AccuTOF™

A new method for pesticides identification: fast GC/time-of-flight mass spectrometry

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Introduction

Pesticides have been widely used all over the world. Although the use of pesticides is strictly regulated in many countries, laboratories still monitor their residues due to their toxicity and highly persistent nature. The most common method for pesticides identification is GC/MS with select ion monitoring (SIM). Since most of samples contain many different components, a long GC separation is generally needed when a low-resolution SIM MS is used. This is very time-consuming. Fast GC has been available for several years; however, the combination of fast GC with mass spectrometry had not been commercially available until high acquisition rate time-of-flight mass spectrometry was introduced. Here, we describe a new method by using fast GC/time-of-flight MS to identify 67 pesticides. The high resolution time-of-flight MS always yields high quality library searchable spectrums without compromising the sensitivity. The method is simple, fast, and reliable.

Experimental

All solvents used were of HPLC grade. The pesticide standards used are listed in Table 1. They were prepared in ethyl acetate with concentration of 100 ppb.

An Agilent 6890N gas chromatograph was used. Samples were injected onto an HP-5MS capillary column (10 x 0.18 mm, 0.18 μm film thickness) with splitless injection mode. Helium was used as the carrier gas and set at 0.6 mL/min. The injector temperature was set at 200 °C. The oven temperature was held at 40 °C for 1 min and then increased to 300 °C at a rate of 50 °C/min.

Pesticide	Formula	Pesticide	Formula	Pesticide	Formula
Simazine	C7H12ClN5	Thiobencarb	C12H16ClNOS	Isoxathion	C13H16NO4PS
Diazinon	C12H21N2O3PS	Fenitrothion	C9H12NO5PS	Isoprothiolane	C12H18N4S2
Chlorothalonil	C8Cl4N2	Propyzamide	C12H11Cl2NO	Dichlorvos	C4H7Cl2O4P
Fenobcarb	C12H17NO2	Chlornitrofen	C12H6Cl3NO3	CNP-amino	C12H8Cl3NO
Iprobenfos	C13H21O3PS	EPN	C14H14NO4PS	Isofenphos	C15H24NO4PS
Chlorpyrifos	C9H11Cl3NO3PS	Pyridafenthion	C14H17N2O4PS	Iprodione	C13H13Cl2N3O3
Etridiazole	C5H5Cl3N2OS	Captan	C9H8Cl3NO2S	Chloroneb	C8H8Cl2O2
Tolclofos-methyl	C9H11Cl2O3PS	Flutolanil	C17H16F3NO2	Pencycuron	C19H21ClN2O
Metalaxyl	C15H21NO4	Mepronil	C17H19NO2	Dithiopyr	C15H16F5NO2S2
Terbucarb	C17H27NO2	Napropamide	C17H21NO2	Pyributicarb	C18H22N2O2S
Butamifos	C13H21N2O4PS	Benfluralin	C13H16F3N3O4	Pendimethalin	C13H19N3O4
Methyldymron	C17H20N2O	Alachlor	C14H20ClNO2	Edifenphos	C14H15O2PS2
Pyroquilon	C11H11NO	Phthalide	C8H2Cl4O2	Mefenacet	C16H14N2O2S
Pretilachlor	C17H26ClNO2	Isoprocarb	C11H15NO2	Thenylchlor	C16H18ClNO2S
Methidathion	C6H11N2O4PS3	Bromobutide	C15H22BrNO	Molinate	C9H17NOS
Procymidone	C13H11Cl2NO2	Anilofos	C13H19ClNO3PS2	Atrazine	C18H14ClN5
Dichlobenil	C7H2Cl2N	Dimethoate	C5H12NO3PS2	Endosulphan	C9H6Cl6O3S
Etofenprox	C25H28O3	Fenthion	C10H15O3PS2	Malathion	C10H19O6PS2
Simetryne	C8H15N5S	Dimepiperate	C15H21NOS	Phenthoate	C12H17O4PS2
Buprofezin	C16H23N3OS	Ethyl thiometon	C8H19O2PS3	Esprocarb	85785-20-2
Bifenox	C14H9Cl2NO5	Piperophos	C14H28NO3PS2	Dimethametryn	C11H21N5S
Propiconazole	C15H17Cl2N3O2	Pyriproxyfen	C20H19NO3	Trifluralin	C13H16F3N3O4
Cafenstrole	C16H22N4O3S				

Table 1. List of 67 pesticides

The mass spectrometer system consisted of JEOL AccuTOF-GC™ time-of-flight mass spectrometer with EI source and JEOL MassCenter™ workstation. The source and transfer line temperature were set at 250°C, respectively. The detector voltage was set at 2500V. The acquisition range is from m/z 35 to 500 with spectrum recoding interval of 0.05 s. The system was tuned with PFK to achieve a resolution of 6,000 (FWHM) at m/z 292.9824.

Results

Figure 1 shows the TICs of 67 pesticides separated by the AccuTOF™ GC/MS system. The high acquisition rate of this GC/MS system makes fast GC separation possible. The running time is only 6.5 min.

In order to determine the data quality for the unresolved chromatographic peaks, we chose tolclofos-methyl and alachlor. Their retention times have only 0.008 min difference. Since time-of flight mass spectrometer always runs at high resolution and full mass range without compromising the sensitivity, a full mass-range spectrum can be obtained for each pesticide.

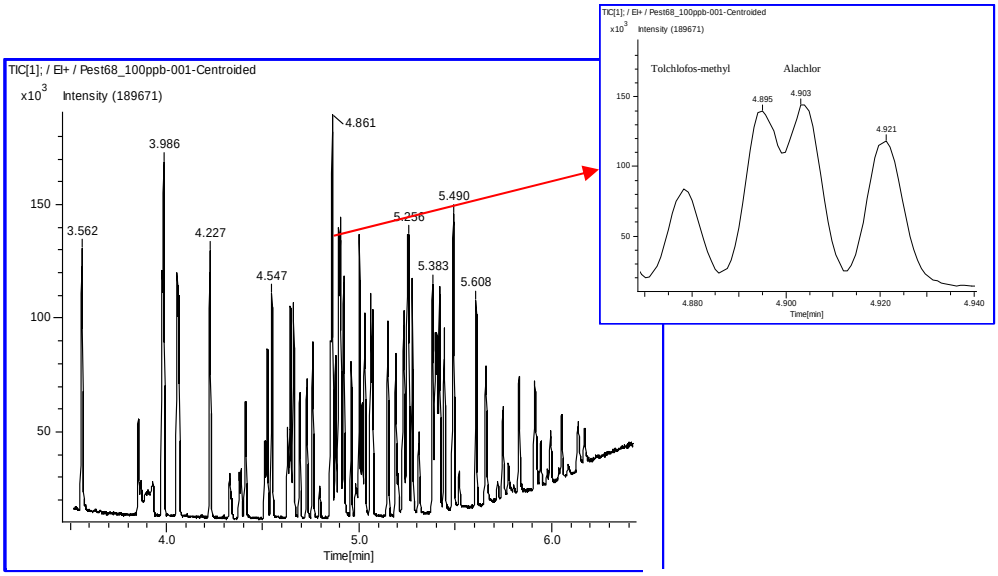

Fig 1. Total ion chromatogram of 67 pesticides.

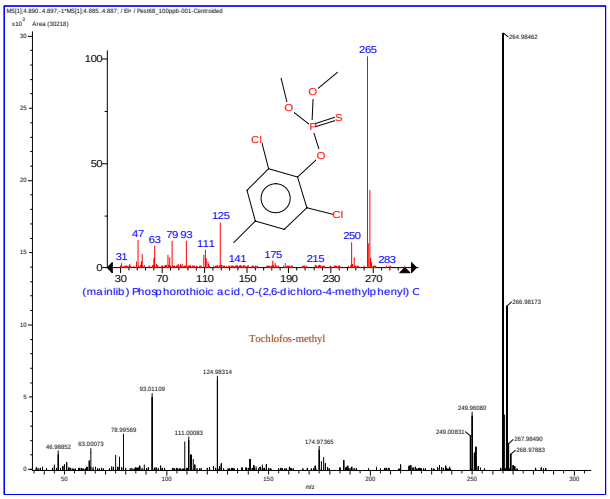

Fig. 2 Mass spectra for selected two pesticides

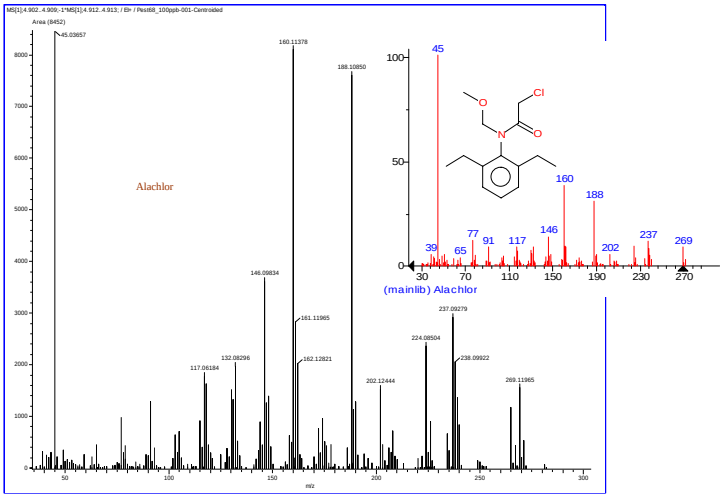

Figure 2 shows the mass spectra for these two pesticides in the sample and their corresponding spectra in the NIST library. An excellent library search was obtained and the results are shown in Figure 3. The probability index for both pesticides is greater than 97%, showing a strong confidence for identification results.

In addition, the high-resolution time-of-flight MS system has the capability for exact mass measurement. Possible elemental compositions for each pesticide and its fragments are ready obtained. The exact mass measurement results for two selected pesticides are listed in Table 2. The errors for all selected ions are less than 2 mmu.

The elemental composition estimation combined with full mass range spectrum make the identification unambiguous.

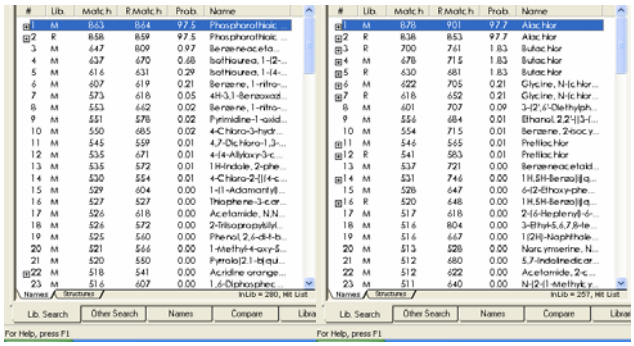

Fig 3. NIST library research.

Tolclofos-methyl			
Measured m/z	Calc. m/z	Error (mmu)	Formula
124.9831	124.9826	0.5	$C_2H_6O_2PS$
174.9737	174.9717	2.0	$C_7H_5Cl_2O$
249.9608	249.9620	-1.2	$C_8H_8ClO_3PS$
264.9846	264.9855	-0.9	$C_9H_{11}ClO_3PS$
Alachlor			
146.0983	146.0970	1.3	$C_{10}H_{13}N$-H
160.1138	160.1126	1.2	$C_{11}H_{15}N$-H
174.0925	174.0919	0.6	$C_{11}H_{13}NO$-H
188.1085	188.1075	1.0	$C_{12}H_{15}NO$-H
202.1244	202.1232	1.2	$C_{13}H_{17}NO$-H
224.0850	224.0842	0.8	$C_{12}H_{15}ClNO$
237.0928	237.0920	0.8	$C_{13}H_{17}ClNO$
269.1197	269.1183	1.4	$C_{14}H_{20}ClNO_2$

Table 2. Exact mass measurement results for major fragment ions for two selected pesticides.

Conclusion

Fast GC/time-of-flight mass spectrometry was used to identify 67 pesticides in 6.5 minutes. Full mass range spectrum and exact mass measurement provide positive identification.

References

1. Lehotay SJ. *Journal of AOAC International.* 83(3):680-97, 2000 May-Jun.
2. http://www.leco.org/customersupport/apps/separationscience/-227.pdf