

Rapid Analysis of SVOCs, PCBs and Pesticides in Crude Soil Extracts by GC-TOFMS

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Key Words: GC-TOFMS, Environmental, Pesticides, PCBs

1. Introduction

In busy routine laboratories, there are clear incentives to minimize the number of routine procedures performed by increasing the number of determinands included in each analytical method. This leads to reduced costs, faster turn-around times, and greater flexibility in the way in which laboratory resources can be deployed.

Soil samples are a particular challenge due to the complex and variable nature of the matrix, and are usually associated with lengthy sample preparation procedures and long analysis times.

Once a soil sample has been extracted, the crude extract is usually opaque with large amounts of matrix co-extractives. If no clean-up is applied then the matrix masks target compounds, and instrument downtime becomes excessive due to contamination. As a consequence, it is usual to apply a clean-up step (often SPE or GPC); unfortunately, it is very often the case that this clean-up step reduces recoveries or removes target analytes altogether, along with matrix components.

Fast Gas Chromatography—Time-of-Flight Mass Spectrometry (GC-TOFMS) offers a practical way of resolving this dilemma. Presented here are the results from the analysis of 140 SVOCs, PCBs, and pesticides (including internal standards and surrogates) in crude soil extracts, with no clean-up and a run time of 23 minutes.

2. Experimental Conditions

Instrumentation

- CTC CombiPal Autosampler
- Agilent 6890 Gas Chromatograph
- LECO Pegasus® III GC-TOFMS
- LECO ChromaTOF® Software

Standards

No standard exists for this very large suite of compounds; therefore a mixture of an SVOC, a PCB, and a pesticide standard (consisting of OCPs, OPPs and Herbicides) was made, resulting in each sub-suite being at different concentrations. Hexachlorobenzene was present in two of these sub-suites and therefore is present at different levels again. Five surrogate compounds and six internal standards were used which eluted throughout the course of the GC run.

Soil Extraction

A 10 gram sample was extracted sequentially in acetone; 1:1 acetone/DCM; and DCM, by mechanical shaker. These extracts were combined to give solutions in 1:1 acetone/DCM before concentration by evaporation.

Extract Clean Up

None.

GC-TOFMS Analysis

A splitless injection (1 μ L) into a standard Agilent splitless liner, run on a J&W column (0.25 mm i.d.) with a fast column flow and ramp rate. Data analysis was performed using LECO ChromaTOF software.

3. Results

Example chromatograms of a sandy soil spiked at 20% of the calibration curve level can be seen in Figures 1 through 4, showing the SVOCs at a concentration of 4 ppm, pesticides at 0.4 ppm, and PCBs at 0.2 ppm. The Pegasus deconvolution software can analytically resolve closely coeluting target analytes, as shown in Figure 2; as well as resolving these analytes from the matrix background, as shown in Figure 4 where the matrix component unique masses are shown and the TIC overlaid. Target analytes at lower concentrations can be deconvoluted from peaks at much higher concentrations, as shown in Figure 1 where the hexachlorobenzene peak is at a higher concentration than the coeluting pesticides; and Figure 3 where dibutyl phthalate is at a much higher concentration than the coeluting PCB and pesticides.

During the method development it was found that a 0.25 mm i.d. column with a thicker film gave better results for the phenols than using a 0.18 mm i.d. column with a thinner film, however analysis of pesticides alone gave better results with the 0.18 mm i.d. column.

The results can be found in Table 1 for the 140 analytes. Two lots of data are presented: data from the solvent standards and the Certified Reference Material soil data. The data from the solvent standards shows the performance of the GC-TOFMS method; however the data from the CRM soil shows the performance of the extraction method as well as the GC-TOFMS, therefore data is also shown on the repeatability of the crude extracts—a total of 12 injections.

The data from the solvent standards shows good linearity (>0.994 , most at 0.999) and repeatability for 5 injections of a low standard with relative standard deviation of below 7% for all compounds and below 4% for most.

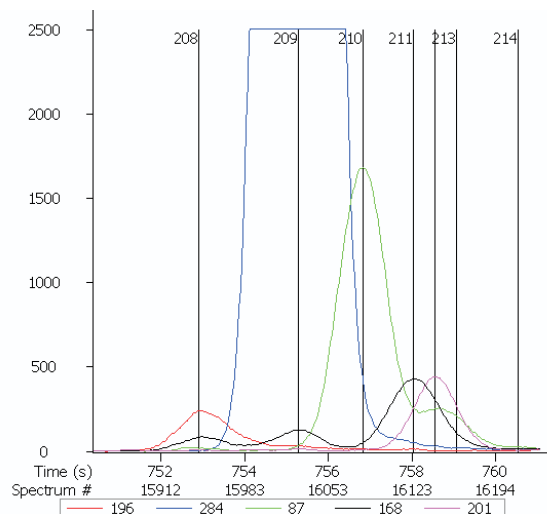


Figure 1. Quantification masses for Atraton (208); Hexachlorobenzene (209); Dimethoate (210); Prometon (211); Simazine (212) in a 20% spiked crude soil sample.

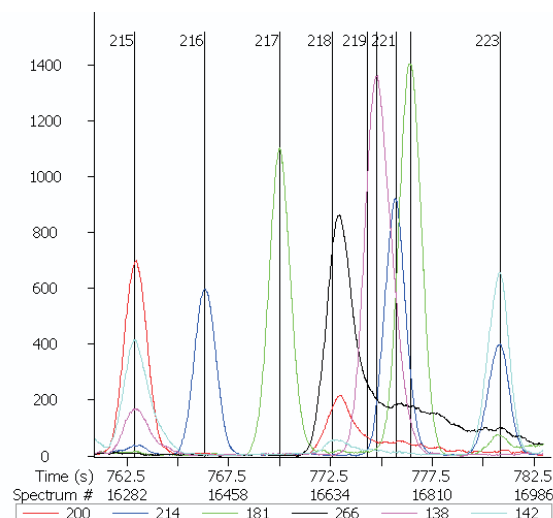


Figure 2. Quantification masses for Atrazine (215); Propazine (216); b-Lindane (217); Pentachlorophenol (218); Propetamphos (220); Terbutylazine (221); Lindane (222); Pentachloronitrobenzene (223) in a 20% spiked crude soil sample.

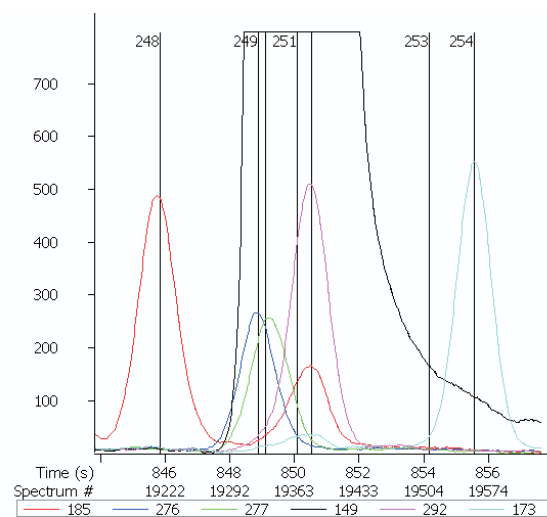


Figure 3. Quantification masses for Terbutryn (248); Pirimiphos methyl (249); Fenitrothion (250); Dibutyl phthalate (251); 1,1'-Biphenyl, 2,2,5,5-Tetrachloro- (252); Malathion (254) in an 80% spiked crude soil sample.

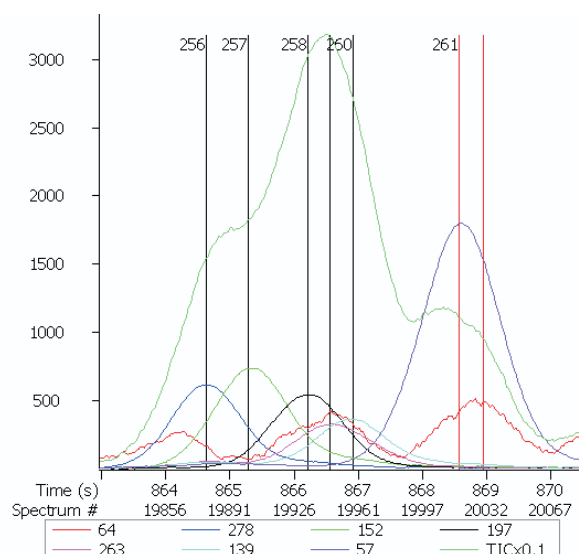


Figure 4. Quantification masses for Fenthion (256); Chlorpyrifos (258); Aldrin (259); Parathion (260); Triadimefon (261); matrix components (257, 262) and TIC x 0.1 in a 20% spiked crude soil sample.

GC-TOFMS analysis was performed on duplicate SVOC CRM soil extracts, from refrigerated storage rather than fresh ones; however, the within-batch precision and repeatability is good. The two CRM soil extracts were injected 6 times each and the results averaged for the 12 injections, giving results very close to the certified reference concentrations. The recoveries are very respectable for many of the analytes, but are poor for some; this could be because of the storage of the samples as the RSD of the 12 injections are good (<10% for the majority).

Example calibration curves are shown in Figures 5 through 10 for SVOCs phenol and 4-chloroaniline; pesticides dimethoate, endosulfan I and azinphos methyl; and PCB 2,2',3,4,4',5,5'-heptachloro-1,1'-biphenyl.

Name	Retention Time (sec.)	Type	Correlation Coefficient R2	RSD (%)	CRM Mean (mg/kg)	CRM Reference (mg/kg)	Spike Recovery (%)	RSD
Phenol-d6- **	332.085	Surrogate	0.99882	0.83	1.107	1.00	110.7	6.1
Phenol	332.965	Analyte	0.99903	1.07	12.414	14.70	84.4	7.5
Bis(2-chloroethyl) ether	341.059	Analyte	0.99967	0.53				
Phenol, 2-chloro-	344.609	Analyte	0.99919	0.52	6.480	8.45	76.7	8.5
Benzene, 1,3-dichloro-	356.708	Analyte	0.99949	0.29				
1,4-Dichlorobenzene-D4	359.718	IS	N/A	0.00				
Benzene, 1,4-dichloro-	361.110	Analyte	0.99866	0.25				
Benzene, 1,2-dichloro-	377.070	Analyte	0.99913	0.35				
Phenol, 2-methyl-	383.517	Analyte	0.99945	0.54				
Bis(2-chloroisopropyl) ether	387.323	Analyte	0.99982	0.33				
Phenol, 4-methyl-	395.985	Analyte	0.99941	0.93				
1-Propanamine, N-nitroso-N-propyl-	399.251	Analyte	0.99485	1.28				
Ethane, hexachloro-	403.539	Analyte	0.99973	0.35	5.152	8.49	60.7	5.7
Nitrobenzene-D5 ***	409.958	Surrogate	0.99130	1.18	0.611	0.50	122.2	4.0
Benzene, nitro-	411.548	Analyte	0.99973	1.01	8.906	11.30	78.8	5.9
Isophorone	432.592	Analyte	0.99841	0.74	3.343	4.24	78.8	10.0
Phenol, 2-nitro-	440.374	Analyte	0.99745	0.74	4.062	8.08	50.3	7.5
Phenol, 2,4-dimethyl-	444.038	Analyte	0.99871	1.41				
Methane, bis(2-chloroethoxy)-	453.779	Analyte	0.99705	1.47				
Phenol, 2,4-dichloro-	461.049	Analyte	0.99879	0.78	4.799	8.02	59.8	7.9
Benzene, 1,2,4-trichloro-	469.683	Analyte	0.99478	1.23	8.520	8.81	96.7	4.6
Naphthalene-D8	473.432	IS	N/A	0.00				
Naphthalene	475.164	Analyte	0.98181	0.62	13.199	13.05	101.1	2.6
4-Chloroaniline	482.321	Analyte	0.99909	1.38				
1,3-Butadiene, 1,1,2,3,4,4-hexachloro-	492.886	Analyte	0.99850	1.50				
Dichlorvos	507.938	Analyte	0.99810	1.57				
Phenol, 4-chloro-3-methyl-	528.045	Analyte	0.99848	1.83	3.889	6.42	60.6	8.8
Naphthalene, 2-methyl-	540.456	Analyte	0.99664	1.01				
1,3-Cyclopentadiene, 1,2,3,4,5,5-hexachloro-	562.636	Analyte	0.99753	1.44				
Phenol, 2,4,6-trichloro-	570.020	Analyte	0.99701	0.74	2.527	4.25	59.5	2.5
Phenol, 2,4,5-trichloro-	573.002	Analyte	0.99773	1.59				
1,1'-Biphenyl, 2-fluoro- ***	578.114	Surrogate	0.99683	0.76	0.395	0.50	78.9	5.5
Naphthalene, 2-chloro-	586.577	Analyte	0.99483	0.58				
2-Nitroaniline	599.925	Analyte	0.99495	0.81				
Mevinphos	607.820	Analyte	0.99648	1.36				
Dimethyl phthalate	622.049	Analyte	0.99890	1.49				
Acenaphthylene	627.161	Analyte	0.99689	0.73	6.236	9.22	67.6	5.6
2,6-Dinitrotoluene	627.842	Analyte	0.99907	0.85	1.873	2.30	81.5	2.9
3-Nitroaniline	640.083	Analyte	0.99747	1.66				
Acenaphthene-d10	642.298	IS	N/A	0.00				
Acenaphthene	645.308	Analyte	0.99427	1.36	9.100	10.20	89.2	4.3
Phenol, 2,4-dinitro-	649.852	Analyte	0.99476	1.75				
Phenol, 4-nitro-	656.072	Analyte	0.99620	3.71	9.498	10.20	93.1	3.1
Dibenzofuran	660.559	Analyte	0.98834	2.59	3.340	8.65	39.6	14.0
2,4-Dinitrotoluene	665.188	Analyte	0.99615	0.89	1.939	2.26	85.8	5.2
Diethyl Phthalate	691.089	Analyte	0.99943	1.40	8.691	9.92	87.6	9.2
Fluorene	694.100	Analyte	0.99673	1.50	3.019	3.50	86.3	6.0
4-Chlorophenyl phenyl ether	695.264	Analyte	0.99513	1.85	10.571	10.2	103.6	4.1
4-Nitroaniline	699.325	Analyte	0.99488	4.25				
Tecnazene	701.796	Analyte	0.99873	2.66				
Phenol, 2-methyl-4,6-dinitro-	703.926	Analyte	0.99411	1.03				
Azobenzene	710.344	Analyte	0.99729	1.38				
Phenol, 2,4,6-tribromo- **	719.177	Surrogate	0.99560	0.70	1.086	1.00	108.6	2.2
Trifluralin	727.867	Analyte	0.99856	2.69				
4-Bromophenyl phenyl ether	742.294	Analyte	0.99928	0.92	11.125	12.50	89.0	5.8
α-Lindane	747.747	Analyte	0.99979	1.08				
Atraton	752.802	Analyte	0.99716	4.64				
Benzene, hexachloro- *	755.387	Analyte	0.99609	1.77	9.749	10.40	93.7	5.9
Dimethoate	756.920	Analyte	0.99900	4.42				
Prometon	757.914	Analyte	0.99680	3.05				
Simazine	758.795	Analyte	0.99751	1.67				
Atrazine	763.140	Analyte	0.99779	2.27				
Propazine	766.463	Analyte	0.99646	2.85				
β-Lindane	770.297	Analyte	0.99935	1.63				
Phenol, pentachloro-	772.739	Analyte	0.99672	1.34	1.780	6.99	25.5	4.1
Propetamphos	774.869	Analyte	0.99754	2.54				
Terbutylazine	775.806	Analyte	0.99684	2.49				
Lindane	776.488	Analyte	0.99980	1.81				
Benzene, pentachloronitro-	780.975	Analyte	0.99868	0.75				
Phenanthrene-D10-	784.667	IS	N/A	0.00				

Name	Retention Time (sec.)	Type	Correlation Coefficient R2	RSD (%)	CRM Mean (mg/kg)	CRM Reference (mg/kg)	Spike Recovery (%)	RSD
Diazinon	784.843	Analyte	0.99916	2.57				
Phenanthrene	786.684	Analyte	0.99643	1.46	7.453	8.29	89.9	2.1
Anthracene	791.029	Analyte	0.99479	1.29	5.408	8.98	60.2	4.6
Erimfos	798.129	Analyte	0.99742	0.86				
Triallate	799.151	Analyte	0.99695	1.23				
Chlorothalonil	800.032	Analyte	0.99768	2.30				
Carbazole	807.558	Analyte	0.99207	1.62				
1,1'-Biphenyl, 2,4',5-trichloro-	822.950	Analyte	0.99875	1.85				
Methyl parathion	827.665	Analyte	0.99857	1.86				
Methyl chlorpyrifos	827.920	Analyte	0.99761	2.89				
Simetryn	828.744	Analyte	0.99267	7.35				
Ametryn	831.982	Analyte	0.99700	7.47				
Prometryn	834.367	Analyte	0.99619	3.72				
Heptachlor	837.605	Analyte	0.99883	2.05				
Terbutryn	845.642	Analyte	0.99785	3.67				
Pirimiphos methyl	848.794	Analyte	0.99783	1.60				
Fenitrothion	849.171	Analyte	0.99700	2.78				
Dibutyl phthalate	850.101	Analyte	0.99774	0.77	5.161	6.87	75.1	9.3
1,1'-Biphenyl, 2,2',5,5'-Tetrachloro-	850.442	Analyte	0.99824	2.67				
Malathion	855.497	Analyte	0.99741	3.14				
Fenthion	864.556	Analyte	0.99795	5.10				
Chlorpyrifos	866.317	Analyte	0.99758	6.07				
Aldrin	866.715	Analyte	0.99832	5.58				
Parathion	867.027	Analyte	0.99759	5.86				
Triadimefon	868.447	Analyte	0.99612	2.93				
Pendimethalin	892.161	Analyte	0.99841	1.39				
Heptachlor epoxide	897.864	Analyte	0.99859	4.96				
Clafenvinfos	897.926	Analyte	0.99787	3.33				
Fluoranthene	902.953	Analyte	0.99924	1.19	4.729	5.96	79.4	8.3
o,p'-DDE	917.409	Analyte	0.99935	4.90				
1,1'-Biphenyl, 2,2',4,5,5'-Pentachloro-	919.340	Analyte	0.99947	2.00				
Pyrene	924.253	Analyte	0.99619	1.67	1.472	2.51	58.6	4.1
Endosulfan I	927.065	Analyte	0.99969	5.06				
p,p'-DDE	940.924	Analyte	0.99938	2.26				
p-Terphenyl-d14 ***	942.742	Surrogate	0.99800	2.26	0.306	0.50	61.2	5.8
Dieldrin	947.115	Analyte	0.99972	2.92				
o,p'-DDD	948.336	Analyte	0.99967	3.45				
Endrin	964.581	Analyte	0.99930	3.91				
1,1'-Biphenyl, 2,3',4,4',5-Pentachloro-	967.592	Analyte	0.99837	3.96				
Endosulfan II	971.142	Analyte	0.99935	5.85				
p,p'-DDD	973.016	Analyte	0.99948	4.40				
Ethion	974.692	Analyte	0.99937	4.41				
o,p'-DDT	976.594	Analyte	0.99959	2.54				
Triazophos	983.552	Analyte	0.99955	2.40				
1,1'-Biphenyl, 2,2',4,4',5,5'-Hexachloro-	983.836	Analyte	0.99948	5.77				
Carbophenothion	992.442	Analyte	0.99969	1.88				
Benzyl butyl phthalate	995.310	Analyte	0.99893	2.00				
p,p'-DDT	1001.470	Analyte	0.99937	4.36				
Endosulfan sulfate	1002.640	Analyte	0.99820	3.67				
1,1'-Biphenyl, 2,2',3,4,4',5'-Hexachloro-	1005.340	Analyte	0.99877	3.19				
Methoxychlor	1007.780	Analyte	0.99951	5.12				
Benz[a]anthracene	1041.550	Analyte	0.99959	1.73				
Chrysene-D12	1043.080	IS	N/A	0.00				
Chrysene	1045.460	Analyte	0.99789	1.21				
1,1'-Biphenyl, 2,2',3,4,4',5,5'-Heptachloro-	1054.100	Analyte	0.99933	3.79				
Bis(2-ethylhexyl) phthalate	1054.500	Analyte	0.99914	2.84	9.709	11.20	86.7	4.9
Phosalone	1065.340	Analyte	0.99983	5.35				
Azinphos-Methyl	1067.360	Analyte	0.99942	4.45				
Azinphos-ethyl	1091.610	Analyte	0.99916	3.10				
Permethrin	1105.620	Analyte	0.99882	3.57				
Permethrin-2	1110.240	Analyte	0.99991	1.32				
Di-n-octyl phthalate	1110.470	Analyte	0.99997	1.53				
Benzo[b]fluoranthene	1140.210	Analyte	0.99997	0.92				
Benzo[k]fluoranthene	1142.080	Analyte	0.99977	1.21				
Benzo[a]pyrene	1166.850	Analyte	0.99975	0.86				
Perylene-D12	1171.790	IS	N/A	0.00				
Indeno[1,2,3-cd]pyrene	1259.490	Analyte	0.99969	1.04				
Dibenz[a,h]anthracene	1260.740	Analyte	0.99957	1.48				
Benzo[ghi]perylene	1283.510	Analyte	0.99975	0.54				

Table 1. Calibration data (an SVOC, a PCB and a pesticide standard were mixed to produce the large standard mixture resulting in compounds at different concentrations): SVOCs 1-20 µg/mL; Pesticides 0.1-2 µg/mL; PCBs 0.05-1 µg/mL; HCB (present in 2 original standards) 1.1-22 µg/mL; Surrogates ** 1-20 µg/mL and * 0.5-10 µg/mL; Internal standards 10 µg/mL. Repeatability: % RSD of low Std2 n=5.**

CRM data: SVOC CRM 117-100 (results corrected for 10x dilution), Matrix: Sandy Loam; Mean of two soil extracts each injected six times n=12; spike recovery against certified soil. Note: CRM data from stored soil extracts not fresh extracts.

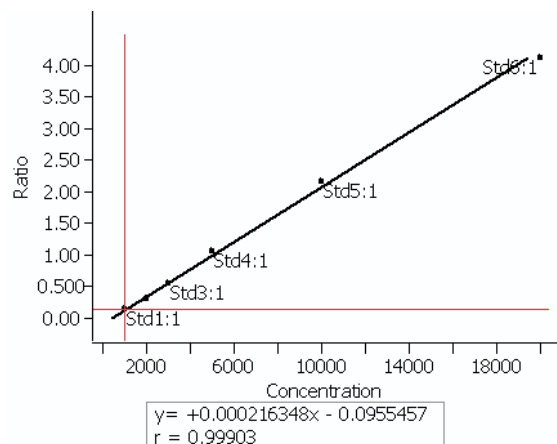


Figure 5. Phenol 1000-20000 µg/L (100-2000 µg/kg).

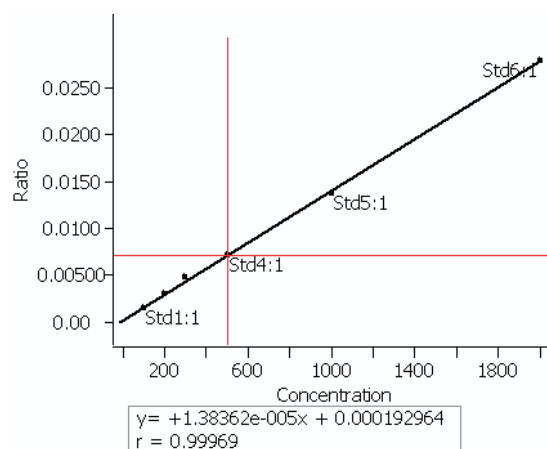


Figure 8. Endosulfan I 100-2000 µg/L (10-200 µg/kg).

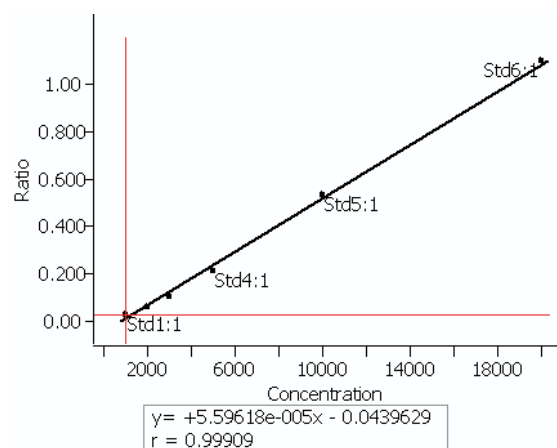


Figure 6. 4-Chloroaniline 1000-20000 µg/L (100-2000 µg/kg).

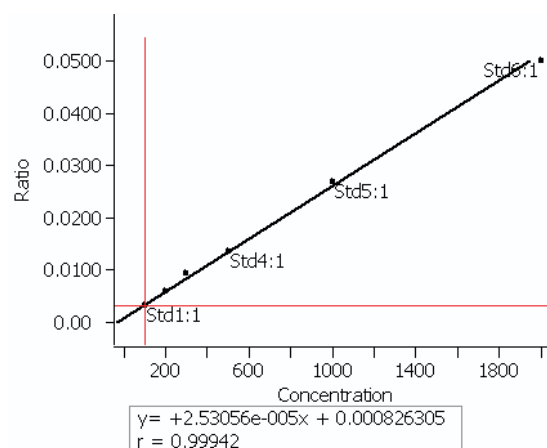


Figure 9. Azinphos methyl 100-2000 µg/L (10-200 µg/kg).

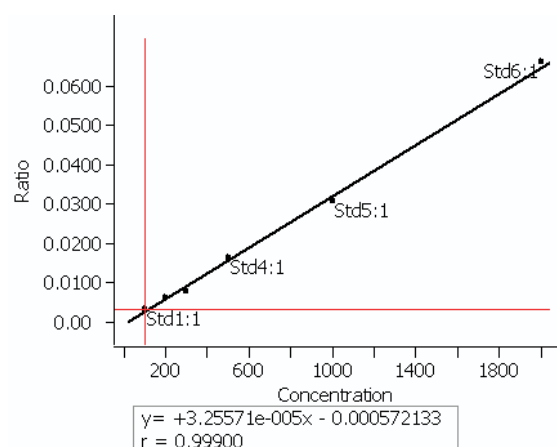


Figure 7. Dimethoate 100-2000 µg/L (10-200 µg/kg).

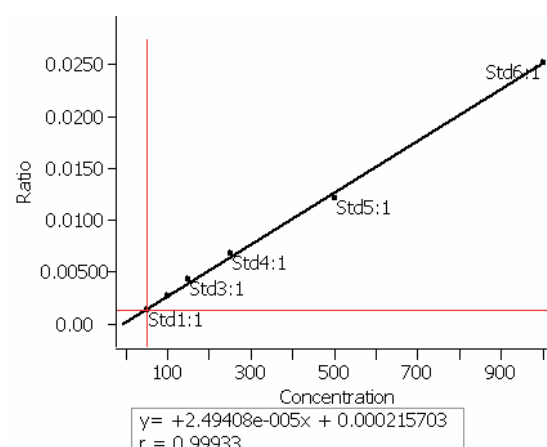


Figure 10. 1,1'-Biphenyl, 2,2',3,4,4',5,5'-Heptachloro- 50-1000 µg/L (5-100 µg/kg).

4. Conclusions

The ability of the fast GC-TOFMS to cope with high levels of matrix background greatly reduces the need for sample clean-up and reduces the potential losses of some analytes during this process. With spectral deconvolution, analysis times can be greatly reduced and a much larger number of analytes accurately identified using the full mass spectrum rather than using target and qualifying ions.

However, although the detector needs very little maintenance (it isn't necessary to clean the ion source on the TOFMS), rigorous maintenance of the GC inlet and column is even more crucial due to the nature of the samples being injected. Through the development of liner exchange systems, Anatune hopes to further improve this application.

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ALcontrol Laboratories



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