorus, sulfur, and/or electron capture data [2]. The selective detector chromatograms can highlight suspect compounds even if they are not in the MS target list. They can also offer an alternative means for quantitation of target analytes.

The introduction of the synchronous SIM/Scan feature allows for the simultaneous acquisition of both full scan and SIM data from the same injection [2, 3]. The scan data can be used for screening the full list of targets in the database while the SIM data looks for a high priority subset of compounds down to very low levels.

One of the most significant tools developed for dealing with complex matrices is Agilent's Deconvolution Reporting Software (DRS) [4]. It uses advanced computational techniques to extract the spectra of targets from those of overlapped interference peaks. It then compares the extracted spectrum with a library to determine if the target is present. Any hits are confirmed by searching against the main NIST MS reference library. This process is automated and provides significant time savings in data interpretation. Since it deals with the entire spectrum instead of just four ions, DRS can often correctly identify a target in the presence of interferences where the typical approach would fail. The use of DRS substantially reduces the number of both false positives and false negatives.

This application note describes the combination of the above techniques with a database of 731 hazardous chemicals, the Agilent Hazardous Chemical DBL (HCD), to be used for screening purposes. The compounds were chosen because of their significance in environmental or food safety analysis. The reasoning is that if the materials are manufactured in significant quantities and are toxic, they would be likely to appear in an

environmental method. The pesticides are included because many exhibit toxicity.

The list is comprised of:

- Chlorinated Dioxins and Furans: EPA 8280A, 10 compounds
- Polychlorinated biphenyls: EPA 8082, 19 compounds
- Volatiles: EPA 502/524, 60 compounds
- Semivolatiles: EPA 8270C Appendix IX, 140 compounds
- Pesticides: Agilent RTL Pesticide Database (adapted), 567 compounds
- Total: 796 compounds, with 65 compounds in two groups, or 731 individual compounds

The names of all the compounds in the database are listed in Appendix A at the end of this note.

The above list by no means contains all of the hazardous chemicals that could be encountered. However, it does screen for a large number of known hazards and with the addition of selective detection can highlight other nontarget compounds that may be of interest.

The chromatographic conditions chosen for development of the database are general in nature and are compatible with the analysis of other types of compounds beyond those in the table. For example, laboratories with access to calibration standards for chemical warfare agents (CWA) can add CWA data to the tables and screen for them as well.

The RTs for compounds in the database were collected with the column outlet pressure at 3.8 psig using a microfluidic splitter. This was done to assure that the RTs observed during sample analysis would closely match those in the database when a microfluidic splitter or QuickSwap is used.

The chromatographic conditions for the database were chosen to be compatible with the method translation technique. Constant pressure mode was used in the GC inlet so that method translation can be used to precisely time scale the methods for faster operation [5]. Provided with the Agilent Hazardous Chemicals DBL are the files to run the analysis precisely threefold (3X) and sevenfold (7X) faster than the primary database (1X). Also, each of the three-speed variations of the database are provided in two forms: one with the entire set of 731 compounds and one with the 36 aromatic hydrocarbons removed. The latter is provided for use with samples known to contain fuels and where the fuel components are not of interest. In the examples shown below the database with hydrocarbons removed was used, since fuels were used as prototype matrices.

System Configuration

The system configurations used are shown in Figure 1A and 1B.

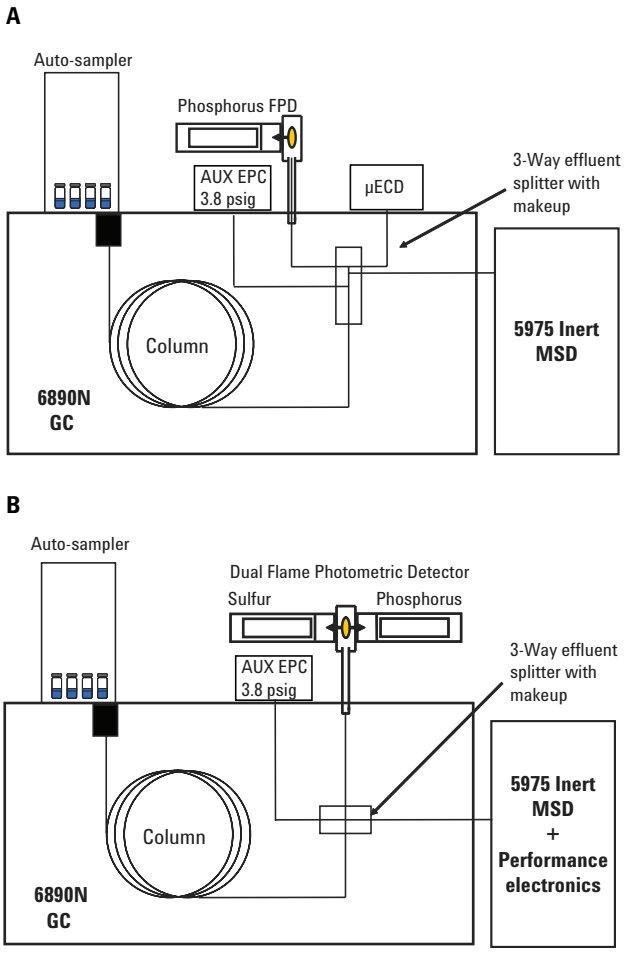


Figure 1. System configurations. A). GC/MS/ECD/FPD system used for 1X and 3X screening analyses. B). GC/MS/DFPD system used for 7X screening analyses.

Key components are:

Fast Oven

The primary 1X method only requires the 120V oven. With the 6890N 240V oven (option 002), the screening analysis method can be run precisely three times faster (14.33 min) using a 15-m HP-5MS column. If the 240V GC is further equipped with SP1 2310-0236 (puts MSD interface in back of oven under rear injection port) and

using the G2646-60500 oven-insert accessory, the speed can be increased to seven times faster (6.14 min) with a 5-m HP-5MS column. Note that use of the oven insert prevents use of the front inlet and detector positions. Only one detector is available for splitting. The DFPD is a good choice for this configuration, as it uses only one detector position but generates two signals.

µECD

The 6890N Option 231 is a µECD. The signal from the electron capture detector (ECD) is collected, stored, and processed by the MS ChemStation simultaneously with the MS data. ECDs are selective in nature and exhibit very sensitive response to halogenated compounds, with detection limits below 1 pg for polyhalogenates. They also respond to several other functional groups like nitro compounds. They do, however, also respond to some fairly low-priority compounds, like phthalate esters. The ECD data can be used in several ways. Nontarget halogenated or nitro compounds are highlighted. The presence of an electrophore at the RT of an identified compound can be used to support confirmation of identity. The response on the ECD can be used for quantitative analysis, but only after calibration with a standard, as the response factors are compound dependent and can vary significantly with compound class.

Single FPD

The 6890N Option 240 is a single FPD. It is used to selectively detect either sulfur or phosphorus. The detector is usually run in the phosphorus mode to highlight such compounds as organophosphorus pesticides and nerve agents. In the phosphorus mode, the detector is highly selective ($>10^6$) with a very low (~0.050 pg) detection limits for phosphorus. The ability of the FPD to uncover nontarget organophosphorus compounds like new pesticides or designer nerve agents is especially helpful. The presence of phosphorus at the RT of an identified compound can be used to support confirmation of identity. Because the response per unit weight of phosphorus is relatively consistent from compound to compound, the FPD can be used for semi-quantitative analysis in situations where no calibration standard is available for an identified analyte.

Dual FPD

The 6890N Option 241 is a DFPD with two optical detection channels that measures sulfur and phosphorus simultaneously. The DFPD sulfur response is also selective ($>10^4$) and sensitive (detection limits <10 pg) , although not as much as phosphorus. The sulfur signal is also quadratic with respect to the amount of sulfur injected. It is often used to detect sulfur-mustard agents and for confirmation of sulfur-containing pesticides. The response per unit weight of sulfur is relatively consistent from compound to compound, but varies more than that of the phosphorus signal.

Microfluidic Splitter

The 6890N Option 890 (3-way splitter) or Option 889 (2-way splitter) uses diffusion-bonded plate technology combined with metal column ferrules to make an inert, easy-to-use, leak free, high-temperature column-effluent splitter. The splitter uses Auxiliary EPC for constant pressure makeup (6890N Option 301). The Auxiliary EPC makeup can be pressure programmed at the end of the run to higher pressure, while at the same time the inlet pressure is lowered to near ambient. This causes the flow in the column to reverse direction, backflushing heavy materials out the split vent of the inlet. Backflushing can greatly reduce analysis times for samples that contain high-boiling matrix components [6]. The Aux EPC also allows column changing and maintainance without venting the MSD. When the column fitting is removed from the splitter, helium from the makeup supply purges the fitting, preventing air from entering the MSD. If the column is attached to the splitter but removed from the inlet, helium flows backwards through the column and out the inlet end. Inlet maintainance or column headtrimming can be done without cooling and venting the MSD to prevent sucking air into a hot source.

MSD System

The 5975 inert MSD with performance turbo (G3243A) or 5973N inert MSD with performance electronics and performance turbo (G2579A), EI (electron impact ionization mode) MSD is used. These configurations provide faster full scan rates while maintaining sensitivity. The scan rates are compatible with the narrower peaks generated by fast chromatography. The performance turbo pump is required to handle the higher flows associated with the screening method.

Synchronous SIM/Scan

The D.02.00 (or higher) revision of the Agilent MSD ChemStation is used because it supplies the synchronous SIM/Scan feature. SIM/Scan operates by collecting SIM data every other cycle and scan data on alternate cycles throughout the entire chromatogram. The signal-to-noise performance of the collected SIM and scan data is virtually identical to that obtained with SIM-only and scan-only

methods. As with conventional SIM methods, not all 731 targets can be monitored in a single run due to the required time separation between SIM groups. In general, the acquisition of SIM data is set up to collect high-priority targets at very low levels. Examples would be the chlorinated dioxins and CWAs.

DRS Software (G1716AA)

Spectral deconvolution of the MS data enables identification of analytes in the presence of overlapped matrix peaks [4]. This significantly reduces chromatographic resolution requirements, which allows detection of targets in higher levels of matrix or can be used with fast chromatography to shorten analysis times. DRS uses the AMDIS deconvolution program from NIST, originally developed for trace chemical-weapons detection in complex samples. DRS presents the analyst with three distinct levels of compound identification:

- ChemStation, based on RT and four-ion agreement
- AMDIS, based on "cleaned spectra" full-ion matching and locked RT
- NIST05 search using a 163000 compound library

Hazardous Chemical DBL (G1671AA)

This supplies the mass spectral library, method, and DRS files for the 731 compound-screening method.

Instrument Operating Parameters

The instrument operating parameters used (unless noted otherwise) are listed in Table 1. These are starting conditions and may have to be optimized.

The split/splitless injection port was used for all work described here. It was chosen for its flexibility, allowing splitless injections for clean samples and split injections for dirty or high-concentration samples. It is also compatible with column backflushing. For all cases (except ambient headspace), the inlet liner used was the 4-mm id Siltek Cyclosplitter (Restek, part number 20706-214.1). This inlet liner was found to be of low activity, as it does not contain glass wool. Proper mixing for split injections is done by the internal liner geometry. Except as noted, split injections with a split ratio of 10:1 were used. For high matrix samples, this roughly matches the amount of matrix injected with the column capacity. If excess amounts of matrix are injected, the RTs of targets can shift. Split injection is also the easiest and most reliable way of screening samples for analytes ranging in volatility from gases to large polynuclear aromatic hydrocarbons (PAHs). Splitless injections are usually incompatible with the lowest boiling volatiles due to problems with the solvent. For low matrix samples where semivolatiles are of interest, splitless injections can be used.

For ambient headspace analysis [7], the conditions are listed separately at the bottom of Table 1. The liner used for ambient headspace was 1-mm id straight through (no glass wool) and Siltek coated (Restek, part number 20973-214.5). The auto injector parameters are critical in ambient headspace and are listed in Table 1. The volatiles samples run by ambient headspace were prepared as described in Reference 7.

While the targets in the table cover a very broad range of boiling points, it is usually not practical to screen for all of them in one run. This is because an analysis for semivolatile compounds would be done with a solvent that would occlude the lowest boiling volatiles in the table. Conversely, a method for injecting the lowest boiling compounds would usually not be suitable for the highest boiling. The MSD solvent delays listed in Table 1 are based on isooctane as the solvent in a semivolatiles analysis. If a lower boiling solvent is used, it may be possible to reduce these delays accordingly.

Some of the target compounds were found to have sufficiently high boiling points to require higher inlet and detector temperatures. These were the higher molecular weight PAHs, the polychlorinated dioxins, and the polychlorinated furans. For these compounds the inlet temperature, MS source, and transfer line were also raised to 300 °C. Without this increase in temperature, the compounds would exhibit tailing and in some cases reduction in signal. The trade-off with temperature is that the performance of some thermally labile compounds is degraded at the higher temperatures.

The MSD data acquisition sampling rates listed in Table 1 are for scan mode only. For volatiles analysis, the scan rate is increased one step. It is also increased one step when SIM/Scan is used. In SIM/Scan mode the SIM dwell time was set to 40 milliseconds for each ion monitored.

The microfluidic splitter parameters are chosen to provide the desired flow ratio between detectors while meeting the flow requirements of the detectors used. A primary consideration is to make sure that the flow to the MSD does not exceed ~4 mL/min while collecting analyte data. It was also desired to split the effluent equally between the DFPD and MSD in the 2-way split configuration. In the 3-way configuration, the split to the μECD was reduced

Table 1. Gas Chromatograph and Mass Spectrometer Conditions

	Original 1X Method	3X Method	7X Method
GC			
Agilent Technologies 6890N			
7683 Autoinjector and Tray			
Inlet	EPC Split/Splitless	EPC Split/Splitless	EPC Split/Splitless
Mode	Constant pressure	Constant pressure	Constant pressure
Injection type	Split	Split	Split
Injection volume (uL)	1.0	1.0	1.0
Inlet temp (°C)	250	250	250
Pressure, nominal (psig)	31.17	23.96	8.84
RT Locking compound	Tripropyl phosphate	Tripropyl phosphate	Tripropyl phosphate
RT Locking time (min)	12.874	4.291	1.839
Split ratio	10:1	10:1	10:1
Gas saver	Off	Off	Off
Gas type	Helium	Helium	Helium
Oven			
Voltage (VAC)	120 or 240	240	240 (and pillow)
Initial oven temp (°C)	40	40	40
Initial oven hold (min)	2	0.667	0.286
Ramp rate (°C/min)	10	30	70
Final temp (°C)	300	300	300
Final hold (min)	15	5	2.143
Total run time (min)	43.00	14.33	6.14
Equilibration time (min)	0.5	0.5	0.5
Column			
Type	HP 5-MS inert	HP 5-MS	HP 5-MS
Agilent part number	19091S-433i	19091S-431	Custom
Length (m)	30	15	5
Diameter (mm)	0.25	0.25	0.25
Film thickness (um)	0.25	0.25	0.25
Outlet pressure (AUX EPC, psig)	3.8	3.8	3.8
FPD or DFPD			
Type	Single, Phosphorus	Single, Phosphorus	Dual, S and P
Temperature (°C)	250	250	250
Hydrogen flow (mL/min)	75	75	75
Air flow (mL/min)	100	100	100
Mode: Constant makeup flow			
Nitrogen makeup flow (mL/min)	60	60	60
Data rate (Hz)	5	10	10
µECD			
Temperature (°C)	30 0	300	N/A
Nitrogen makeup flow (mL/min)	60	60	N/A
Mode: Constant makeup flow			
Data rate (Hz)	5	10	N/A
AUX EPC Pressure			
Pressure (psig)	3.8	3.8	3.8
Gas type	Helium	Helium	Helium

Table 1. Gas Chromatograph and Mass Spectrometer Conditions (Continued)

MSD			
Agilent Technologies	5975 inert MSD	5975 inert MSD	5973 inert with Performance Electronics
Tune file	Atune.U	Atune.U	Atune.U
Mode	Scan	Scan	Scan
Solvent delay (min)	2.20	0.82	0.40
EM voltage	Atune voltage	Atune voltage	Atune voltage
Low mass (amu)	35	35	35
High mass (amu)	565	565	565
Threshold	0	0	0
Sampling	1	1	0
Scans/s	5.23	5.23	9.46
Quad temp (°C)	150	150	150
Source temp (°C)	230	230	230
Transfer line temp (°C)	280	280	280
Splitter			
Type	3 way	3 way	2 way
6890N option number	890	890	889
Flow ratio	1:1:0.1 MSD:FPD:ECD	1:1:0.1 MSD:FPD:ECD	1:1 MSD:DFPD
[Deactivated fused silica tubing]			
MSD restrictor length (m)	1.44	1.44	1.44
MSD restrictor id (mm)	0.18	0.18	0.18
FPD/DFPD restrictor length (m)	0.53	0.53	0.53
FPD/DFPD restrictor id (mm)	0.18	0.18	0.18
ECD restrictor length (m)	0.51	0.51	N/A
ECD restrictor id (mm)	0.10	0.10	N/A
Ambient Headspace			
Inlet	EPC Split/Splitless		
Mode	Constant pressure		
Injection type	Split		
Inlet temp (°C)	200		
Pressure, nominal (psig)	31.17		
RT locking compound	Tripropyl phosphate		
RT locking time (min)	12.874		
Split ratio	1:1		
Gas saver	Off		
Gas type	Helium		
Autoinjector			
Sample washes	0		
Sample pumps	3		
Injection volume (µL)	50		
Syringe size (µL)	100		
PreInj Solvent A washes	0		
PreInj Solvent B washes	0		
PostInj Solvent A washes	1		
PostInj Solvent B washes	3		
Viscosity delay (s)	5		
Plunger speed	Fast		
Pre-injection dwell (min)	0		
Post-injection dwell (min)	0		
Sampling depth (mm) [critical!]	20		

to 1/10th that going to the MSD and FPD because of the extreme sensitivity of the detector. The lengths and diameters of the detector restrictors were calculated using the spreadsheet calculator included with the splitter.

The peak recognition windows used in the Agilent ChemStation were set to ±0.2 min and in AMDIS to 12 s. these values were found to be sufficiently wide enough to compensate for some RT drift yet narrow enough to minimize the number of false positives. The minimum match factors setting in AMDIS was set to 45. This value seemed to give the least number of false positives and false negatives.

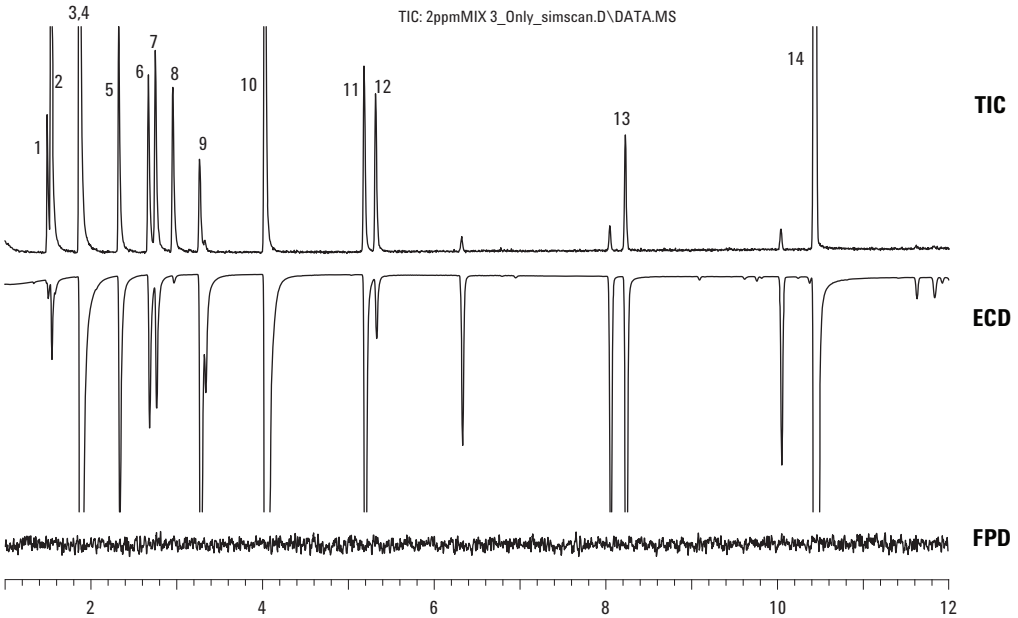
Results

Volatiles

To evaluate the HCD method for volatiles analysis, headspace injection was chosen. Headspace injections are usually done with an automated heated sampler specifically designed for the purpose. Ambient headspace [7] is a variant of the technique that uses a gastight syringe in the liquid autosampler and injects the headspace from a 2-mL vial. It is unheated, and is thus limited to compounds that are volatile at room temperature. Ambient headspace works well for the analysis of relatively non-polar volatiles in water. It is convenient for labs that need to screen samples for volatiles but do not have a dedicated headspace sampler. The conversion from liquid sampling to ambient headspace simply requires changing the inlet liner and the autosampler syringe.

Figure 2 shows the chromatograms from a run using the system in Figure 1A. A mixture of 14 halogenated volatiles was spiked into water at 2 ppm. Fifty microliters of the approximately 1 mL of headspace in the vial was injected. With the exception of peaks 3 and 4, which coelute, the compounds are well separated. The ECD chromatogram is inverted for comparison with the MS total ion chromatogram from the full-scan data. All of the volatiles respond on the ECD, although the response to compounds 1, 2, and 8 is significantly lower than for the rest of the compounds. In general with an ECD the response to a compound increases dramatically with the number of halogens in the molecule. Since none of the compounds contain phosphorus, there is no response on the FPD.

Figure 3 shows the DRS report for the sample. For each compound identified, the RT, Chemical Abstracts number (CAS#), and compound name are listed. A line is generated in the report if a compound is found by either the Agilent ChemStation, AMDIS, or both.



Peak identities

1) 1,2-Dichloroethane
2) 1,1-Dichloropropylene
3) 1,2-Dichloropropane
4) Trichloroethylene
5) *cis*-1,3-Dichloropropylene
6) *trans*-1,3-Dichloropropylene
7) 1,1,2-Trichloroethane
8) 1,3-Dichloropropane
9) 1,2-Dibromoethane
10) 1,1,1,2-Tetrachloroethane
11) 1,1,2,2-Tetrachloroethane
12) 1,2,3-Trichloropropane
13) 3-Chloro-1,2-dibromopropane
14) Hexachlorobutadiene

Figure 2. Ambient headspace analysis of volatile organics in water, spiked at 2 ppm per component.

MSD Deconvolution Report
Sample Name: 2 ppmVOA MIX 3 Only
Data File: C:\msdchem\1\DATA\042205AMHS_SimScan\2ppmMIX 3_Only_simscan.D
Date/Time: 05:13:03 PM Friday, Dec 9 2005

The NIST library was searched for the components that were found in the AMDIS target library.

			Agilent	AMDIS		NIST	
R.T.	Cas #	Compound Name	ChemStation Amount (ng)	Match	R.T. Diff sec.	Reverse Match	Hit Num.
1.497	107062	1,2-Dichloroethane	2.27	97	0.6	94	1
1.540	563586	1,1-Dichloropropylene	7.6	100	0.5	96	1
1.867	78875	1,2-Dichloropropane	4.92	95	0.7	90	1
1.871	79016	Trichloroethylene	7.58	99	0.6	91	1
2.330	10061015	cis-1,3-Dichloropropylene	4.39	98	1.0	92	2
2.677	10061026	trans-1,3-Dichloropropylene	3.3	97	1.5	94	1
2.758	79005	1,1,2-Trichloroethane	2.82	99	1.7	92	1
2.961	142289	1,3-Dichloropropane	3.39	98	1.5	92	1
3.273	106934	1,2-Dibromoethane	2.6	91	1.5	76	4
4.032	630206	1,1,1,2-Tetrachloroethane	5.15	100	1.9	94	1
5.187	79345	1,1,2,2-Tetrachloroethane	2.38	99	2.3	89	1
5.322	96184	1,2,3-Trichloropropane	1.89	98	2.5	94	1
6.323	76017	pentachloroethane	0.08	63	2.0	76	1
8.232	96128	3-Chloro-1,2-dibromopropane	1.62	93	1.6	87	1
10.439	87683	hexachlorobutadiene	16.46	94	0.9	95	1

Figure 3. DRS report for the analysis in Figure 2.

The report shows that a compound has been determined as present by the Agilent ChemStation if a value appears in the Agilent ChemStation Amount column. This means the identification criteria set in the DATA ANALYSIS section of the method have been met. Typically the criteria are that the target ion is present and all three qualifier ions are present in ratios that fall within the percent uncertainty values for that compound.

The Agilent ChemStation Amount listed is a very rough approximation of the amount of the compound, in nanograms, reaching the MS. This is based on the response factor originally observed when the HCD table data was collected. Since valid quantitation requires recent recalibration of response factors on the specific instrument used for analysis, the numbers in this column should never be used to report concentrations of identified analytes. The error in these values can easiliy be a factor of 10 or higher. The purpose of the listed values is to give an approximate amount that can be used to guide standard preparation for quantitative calibration of the compound, if needed.

The match value listed under the AMDIS column is the degree to which the extracted (deconvolved) spectrum of the peak at that RT matched the spectrum in the HCD AMDIS target library. The higher this number, the better the spectra agree. The column “R.T. Diff sec.” lists the difference in seconds between the observed RT and that in the AMDIS target library. The lower this number, the better the RTs agree.

The NIST column lists the reverse-match quality of the extracted spectrum compared with the NIST05 main library spectrum with the same CAS#. The entry “Hit Num.” is the number of the hit in the NIST search results that has the same CAS# as the identified compound. The higher the reverse-match value and the lower the hit number, the better the extracted spectrum matches with NIST05. The NIST column serves as a second opinion on the identity of the extracted spectrum.

The analysis in Figure 2 is of course an easy one, but serves to demonstrate how the system works. All 14 spiked compounds were found by both the Agilent ChemStation and AMDIS. The certainty of identification is very high because:

- The target ion and three qualifier ions are present in appropriate ratios and at the appropriate time as determined by the Agilent ChemStation
- The deconvolved spectrum and the RT at which it appears closely matches the data in the AMDIS target library.

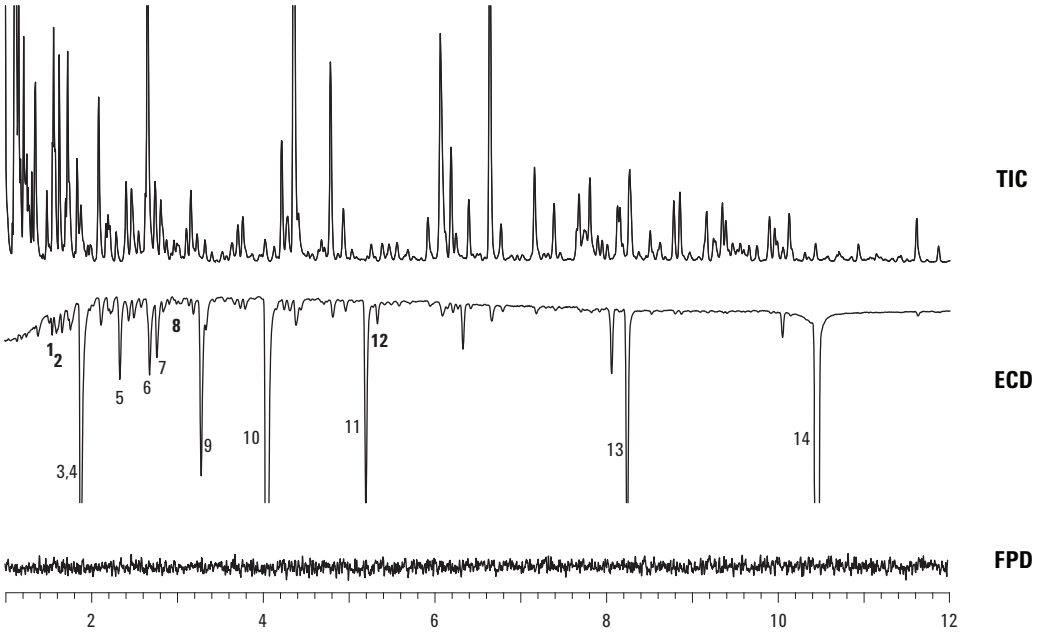
- The extracted spectrum of the identified compound also matches the spectrum with the same CAS # in the NIST05 library.
- The compounds all have a significant response on the ECD, as expected from their halogen content.

To challenge the system in a more realistic way, the effect of matrix and dilution of the analytes was studied. Additional samples were prepared that contained: the same 2-ppm mixture of analytes plus 100 ppm of pump gasoline; 100 ppb of analytes only; and 100 ppb of analytes plus 100 ppm of pump gasoline.

Figure 4 shows the chromatograms from the 100 ppb of analytes with 100 ppm of gasoline. The complexity of the TIC chromatogram illustrates the severe matrix challenge presented by the thousand-fold excess of gasoline. In the ECD chromatogram, interference peaks are now apparent. However, with the exception of peaks 1, 2, 8, and 12, all of the analytes peaks are still visible above the matrix interferences.

Table 2 summarizes the results from the matrix and dilution experiments. In the sample that was 2 ppm of analytes with 100 ppm of gasoline, the Agilent ChemStation (column labeled Quant) found all but two of the compounds. Those two compounds had qualifier ions out of range due to interferences from the matrix. AMDIS successfully found all 14 compounds. Also, with the exception of compound 8, all of the analytes were clearly visible above the matrix responses on the ECD chromatogram.

In the sample that contained 100 ppb of analytes but without gasoline, quant found 7 of the 14 analytes. Using full-scan data, the signal to noise ratio for most of the analytes at the 100-ppb level is very low. This results in difficulties with finding the qualifier ions in ratios that fall within the specified uncertainty range in the quant calibration table. AMDIS found 11 of the 14 compounds. Peak 3 was not found due to a severe overlap with the coeluting peak number 4. Peaks 9 and 13 were missed by AMDIS because the signal to noise ratio was too low.



Peak identities

1) 1,2-Dichloroethane
2) 1,1-Dichloropropylene
3) 1,2-Dichloropropane
4) Trichloroethylene
5) *cis*-1,3-Dichloropropylene
6) *trans*-1,3-Dichloropropylene
7) 1,1,2-Trichloroethane
8) 1,3-Dichloropropane
9) 1,2-Dibromoethane
10) 1,1,1,2-Tetrachloroethane
11) 1,1,2,2-Tetrachloroethane
12) 1,2,3-Trichloropropane
13) 3-Chloro-1,2-dibromopropane
14) Hexachlorobutadiene

Figure 4. Ambient headspace analysis of volatile organics in water. Analytes at 100 ppb plus pump gasoline at 100 ppm.

Table 2. Effect of Matrix and Concentration on DRS Results

			2 ppm STD only		2 ppm STD with 100 ppm gasoline		100 ppb STD only		100 ppb STD with 100 ppm gasoline	
RT (min)	Compound	Peak Number	Quant (ng)	AMDIS (match)	Quant (ng)	AMDIS (match)	Quant (ng)	AMDIS (match)	Quant (ng)	AMDIS (match)
1.491	1,2-Dichloroethane	1	2.27	97	2.47	93		73		65
1.536	1,1-Dichloropropylene	2	7.60	100	7.34	98	0.37	89		85
1.793	1,2-Dichloropropane	3	4.92	95	5.59	64	0.21	**Overlap**		**Overlap**
1.863	Trichloroethylene	4	7.58	99	7.71	97	0.40	90	0.30	82
2.317	*cis*-1,3-Dichloropropylene	5	4.39	98	4.81	98	0.21	88	0.23	74
2.658	*trans*-1,3-Dichloropropylene	6	3.30	97		84		53		**Overlap**
2.735	1,1,2-Trichloroethane	7	2.82	99	3.05	96	0.12	72		**Overlap**
2.938	1,3-Dichloropropane	8	3.39	98	3.50	97		66	0.22	46
3.250	1,2-Dibromoethane	9	2.60	91		95		**S/N**		66
4.003	1,1,1,2-Tetrachloroethane	10	5.15	100	5.32	99		89	0.31	88
5.151	1,1,2,2-Tetrachloroethane	11	2.38	99	2.41	98		48	0.19	53
5.283	1,2,3-Trichloropropane	12	1.89	98	1.85	98	0.07	79	0.14	75
8.208	3-Chloro-1,2-dibromopropane	13	1.62	93	2.40	90		**S/N**		59
10.435	Hexachlorobutadiene	14	16.46	94	3.54	89	0.65	75	0.36	52
	Total Found		14	14	12	14	7	10	7	11

With 100 ppm of gasoline added to the 100-ppb sample, quant again found 7 of the 14 compounds and AMDIS again found 11 of the 14. Curiously, in both cases some of the compounds missed in the absence of matrix were now found. It is possible that the presence of matrix enhances the concentration of some of the analytes in the headspace. The compounds missed in quant were again the result of low signal to noise and/or interference. In AMDIS the three missed peaks were due to severe interferences from the gasoline. As indicated above, the ECD response from 10 of the 14 compounds was still visible above the peaks due to interferences.

SIM/Scan

The quant data in Table 2 was generated using full scan mode. Peak 13 was missed in quant due to low signal to noise ratio. SIM/Scan mode can be used to collect SIM data simultaneously with the scan data. The 100 ppb plus 100-ppm gasoline sample was run in SIM/Scan mode with SIM groups for each of the 14 analytes. Figure 5 compares the target and qualifier extracted ion chromatograms in both modes with the ECD response for peak 13.

The signal-to-noise (peak to peak) for the target ion increases from 34 in full scan mode to 433 in SIM mode. The peaks lost in quant due to low signal-to-noise were all recovered in SIM mode. This example demonstrates the power of SIM/Scan when looking for high-priority targets at low levels. If necessary, the ECD could also be used for quantitation, as it has a high signal to noise ratio and is free from interference.

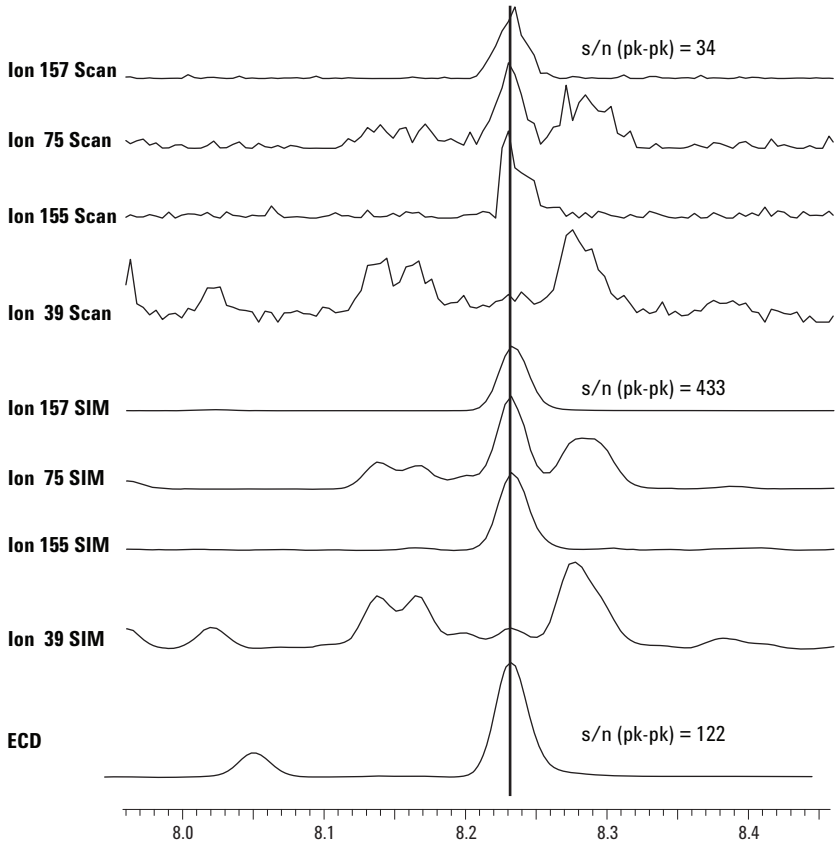


Figure 5. Target and qualifier extracted ion chromatograms for peak 13 (3-Chloro-1,2-dibromopropane) in Figure 4. SIM, scan, and ECD data collected simultaneously.

AMDIS

Figure 6 illustrates the ability of AMDIS to clean the interference ions from the spectrum of an analyte. The raw spectrum at the top of Figure 6 was taken at the apex of peak 13 in the 100 ppb plus 100-ppm gasoline sample. When searched against the NIST05 library using the NIST search program, the actual compound (3-Chloro-1,2-dibromopropane) was the 70th hit in the search results. Using manual subtraction of nearby spectra in the Agilent ChemStation data analysis program improved the quality of the spectrum so that it was now the second hit when searched in NIST. This is a tedious process, however, when dealing with a large number of analytes. The spectrum as deconvolved by AMDIS is shown in Figure 6 above the NIST05 library spectrum. When this spectrum is searched, it is the first hit in the results. The automated deconvolution provided by AMDIS saves an enormous amount of time in the data review process.

Fast Methods

When a retention time locked database is constructed, the RTs are (or at least should be) collected under the highest resolution conditions expected for the application. If the database is collected under constant pressure mode, method translation can then be used to adjust the speed of the method to meet the needs of different situations.

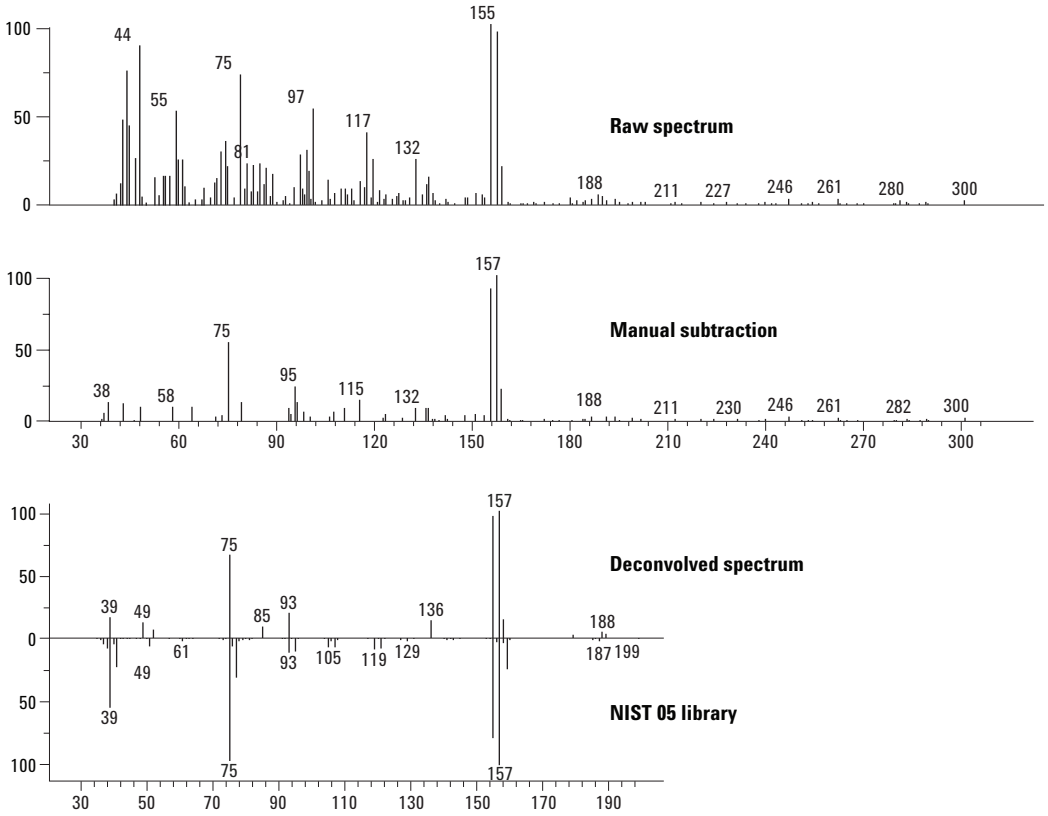


Figure 6. Comparison of raw, manually subtracted, AMDIS deconvoluted, and NIST05 reference spectra for peak 13 (3-Chloro-1,2-dibromopropane) in Figure 4.

The 3X method uses RTs in its database that are simply the RTs from the 1X method divided by exactly 3. The 7X method likewise uses RTs that are 1/7 of those in the original database. The quality of RTs matching between the two new faster methods and the new divided databases is demonstrated in Figure 7. Three different mixtures containing 13 chlorinated hydrocarbons and 36 pesticides were run with the two methods. The RTs were compared to those in the two new databases. The graph at the top of Figure 7 plots the database RT on the x-axis versus the difference of the measured RT from the database on the y axis.

If the RT matching were perfect, the plot would be a straight horizontal line at zero height on the y axis. The maximum deviation from the table values for the 3X method was –0.047 min. The plot indicates that a peak recognition window of ±0.1 min should be sufficient. The maximum deviation in the 7X plot at the bottom of Figure 8 is +0.032 min indicating that the same peak recognition window could be used here as well. In general the RTs in scaled methods agree very well with the predicted RTs.

The conditions for the two higher-speed methods were chosen to increase speed while maintaining the same column capacity. The capacity is important for both the dynamic range of quantitative measurements and for minimizing analyte RT shifts in samples with high levels of matrix. In gas chromatography, the well-known triangle of speed, resolution, and capacity dictates that if the capacity is to be maintained and the speed is to be increased, then the resolution will decrease.

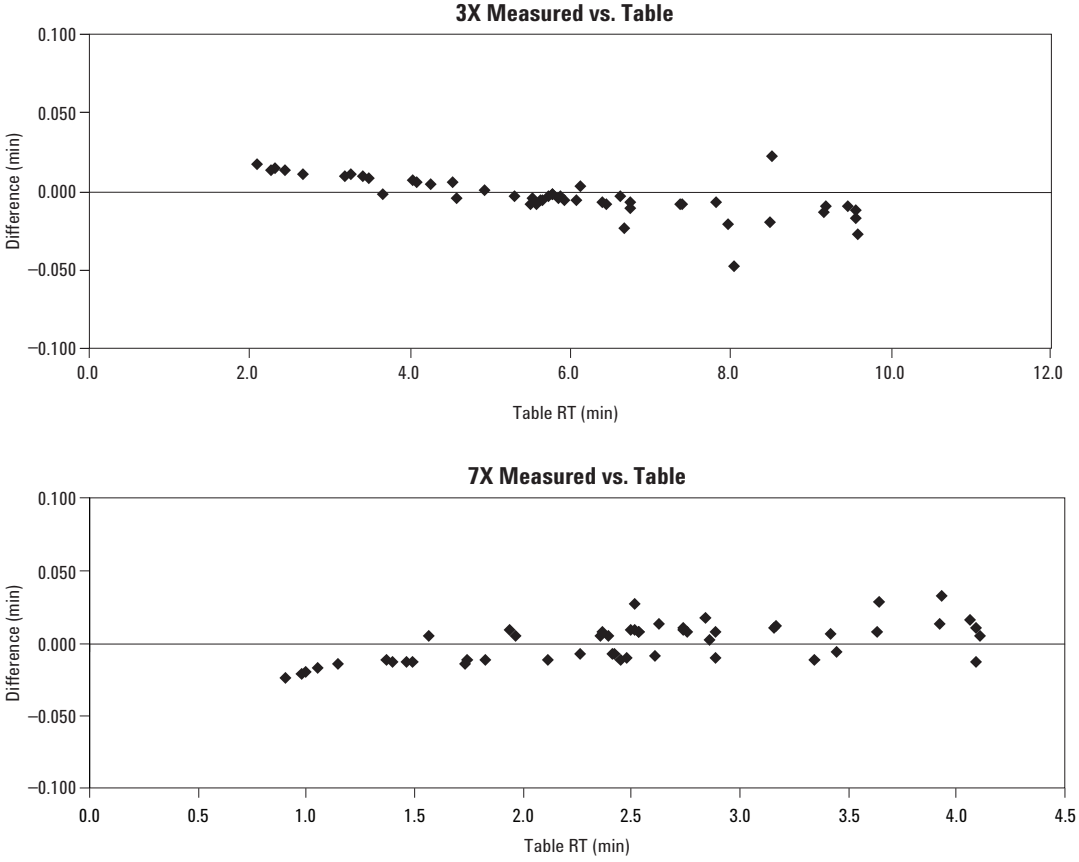
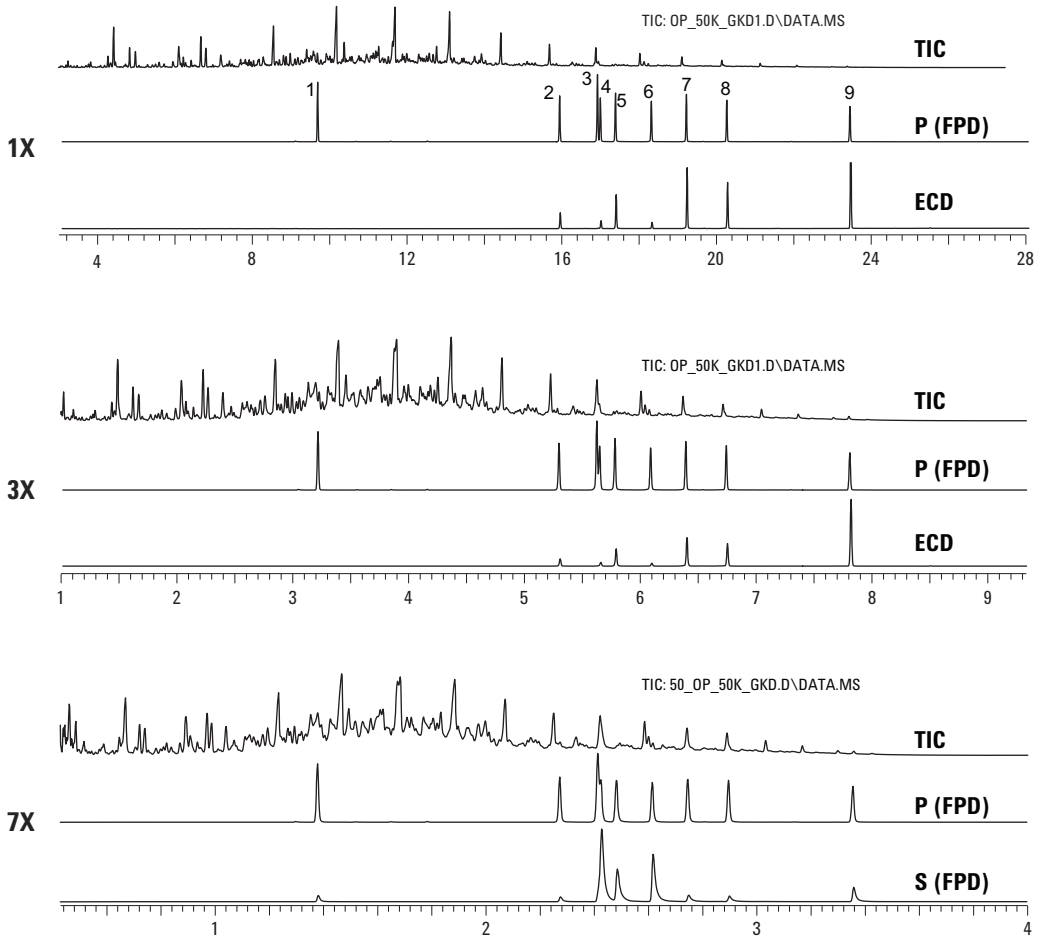


Figure 7. Difference between scaled HCD table and experimental retention times for 50 compound test set. Y axis is table value minus experimental, X axis is table RT. Top plot is 3X, bottom is 7X.

Figure 8 shows three sets of chromatograms using the HCD database at three different speeds. The sample consists of nine organophosphorus pesticides (identified in the caption to Figure 8) at 50 ppm and a matrix consisting of an equal volume mixture of gasoline, kerosene, and diesel fuel spiked at 50,000 ppm total mixture. The 1X and 3X data were collected on the three-way splitter instrument and the 7X was collected on the DFPD instrument. All nine compounds also contained sulfur as can be seen in the DFPD sulfur chromatogram at the bottom of Figure 8. Note that the sulfur tails somewhat compared to the phosphorus.



Peak identities

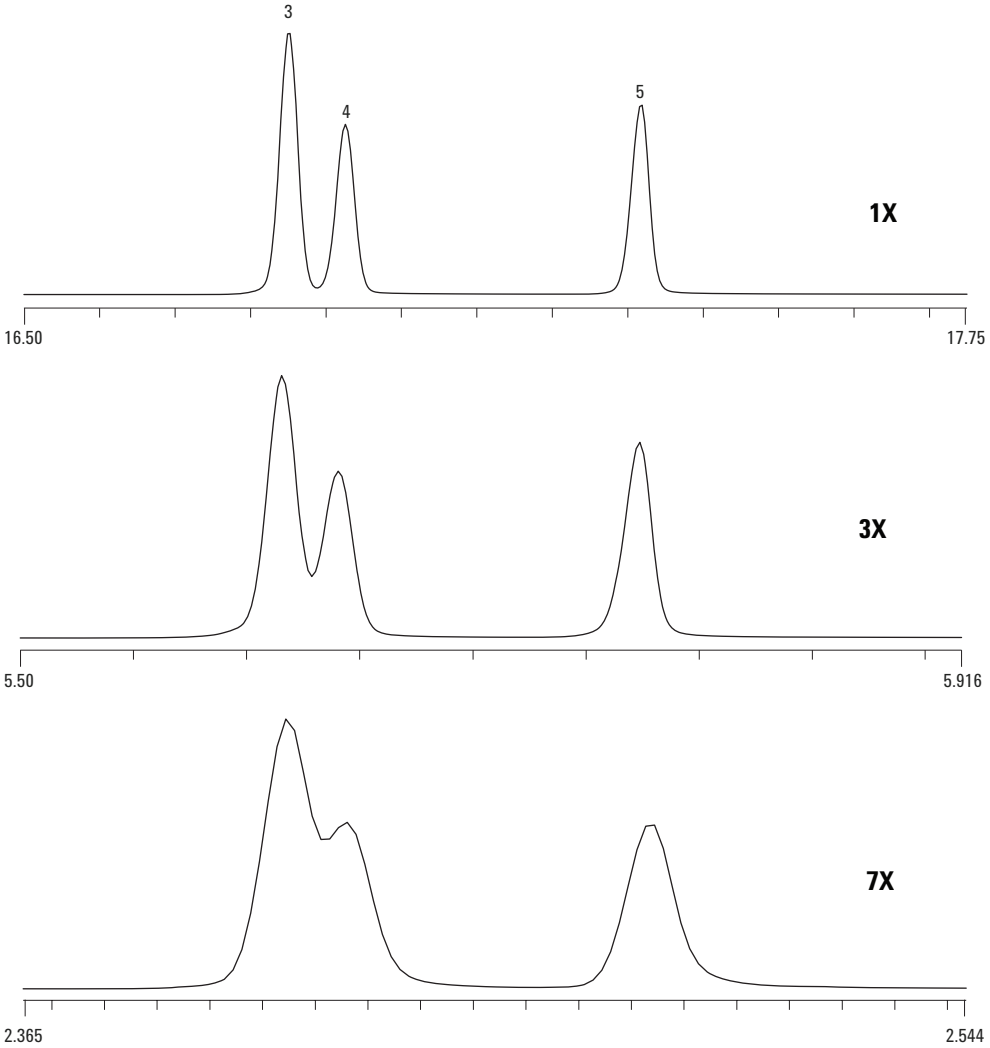
1) O,O,O-triethyl phosphorothioate
2) Thionazin
3) Sulfotepp
4) Phorate
5) Dimethoate
6) Disulfoton
7) Methyl parathion
8) Parathion
9) Famphur

Figure 8. Comparison of 1X, 3X, and 7X chromatograms. 1X and 3X were run on GC/MS/ECD/FPD system, 7X on GC/MS/DFPD.

Figure 9 expands the RT region of the phosphorous chromatogram containing peaks 3, 4, and 5 from Figure 8. The decrease in resolution with increasing speed is clearly evident.

If only the standard target and three qualifier ion approach is used, the loss in resolution causes a significant problems. With the 1X method, all nine of the analytes are identified and eight false positives are reported. With the 3X method, all analytes are again found but now with 25 false positives. With the significantly decreased resolution of the 7X method, only seven of the nine analytes are identified and 48 false positives are reported.

The situation is much different when using the approach described here. Even in the worst situation, the 7X method, AMDIS finds all nine analytes with high-quality matches and only three false positives. The DRS report for the 7X analysis is shown in Table 3. To simplify the table, the 48 false positives that only appear in the quant column are not shown. The analyte compounds are shown in bold. All show close RT and high-quality spectral matches to both the AMDIS target library and to the NIST05 library.



Peak identities
3) Sulfotepp
4) Phorate
5) Dimethoate

Figure 9. Comparison of FPD phosphorus chromatograms from 1X, 3X, and 7X runs in Figure 8.

Table 3. DRS Report for 7x Analysis of 50 ppm Pesticides In 50,000 ppm Gasoline/Kerosine/Diesel Matrix

RT	Cas #	Compound name	Agilent ChemStation amount (ng)	AMDIS match	RT Diff (sec.)	NIST reverse match	Hit number
0.973	98862	Acetophenone		71	–9.5	74	50
1.380	**126681**	**O,O,O-triethyl phosphorothioate**	**13.92**	**69**	**0.7**	**71**	**1**
1.520	94597	Safrole		46	–7.6		
1.520	52417502	Benzeneacetaldehyde, à,2,5-trimethyl-				74	1
2.113	132649	Dibenzofuran	0.35	64	0.6	80	3
2.138	90437	o-Phenylphenol		55	2.3		
2.138	2131411	Naphthalene, 1,4,5-trimethyl-				85	1
2.275	**297972**	**Thionazin**	**89.2**	**91**	**0.5**	**85**	**1**
2.417	**3689245**	**Sulfotepp**		**88**	**0.5**	**83**	**1**
2.427	**298022**	**Phorate**	**23.31**	**90**	**0.6**	**85**	**1**
2.485	**60515**	**Dimethoate**	**27.34**	**84**	**0.7**	**85**	**1**
2.619	**298044**	**Disulfoton**	**22.7**	**92**	**0.6**	**88**	**1**
2.748	**298000**	**Methyl parathion**	**25.12**	**92**	**0.6**	**82**	**1**
2.901	**56382**	**Parathion (ethyl)**		**91**	**0.7**	**85**	**1**
3.360	**52857**	**Famphur**		**93**	**0.8**	**85**	**1**
		(48 quant-only hits not shown)					

The peak at 0.973 minutes is a reasonable spectral match to acetophenone, but the large time difference and being the 50th hit in the NIST search results suggests that this is not the compound. The peak at 1.520 min is a poor spectral match with a large time difference. The absence of a NIST reverse search and hit entry means that the listed compound was not in the top 100 hits in the NIST search. The next compound listed at 1.520 min is the top entry from the NIST search. It is quite clear that safrole is not present.

The peak at 2.113 min, dibenzofuran, was not one of the analytes added to the sample. However, it probably is present in the diesel fuel matrix. Its presence is supported by both reasonably good spectral matches and close time matching with a database.

The last extraneous peak at 2.138 min is also questionable. The time match is somewhat poor and the NIST reverse search suggests the identification is not correct.

All nine analytes are detected with the FPD on both the phosphorus and sulfur chromatograms. All analytes except peak 1 are detected selectively on the ECD as well.

These results suggest that while the loss of resolution in going to 7X is unacceptable when using only conventional screening approaches, with the method discussed here, it is a viable option. By using the DRS report combined with the selective detector data, the number of false positives and false negatives are significantly reduced. For those situations where speed is a critical factor, for example in response to homeland security incidents, the fastest method may be the one of choice.

For many laboratories, the 3X method would be an attractive choice. It has higher resolution than the 7X and higher speed than the 1X and still allows the use of two GC detectors in parallel with the MSD. It also only requires a 240V oven, not the repositioning of the MSD to the back position.

Conclusions

The systems described here offer several advantages when screening samples for the presence of hazardous chemicals. The advantages derive from a combination of techniques that result in both faster and more accurate screening results.

- Retention time locked target database of 731 hazardous chemicals for screening with MS
- Microfluidic splitter - using selective detection simultaneous with MS data for added confirmation, finding non-target suspect compounds, and alternate quantitation
- SIM/Scan - Acquire SIM data on high priority targets simultaneously with scan data. Saves time by eliminating need to run samples in both modes.
- DRS - automated deconvolution dramatically increases accuracy of target identification, even in the most challenging matrices. The reduction of data interpretation from hours to minutes is especially useful for response to hazardous chemical incidents.
- Fast chromatography using shorter columns, faster ovens, and backflushing to greatly reduce run times.

This combination of techniques offers a viable solution to the hazardous chemicals challenge.

References

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2. Chin Kai-Meng and Bruce Quimby, “Identifying Pesticides with Full Scan, SIM, μECD, and FPD from a Single Injection”, Agilent Technologies, publication 5989-3299EN www.agilent.com/chem
3. Chin-Kai Meng, “Improving Productivity with Synchronous SIM/Scan”, Agilent Technologies, publication 5989-3108EN www.agilent.com/chem
4. Philip Wylie, Michael Szelewski, Chin-Kai Meng, Christopher Sandy, “Comprehensive Pesticide Screening by GC/MSD using Deconvolution Reporting Software”, Agilent Technologies, publication 5989-1157EN www.agilent.com/chem
5. B. D. Quimby, L. M. Blumberg, M. S. Klee, and P. L. Wylie, “Precise Time-Scaling of Gas Chromatographic Methods Using Method Translation and Retention Time Locking”, Agilent Technologies, publication 5967-5820E www.agilent.com/chem
6. Michael J. Szelewski and Bruce Quimby, “New Tools for Rapid Pesticide Analysis in High Matrix Samples”, Agilent Technologies, publication 5989-1716EN www.agilent.com/chem
7. Michael J. Szelewski and Bruce D. Quimby, “Ambient Headspace GC and GC-MSD Analysis of Nonpolar Volatiles in Water”, Agilent Technologies, publication 5968-9455E www.agilent.com/chem

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Lists of Compounds in Databases

Volatiles:
EPA 502/524, 60 compounds

1,1,1,2-Tetrachloroethane
1,1,1-Trichloroethane
1,1,2,2-Tetrachloroethane
1,1,2-Trichloroethane
1,1-Dichloroethane
1,1-Dichloroethylene
1,1-Dichloropropylene
1,2,3-trichlorobenzene
1,2,3-Trichloropropane
1,2,4-trichlorobenzene
1,2,4-trimethylbenzene
1,2-Dibromoethane
1,2-dichlorobenzene
1,2-Dichloroethane
1,2-Dichloropropane
1,3,5-trimethylbenzene
1,3-dichlorobenzene
1,3-Dichloropropane
1,4-dichlorobenzene
2,2-Dichloropropane
2-chlorotoluene
3-Chloro-1,2-dibromopropane
4-chlorotoluene
Benzene
Bromobenzene
Bromochloromethane
Bromodichloromethane
Bromoform
Bromomethane
Carbon Tetrachloride
Chlorobenzene
Chlorodibromomethane
Chloroethane
Chloroform
Chloromethane
cis-1,2-Dichloroethylene
cis-1,3-Dichloropropylene
Dibromomethane
Dichlorodifluoromethane
Ethylbenzene
Hexachlorobutadiene
Isopropylbenzene
Methylene Chloride
m-xylene
Naphthalene
n-butylbenzene
n-propylbenzene
o-Xylene
p-isopropyltoluene
p-xylene
Styrene
tert-butylbenzene
Tetrachloroethylene
Toluene
trans-1,2-Dichloroethylene
trans-1,3-Dichloropropylene
Trichloroethylene
Trichlorofluoromethane
Vinyl chloride

Semivolatiles:
EPA 8270C Appendix IX,
140 compounds
1,2,4,5-tetrachlorobenzene
1,2,4-trichlorobenzene
1,2-dichlorobenzene
1,3,5-trinitrobenzene
1,3-dichlorobenzene
1,4-dichlorobenzene
1,4-naphthoquinone
1-naphthylamine
2,3,4,6-tetrachlorophenol
2,4,5-trichlorophenol
2,4,6-trichlorophenol
2,4-dichlorophenol
2,4-dimethylphenol
2,4-dinitrophenol
2,4-dinitrotoluene
2,6-dichlorophenol
2,6-dinitrotoluene
2-acetylaminofluorene
2-chloronaphthalene
2-chlorophenol
2-methyl-4,6-dinitrophenol
2-methylnaphthalene
2-naphthylamine
2-nitroaniline
2-nitrophenol
2-picoline
3,3'-dichlorobenzidine
3,3'-dimethylbenzidine
3-methylcholanthrene
3-nitroaniline
4,4'-DDD
4,4'-DDE
4,4'-DDT
4-aminobiphenyl
4-bromophenyl phenyl ether
4-chloro-3-methylphenol
4-chloroaniline
4-chlorophenyl phenyl ether
4-nitroaniline
4-nitrophenol
4-nitroquinoline-1-oxide
5-nitro-o-toluidine
7,12-dimethylbenz[a]anthracene
a,a-dimethylphenethylamine
Acenaphthene
Acenaphthylene
Acetone
Acetophenone
Aldrin
Alpha-BHC (alpha-HCH)
Aniline
Anthracene
Aramite (total)
Benz[a]anthracene
Benzene
Benzo[a]pyrene
Benzo[b]fluoranthene
Benzo[ghi]perylene
Benzo[k]fluoranthene
Benzyl alcohol
Beta-BHC (beta-HCH)
Bis(2-chloroethoxy)methane
Bis(2-chloroethyl) ether
Bis(2-chloroisopropyl) ether
Bis(2-ethylhexyl)phthalate
Butyl benzyl phthalate
Chlorobenzilate
Chrysene
Delta-BHC (delta-HCH)
Diallate (total)
Dibenz[a,h]anthracene
Dibenzofuran
Dieldrin
Diethyl phthalate
Dimethoate
Dimethyl phthalate
Di-n-butyl phthalate

Di-n-octyl phthalate
Dinoseb
Diphenylamine
Disulfoton
Endosulfan I
Endosulfan II
Endosulfan sulfate
Endrin
Endrin aldehyde
Ethyl methanesulfonate
Famphur
Fluoranthene
Fluorene
Gamma-BHC (lindane)
Heptachlor
Heptachlor epoxide -isomer B
Hexachlorobenzene
Hexachlorobutadiene
Hexachlorocyclopentadiene
Hexachloroethane
Hexachlorophene
Hexachloropropene
Indeno[1,2,3-cd]pyrene
Isodrin
Isophorone
Isosafrole
Kepone
m-cresol (3-methylphenol)
m-dinitrobenzene
Methapyrilene
Methoxychlor
Methyl methanesulfonate
Methyl parathion
Naphthalene
Nitrobenzene
N-nitrosodiethylamine
N-nitrosodimethylamine
N-nitrosodi-n-butylamine
N-nitrosodi-n-propylamine
N-nitrosodiphenylamine
N-nitrosomethylethylamine
N-nitrosomorpholine
(4-nitrosomorpholine)
N-nitrosopiperidine
(1-nitrosopiperidine)
N-nitrosopyrrolidine (1-nitrosopyrrolidine)
O,O,O-triethyl phosphorothioate
o-cresol (2-methylphenol)
o-toluidine
p-(dimethylamino)azobenzene
Parathion (ethyl)
p-cresol (4-methylphenol)
Pentachlorobenzene
Pentachloroethane
Pentachloronitrobenzene
Pentachlorophenol
Phenacetin
Phenanthrene
Phenol
Phorate
p-phenylenediamine
Pronamide
Pyrene
Pyridine
Safrole
Sulfotepp
Thionazin

Chlorinated Dioxins and Furans:
EPA 8282, 19 compounds

2,3,7,8-Tetrachlorodibenzo-p-dioxin
1,2,3,7,8-Pentachlorodibenzo-p-dioxin
1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin
1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin
Octachlorodibenzo-p-dioxin
2,3,7,8-Tetrachlorodibenzofuran
1,2,3,7,8-Pentachlorodibenzofuran
1,2,3,4,7,8-Hexachlorodibenzofuran
1,2,3,4,6,7,8-Heptachlorodibenzofuran
Octachlorodibenzofuran

Polychlorinatedbiphenyls:
EPA 8082, 19 compounds

2-chlorobiphenyl
2,3-dichlorobiphenyl
2,2',5-trichlorobiphenyl
2,4',5-trichlorobiphenyl
2,2',5,5'-tetrachlorobiphenyl
2,2',3,5'-tetrachlorobiphenyl
2,3',4,4'-tetrachlorobiphenyl
2,2',4,5,5'-pentachlorobiphenyl
2,2',3,4,5'-pentachlorobiphenyl
2,3,3',4',6-pentachlorobiphenyl
2,2',3,5,5',6-hexachlorobiphenyl
2,2',4,4',5,5'-hexachlorobiphenyl
2,2',3,4,5,5'-hexachlorobiphenyl
2,2',3,4,4',5'-hexachlorobiphenyl
2,2',3,4',5,5',6-heptachlorobiphenyl
2,2',3,4,4',5',6-heptachlorobiphenyl
2,2',3,4,4',5,5'-heptachlorobiphenyl
2,2',3,3',4,4',5-heptachlorobiphenyl
2,2',3,3',4,4',5,5',6-nonachlorobiphenyl

Pesticides:
Agilent RTL pesticide database
(adapted), 567 compounds
1,2,4-Trichlorobenzene
1,2-Dibromo-3-chloropropane
17a-Ethynylestradiol
2-(1-naphthyl)acetamide
2-(2-Butoxyethoxy)ethyl thiocyanate
2-(Octylthio)ethanol
2,3,4,5-Tetrachlorophenol
2,3,4,6-Tetrachlorophenol
2,3,5,6-Tetrachlorophenol
2,3,5-Trichlorophenol
2,3,5-Trimethacarb
2,3,5-Trimethylphenyl methyl carbamate
(Trimethacarb)
2,3,7,8-Tetrachlorodibenzofuran
2,3,7,8-Tetrachlorodibenzo-p-dioxin
2,4,5-T methyl ester
2,4,5-Trichlorophenol
2,4,6-Trichlorophenol
2,4-D methyl ester
2,4-D sec-butyl ester
2,4-DB methyl ester
2,4-Dichlorophenol
2,4-Dichlorophenyl benzenesulfonate
2,4-Dimethylaniline
2,6-Dichlorobenzonitrile
2,6-Dimethylaniline
2-[3-Chlorophenoxy]propionamide
2-Ethyl-1,3-hexanediol
2-Hydroxyestradiol
2-Methylphenol
2-Phenoxypropionic acid
3,4,5-Trimethacarb
3,4-Dichloroaniline
3,5-Dichloroaniline
3-Chloroaniline
3-Hydroxycarbofuran
4,4'-Dichlorobenzophenone
4,6-Dinitro-o-cresol (DNOC)
4-Chloroaniline
4-Methylphenol
5,7-Dihydroxy-4'-methoxyisoflavone
9,10-Anthraquinone
Acephate
Acetochlor
Acifluorfen methyl ester
Alachlor
Aldrin
Allidochlor
Ametryn
Amidithion
Aminocarb
Amitraz
Ancymidol
Anilazine
Aniline
Atraton
Atrazine
Azaconazole
Azamethiphos
Azinphos-ethyl
Azinphos-methyl Aziprotryne
Azobenzene
Barban

Benalaxyl
Benazolin-ethyl
Bendiocarb
Benfluralin
Benfuresate
Benodanil
Bentazone
Bentazone methyl derivative
Benthiocarb
Benzo(a)pyrene
Benzophenone
Benzoylprop ethyl
b-Estradiol
BHC alpha isomer
BHC beta isomer
BHC delta isomer
Bifenox
Bifenthrin
Binapacryl
Bioallethrin
Bioallethrin S-cyclopentenyl isomer
Bioresmethrin
Biphenyl
Bis(2-ethylhexyl)phthalate
Bisphenol A
Bitertanol I
Bitertanol II
Bromacil
Bromobutide
Bromocyclen
Bromophos
Bromophos-ethyl
Bromopropylate
Bromoxynil
Bromoxynil octanoic acid ester
Buprofezin
Butachlor
Butamifos
Butoxycarboxim
Butralin
Butyl benzyl phthalate
Butylate
Butylated hydroxyanisole
Captafol
Captan
Carbaryl
Carbetamide
Carbofuran
Carbofuran-3-keto
Carbophenothion
Carbosulfan
Carboxin
Chinomethionat
Chloramben methyl ester
Chloranocryl
Chlorbenside
Chlorbromuron
Chlorbufam
Chlordecone
Chlordimeform
Chlorfenethol
Chlorfenprop-methyl
Chlorfenson
Chlorfenvinphos
Chlorflurecol-methyl ester
Chlormefos
Chlornitrofen
Chlorobenzilate
Chloroneb
Chloropropylate
Chlorothalonil
Chlorotoluron
Chlorpropham
Chlorpyrifos
Chlorpyrifos Methyl
Chlorthal-dimethyl
Chlorthiamid
Chlorthion
Chlorthiophos
Chlorthiophos sulfone
Chlorthiophos sulfoxide
Chlozolinate
cis-Chlordane
Clomazone
Coumaphos
Crimidine
Crotoxyphos
Crufomate
Cyanazine
Cyanofenphos
Cyanophos
Cycloate
Cycluron
Cyfluthrin I
Cyfluthrin II
Cyfluthrin III
Cyfluthrin IV
Cyhalothrin I (lambda)
Cymoxanil
Cypermethrin I
Cypermethrin II
Cypermethrin III
Cypermethrin IV
Cyprazine
Cyprofuram
Cyromazine
d-(*cis-trans*)-Phenothrin-I
d-(*cis-trans*)-Phenothrin-II
Dazomet
Decachlorobiphenyl
Deltamethrin
Demephion
Demeton-S
Demeton-S-methylsulfon
Desbromo-bromobutide
Desmedipham
Desmetryn
Dialifos
Di-allate I
Di-allate II
Diamyl phthalate
Diazinon
Dibrom (naled)
Dicamba
Dicamba methyl ester
Dicapthon
Dichlofenthion
Dichlofluanid
Dichlone
Dichlormid
Dichlorophen
Dichlorprop
Dichlorprop methyl ester
Dichlorvos
Diclobutrazol
Diclofop methyl
Dicloran
Dicrotophos
Dicyclohexyl phthalate
Dicyclopentadiene
Dieldrin
Diethatyl ethyl
Diethofencarb
Diethyl dithiobis(thionoformate) (EXD)
Diethyl phthalate
Diethylene glycol
Diethylstilbestrol
Difenoconazol I
Difenoconazol II
Diflufenican
Dimefox
Dimethachlor
Dimethametryn
Dimethipin
Dimethoate
Dimethylphthalate
Dimethylvinphos(z)
Dimetilan
Di-n-butylphthalate
Diniconazole
Dinitramine
Dinobuton
Dinocap I
Dinocap II
Dinocap III
Dinocap IV

Dinoseb
Dinoseb acetate
Dinoseb methyl ether
Dinoterb
Dinoterb acetate
Di-n-propyl phthalate
Dioxacarb
Dioxathion
Dioxydemeton-S-methyl
Diphacinone
Diphenamid
Diphenylamine
Dipropetryn
Disulfoton
Ditalimfos
Dithiopyr
Diuron
Dodemorph I
Dodemorph II
Drazoxolon
Edifenphos
Endosulfan (alpha isomer)
Endosulfan (beta isomer)
Endosulfan ether
Endosulfan lactone
Endosulfan sulfate
Endrin
Endrin aldehyde
Endrin ketone
EPN
Epoxiconazole
EPTC
Erbon
Esfenvalerate
Esprocarb
Etaconazole
Ethalfluralin
Ethiofencarb
Ethiolate
Ethion
Ethofumesate
Ethoprophos
Ethoxyquin
Ethylenethiourea
Etridiazole
Etrimfos
Famphur
Fenarimol
Fenazaflor
Fenbuconazole
Fenchlorphos
Fenfuram
Fenitrothion
Fenobucarb
Fenoprop
Fenoprop methyl ester
Fenoxycarb
Fenpropathrin
Fenson
Fensulfothion
Fenthion
Fenthion sulfoxide
Fenuron
Fenvalerate I
Fenvalerate II
Fepropimorph
Flamprop-isopropyl
Flamprop-methyl
Fluazifop-p-butyl
Flubenzimine
Fluchloralin
Flucythrinate I
Flucythrinate II
Flumetralin
Fluometuron
Fluorodifen
Fluotrimazole
Flurenol-butyl ester
Flurenol-methylester
Fluridone
Flurochloridone I
Flurochloridone II
Fluroxypyr-1-methylheptyl ester
Flusilazole
Flutolanil
Flutriafol
Fluvalinate-tau-I
Fluvalinate-tau-II
Folpet
Fonofos
Formothion
Fuberidazole
Furalaxyl
Furathiocarb
Furmecyclox
Heptachlor
Heptachlor epoxide
Heptachlor exo-epoxide isomer B
Heptenophos
Hexabromobenzene
Hexachlorobenzene
Hexachlorophene
Hexaconazole
Hexazinone
Hexestrol
Imazalil
Ioxynil
Iprobenfos
Iprodione
Isazophos
Isobenzan
Isobornyl thiocyanoacetate
Isocarbamide
Isodrin
Isofenphos
Isomethiozin
Isoprocarb
Isopropalin
Isoprothiolane
Isoproturon
Isoxaben
Isoxathion
Jodfenphos
Kinoprene
Lenacil
Leptophos
Leptophos oxon
Lindane
Linuron
Malathion
Malathion-o-analog
MCPA methyl ester
MCPB methyl ester
m-Cresol
Mecarbam
Mecoprop methyl ester
Mefenacet
Mefluidide
Menazon
Mephosfolan
Mepronil
Metalaxyl
Metamitron
Metasystox thiol
Metazachlor
Methacrifos
Methamidophos
Methfuroxam
Methidathion
Methiocarb
Methiocarb sulfone
Methiocarb sulfoxide
Methomyl
Methoprene I
Methoprene II
Methoprotryne
Methoxychlor
Methyl paraoxon
Methyl parathion
Methyl-1-naphthalene acetate
Methyldymron
Metobromuron
Metolachlor
Metolcarb
Metribuzin
Mevinphos
Mirex
Molinate
Monalide
Monocrotophos
Monolinuron

Myclobutanil
N,N-Diethyl-m-toluamide
N-1-Naphthylacetamide
Naphthalic anhydride
Napropamide
Nicotine
Nitralin
Nitrapyrin
Nitrofen
Nitrothal-isopropyl
N-Methyl-N-1-naphthyl acetamide
Norflurazon
Nuarimol
o,p'-DDD
o,p'-DDE
o,p'-DDT
Octachlorostyrene
o-Dichlorobenzene
Omethoate
o-Phenylphenol
Oryzalin
Oxabetrinil
Oxadiazon
Oxadixyl
Oxamyl
Oxycarboxin
Oxychlordane
Oxydemeton-methyl
Oxyfluorfen
p,p'-DDD
p,p'-DDE
p,p'-DDT
Paclobutrazol
Paraoxon
Parathion
p-Dichlorobenzene
Pebulate
Penconazole
Pendimethalin
Pentachloroaniline
Pentachloroanisole
Pentachlorobenzene
Pentachloronitrobenzene
Pentachlorophenol
Pentanochlor
Permethrin I
Permethrin II
Perthane
Phenamiphos
Phenkapton
Phenoxyacetic acid
Phenthoate
Phorate
Phosalone
Phosfolan
Phosmet
Phosphamidon I
Phosphamidon II
Phthalide
Picloram methyl ester
Pindone
Piperalin
Piperonyl butoxide
Piperophos
Pirimicarb
Pirimiphos-ethyl
Pirimiphos-methyl
Plifenat
p-Nitrotoluene
Pretilachlor
Probenazole
Prochloraz
Procymidone
Profenofos
Profluralin
Promecarb
Prometon
Prometryn
Propachlor
Propamocarb
Propanil
Propargite
Propazine
Propetamphos
Propham
Propiconazole-I
Propiconazole-II
Propoxur
Propyzamide
Prothiofos
Prothoate
Pyracarbolid
Pyrazon
Pyrazophos
Pyrazoxyfen
Pyributicarb
Pyridaben
Pyridaphenthion
Pyridate
Pyridinitril
Pyrifenox I
Pyrifenox II
Pyrimethanil
Pyroquilon
Quinalphos
Quinoclamine
Quizalofop-ethyl
Resmethrin
S,S,S-Tributylphosphorotrithioate
Sebuthylazine
Secbumeton
Simazine
Simetryn
Sulfotep
Sulfur (S8)
Sulprofos
Swep
Tamoxifen
TCMTB
Tebuconazole
Tebutam
Tecnazene
Temephos
Terbacil
Terbucarb
Terbufos
Terbumeton
Terbuthylazine
Terbutryne
Tetrachlorvinphos
Tetradifon
Tetraethylpyrophosphate (TEPP)
Tetramethrin I
Tetramethrin II
Tetrapropyl thiodiphosphate
Tetrasul
Thenylchlor
Thiabendazole
Thiofanox
Thiometon
Thionazin
Tiocarbazil I
Tiocarbazil II
Tolclofos-methyl
Tolylfluanid
trans-Chlordane
Triadimefon
Triadimenol
Tri-allate
Triamiphos
Triazophos
Tributyl phosphate
Tributyl phosphorotrithioite
Trichlorfon
Trichloronate
Triclopyr methyl ester
Tricyclazole
Tridiphane
Trietazine
Triflumizole
Trifluralin
Tryclopyrbutoxyethyl
Tycor (SMY 1500)
Uniconizole-P
Vamidothion
Vernolate
Vinclozolin

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Printed in the USA
February 9, 2006
5989-4834EN

Agilent Technologies