RESIDUES AND TRACE ELEMENTS

Analysis of Pesticide Residues in Fruits, Vegetables, and Milk by Gas Chromatography/Tandem Mass Spectrometry

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A method for detection, quantitation, and confirmation of more than 100 pesticides by gas chromatography (GC) with ion trap mass spectrometry (MS/MS) has been developed. The sensitivity of this method for many analytes is equal to or lower than those of selective GC detectors such as flame photometric detectors and electrolytic conductivity detectors. Using MS/MS, very low detection limits and good confirmation (1 precursor ion and 2 or more product ions) are achieved simultaneously. The entire list of pesticides is screened with 2 injections per sample. Samples are introduced onto the column by a temperature-programmed cold injection to maximize response. Each pesticide is run with its own unique set of parameters, which fragment the compound, retaining only the precursor ion. This ion is then refragmented to create a product spectrum. The selectivity of MS/MS gives a very clean spectrum, making compound identification and confirmation clear, even with a relatively dirty food matrix. If care is taken to maintain the injection port and guard column, this method can reliably identify and confirm more than 100 pesticides at the low parts-per-billion range.

Contamination of food commodities with trace amounts of pesticides has become a growing source of concern for the general population. For many years, the New York State Department of Agriculture has analyzed fruits, vegetables, and milk for phosphated and chlorinated pesticides at low parts-per-billion levels by using selective detectors combined with mass spectrometric confirmation through selective-ion monitoring (SIM; 1). Many pesticides seem to have endocrine-disrupting effects even at low levels, prompting regulatory agencies to request very sensitive analytical methods (2). Determining the effect of repeated low-level exposure to pesticides on humans, especially children, cannot be made without extremely low detection limits. Many of these compounds, such as the organochlorinated pesticides, also have been shown to bioaccumulate in the fat tissue of animals (3). Several years of monitoring have shown that most reported amounts of these compounds, obtained by gas chromatography (GC) with selective detectors, are near the method detection limit. Without these low detection limits, many residues would have gone unreported. Selective detectors such as electrolytic conductivity detectors (ELCD) and flame photometric detectors (FPD) are very sensitive but do not detect pesticides without phosphorus or chlorine. If pesticides must be confirmed by mass spectrometry, the detection limits are determined by the detection limits of the mass spectrometer. Also SIM confirmations, especially at low levels, can be suspect.

Typically, the usefulness of a benchtop mass spectrometer for screening pesticides is limited by its poor sensitivity compared with those of GC detectors. The use of GC with tandem mass spectrometry (MS/MS) is one method of obtaining confirmation at a sensitivity similar to those of typical GC detectors. MS/MS can achieve excellent sensitivity even with complex matrixes, because it eliminates interference prior to ion measurement (4, 5). In the process, the sample exits the analytical column and becomes ionized in the first stage of MS/MS. At this point, all but a very narrow range of masses are ejected. In the second stage of MS/MS, this retained range of masses is fragmented and the results are then measured.

One technique uses 3 quadrupoles in series to accomplish MS/MS. The first quadrupole functions as a mass filter that retains only ions within a small range of masses. The second quadrupole is the collision chamber, where the isolated ions are fragmented and transferred to the third quadrupole. The third quadrupole filters the results of the fragmentation so they can be scanned as the product spectrum. This triple quadrupole is referred to as a tandem-in-space instrument, because each step in the process requires a unique instrument component (6). While giving excellent confirmatory information, the triple-quadrupole arrangement has poor precision because of transmission losses (7).

A second technique involves the use of an ion trap, in which all MS/MS steps are performed. This paper describes this technique. An ion trap instrument is referred to as a tandem-in-time instrument, because the same ion region is used for all MS/MS processes (8). In a typical ion trap operation, ions are held and selectively ejected from the trap by application of a radio-frequency (rf) voltage to the ring electrode and a fixed-frequency voltage to the end cap electrode. With

Received October 23, 1998. Accepted by JS January 1, 1999.

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proper instructions, the trap can be programmed to eject undesired ions, retaining only those of a narrow range of masses (9–11). To produce product ions, the isolated ions (parent or precursor ions) that are held in the trap are fragmented. Precursor ion fragmentation can be performed 2 ways. With nonresonant excitation, a supplemental low-frequency voltage is applied to the end caps of the trap, resulting in an instantaneous change in potential energy. This energy is converted to vibrational energy, which contributes to dissociation of the ions held in the trapping field. With resonant excitation, a supplemental high-frequency rf voltage is applied to the trap end caps. If the frequency of the applied voltage matches the oscillation frequency of the trapped ion, the kinetic energy of the ion is increased. This increase in energy results in collision-induced dissociation (CID) and product-ion formation. Because resonant excitation selectively adds energy to ions of a particular mass/charge ratio, energy for fragmentation may be added to a precursor ion by increasing the excitation time without ejecting the ion. In this manner, compounds that require many bonds to be broken in order to produce fragmentation may be analyzed.

With both methods of product ion formation, the ion trap must be told how and when to apply these functions. Each analyte must have its own list of parameters that will create the desired product spectrum. These parameters are entered by the user and saved as instructions that the computer uses to control the ion trap. These files are known as ion-preparation method (IPM) files.

GC/MS/MS is effective in identifying pesticides in agricultural matrixes at parts-per-billion levels (12). Varian's Saturn 2000 tandem mass spectrometer has proven to be as sensitive as selective detectors for most pesticides, and is not limited to detecting compounds with a heteroatom such as chlorine or phosphorus. It also offers confirmation without reinjection and is less susceptible than selective detectors to interfering coextractives because the parent ion is isolated prior to the second stage of MS/MS.

METHOD

Apparatus

(**a**) *Blender*.—1 quart glass (explosion proof; Waring, New Hartford, CT).

(**b**) *Liquid concentrator*.—Turbovap 6 cell evaporator (Zymark, Hopkinton, MA) with graduated 200 mL tubes.

(**c**) *Centrifuge*.—200 mL bottle capacity.

(**d**) *GC/MS/MS system*.—Saturn 2000 (Varian, Walnut Creek, CA).

Reagents

(**a**) *Solvents*.—Analytical grade ethanol, acetonitrile, toluene, acetone, and methanol (J.T. Baker, Phillipsburg, NJ).

(**b**) *Water*.—Deionized.

(**c**) *Na_2SO_4*.—Anhydrous, 10–60 mesh (Fisher, Fairlawn, NJ).

(**d**) *NaCl*.—Certified ACS (Fisher).

(**e**) *Solid-phase extraction (SPE) tubes*.—Envi-Carb (Supelco, Bellefonte, PA), 5 g–6 mL; SAX and PSA, 3 mL and 500 mg; 75 mL Bond Elut tube reservoir (Varian, Harbor City, CA).

Extraction

Combine 50 g of a chopped sample (or milk) with 100 mL acetonitrile–ethanol (95 + 5, freshly made) in a 1 quart blender. Blend for 5 min. Add 15 g NaCl and blend for 5 min. Remove ca 40 mL (ca 70 mL for milk) of the top organic layer and transfer to a 200 mL centrifuge bottle. Add 15 g Na_2SO_4 and shake well. Centrifuge on high speed for 5 min. Quantitatively transfer 30 mL (50 mL for milk) to a 200 mL Zymark concentrator tube and concentrate to ca 5 mL at 35°C under nitrogen. Place ca 2 cm Na_2SO_4 in the Envi-Carb SPE tube and wash with 5 mL toluene. Wash 1500 mg SAX SPE tube and 1500 mg PSA SPE tube with 5 mL toluene. Connect from top to bottom the 75 mL reservoir and the Envi-Carb, SAX, and PSA tubes and prewet with 5 mL acetonitrile–toluene (3 + 1, made on the day of use). Transfer concentrated sample to reservoir, and with N_2, push sample to Envi-Carb tube. Elute with four 10 mL volumes of 3:1 (v/v) acetonitrile–toluene and collect in a 200 mL Zymark concentrator tube. Concentrate the eluent to <1 mL. Add ca 10 mL acetone and concentrate to 2 mL. For the carbamate analysis via LC, remove 1 mL of the final sample and concentrate to <0.1 mL. Add ca 5 mL methanol and concentrate to 1 mL.

Concentration factors are 7.5 g/mL (50 g sample × 30 mL/100 mL ÷ 2 mL final volume) for fruits and vegetables and 12.5 g/mL for milk (50 g sample × 50 mL/100 mL ÷ 2 mL final volume).

Instrument Conditions

(**a**) *GC/MS/MS system*.—Trap temperature, 200°C; manifold temperature, 35°C; 1079 temperature-programmable injection port: initial temperature, 53°C; initial time, 0.30 min; rate, 300°C/min; final temperature, 250°C; column pressure, 10 psi; split vent valve: initial condition, open; closed at 0.45 min, open at 2.00 min; ratio, 100% open; 8200 autosampler: injection time, 0.1 min; solvent plug, 1.0 µL; injection rate, 0.5 µL/s; lower air gap, yes; upper air gap, yes; air dry, no; needle depth, 90%; uptake speed, 2.0 µL/s; sample volume, 5 µL.

(**b**) *Gas chromatograph*.—Initial temperature, 55°C for 2.0 min, raise to 230°C at 10°C/min, hold for 10 min, raise to to 275°C at 20°C/min, and hold for 19 min.

Results and Discussion

Extraction was based on a previous method using a carbon-based SPE tube (Envi-Carb) to retain analytes (13). Changes were made to obtain a more concentrated final extract. The result was a concentration factor of 7.5 µg/mL, which allows very low detection limits. In addition, the method requires no halogenated solvents.

To maximize sensitivity, 5 µL is injected by a typical large-volume technique. The sample is injected slowly, just

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Table 1. IPM parameters for various pesticides

Pesticide	No. of injections	Parent ion, *m/z*	Quantification ion, *m/z*	Retention time, min	CID amplification, V	CID RF, V
Dichlorvos	1	185	93	11.58	57	66
Diuron	1	187	124	13.05	72	75
Mevinphos-e	1	192	164	14.38	44	75
Mevinphos-z	1	192	164	14.47	44	75
Carbofuran,3-OH	1	180	137	15	29	50
THPA	1	151	79	15.75	42	50
O-phenylphenol	1	169	115	15.87	80	80
PCB	1	250	142	16.13	100	90
Propoxur	1	152	110	17.02	34	75
Propachlor	1	176	134	17.11	27.7	48
Tecnazene	1	259	201	17.18	52	75
Ethalfluralin	1	334	316	17.33	31	75
Trifluralin	1	306	206	17.45	52	75
Phorate	1	231	175	17.98	46	75
Dimethoate	1	125	79	18.73	55	56
Simazine	1	201	186	18.78	66	99
Phosphamidon A	1	264	193	19.2	74	120
Lindane	1	219	183	19.32	71	100
Quintozene	1	295	265	19.32	57	93
Phosphamidon B	1	264	193	20.13	74	120
Chlorpyrifos-m	1	286	208	20.5	78	89
Prometryn	1	242	184	20.69	31	48
Ametryn	1	212	122	20.73	35.7	48
Heptachlor	1	272	237	20.83	59	75
Fenitrothion	1	260	125	21.65	58	75
Chlorpyrifos	1	314	258	21.7	95	172
Phorate sulfone	1	199	171	21.7	70	75
Aldrin	1	295	222	21.78	65	80
Dacthal (DCPA)	1	301	273	21.78	66	80
Parathion	1	291	114	22.1	58	81
Demeton S sulfone	1	197	169	22.85	44	75
Pendamethalin	1	252	208	23.14	26.2	48
Terbufos sulfone	1	199	171	23.15	46	75
Oxychlordane	1	387	351	23.33	44	75
Methadithion	1	145	85	24.4	0.18	70
DDE-*o,p*	1	316	246	24.6	54	75
Chlordane-t	1	375	301	24.78	68	100
Chlordane-c	1	375	301	24.98	68	100
Profenofos	1	339	267	26.03	40	75
DDE-*p,p*	1	316	246	26.05	54	75
Oxyflurofen	1	252	170	26.4	65	71
DDD-*o,p*	1	235	165	26.8	63	75
Ethion	1	231	175	27.9	46	75
Sulprofos	1	322	156	29.38	40	75
Endosulfan II	1	340	267	29.77	60	125

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Table 1. (*continued*)

Pesticide	No. of injections	Parent ion, *m/z*	Quantification ion, *m/z*	Retention time, min	CID amplification, V	CID RF, V
Carbophenothion	1	296	138	30.35	61	100
Propiconazole	1	259	191	30.89	26.6	48
Propiconazole	1	259	191	31.17	26.6	48
Propargite	1	350	137	31.22	30	71
Endosulfan sulfate	1	387	289	31.63	38	71
Fenamiphos sulfoxide	1	304	196	32.45	40	75
Methoxychlor	1	227	153	32.85	72	80
Phosmet	1	160	133	33.1	76	75
Lambda cyhalothrin	1	181	152	34.02	0.58	50
Lambda cyhalothrin	1	181	152	34.47	0.58	50
Azinphos-m	1	160	132	34.77	60	75
Coumaphos-O-analog	1	346	220	37.13	46	75
Cyfluthrin	1	206	151	39.07	80	75
Fenvalerate	1	225	119	44	51	71
Esfenvalerate	1	225	119	44.98	51	75
Methamidophos	2	141	126	11.73	43	65
Acephate	2	136	42	14.87	0.2	35
1-Naphthol	2	144	116	15.87	43	48
Propoxur	2	152	110	17.02	34	75
Omethoate	2	156	141	17.08	54	75
Phorate oxon	2	171	115	17.12	64	75
Ethoprop	2	158	94	17.23	30	48
Diphenylamine	2	168	139	17.37	94	80
Chlorpropham	2	213	171	17.57	59	100
α-BHC	2	219	183	18.48	69	100
HCB	2	284	177	18.67	100	93
Carbofuran	2	164	149	18.73	35	50
Atrazine	2	216	200	18.82	100	143
Terbufos	2	231	175	18.88	76	125
Diazinon	2	305	179	18.95	42	75
Fonofos	2	246	137	19.21	24.7	48
Dichloran	2	176	148	19.22	80	75
Disulfoton	2	274	245	19.38	20	71
β-BHC	2	219	183	20.12	49	71
Acetochlor	2	146	130	20.3	73	75
Vinclozolin	2	212	109	20.42	70	71
Alachlor	2	188	160	20.55	61	75
Metribuzin	2	198	110	20.69	34.5	48
Fenitrothion-O-analog	2	244	109	20.7	62	75
Metylaxyl	2	206	132	20.77	56	75
Parathion-m	2	263	246	20.82	58	98
Carbaryl	2	144	116	20.98	46	50
Pirimiphos-M	2	290	151	21.11	56	75
Malathion	2	173	127	21.23	30	60
Linuron	2	248	61	21.6	0.17	45

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Table 1. (*continued*)

Pesticide	No. of injections	Parent ion, *m/z*	Quantification ion, *m/z*	Retention time, min	CID amplification, V	CID RF, V
Metolachlor	2	238	162	21.66	27	48
Fenthion	2	278	135	21.85	56	75
Phorate sulfoxide	2	277	199	21.95	45	71
Cyanazine	2	225	189	22.17	33.4	48
DCBP	2	215	179	22.7	0.45	60
Chlorfevinfos-e	2	267	159	23.07	81	100
Chlorfevinfos-z	2	267	159	23.22	81	100
Heptachlor epoxide	2	355	263	23.42	47	75
Triadimenol	2	168	85	23.87	38.5	48
Thiabendazole	2	201	174	24.35	68	71
Tetrachlorvinfos (Gardona)	2	331	109	24.42	62	80
Captan	2	149	121	24.55	80	75
Disulfoton sulfone	2	213	153	24.7	0.19	100
Endosulfan I	2	340	267	25.13	60	125
Imazalil	2	173	109	25.9	80	75
Dieldrin	2	277	241	26.47	74	100
Myclobutanil	2	179	152	27.27	0.22	60
DDT-*o,p*	2	235	165	29.04	59	75
DDD-*p,p*	2	235	165	29.45	63	75
Methoxychlor olefin	2	308	238	30.56	54	75
DDT-*p,p*	2	235	165	31.05	62	75
Piperonyl butoxide	2	176	117	31.37	61	71
Bifenthrin	2	181	165	32.17	39	50
Fenamiphos sulfone	2	320	292	32.6	0.15	105
Iprodione	2	315	245	32.87	89	125
Phosalone	2	367	182	34.7	32	80
Permethrin-c	2	183	165	36.5	64	71
Permethrin-t	2	183	165	36.92	68	75
Coumaphos	2	362	334	38.8	44	75
Cypermethrin	2	181	152	40.23	83	75

below the boiling point of the sample solvent (acetone's boiling point is 56°C and so the sample is injected at 53°C). At the time of injection, the split vent is open, and carrier gas (helium) is allowed to evaporate the solvent. The split vent is then closed, and the injection port temperature is raised quickly (300°C/min) to 250°C to focus the analytes at the head of the column (DB-XLB, 30 m, 0.25 mm id, 0.25 μm film thickness; J&W Scientific, Folsom, CA). Because 5 μL is a relatively large injection volume, the amount of sample matrix that enters the column must be minimized with the use of, for example, a Carbofrit (Restek, Bellefonte, PA) injection port insert packing. The Carbofrit packing is a porous carbon plug that retains coextractives that otherwise would be deposited in the column, interfering with chromatography and reducing column life span.

To perform MS/MS, each analyte must have its own IPM, which performs the functions of ionization, isolation, and precursor fragmentation (12). Because an IPM is built with parameters specific to the analyte, each IPM must be executed only during elution of the desired analyte. Therefore, each analyte should be chromatographically separated to maintain more easily the coincidence of the peak and its related IPM.

To maximize separation of pesticides, they are sorted by retention time and placed into 2 groups. The groups are organized to leave at least 0.1 min between peak maxima. Thus, each IPM is performed during elution of the respective peak. When 0.1 min separation is not possible, the 2 IPMs are combined (14). However, no more than 2 waveforms are combined, because combining 3 or more will reduce sensitivity for all compounds involved. Combining 2 IPMs into one involves

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Table 2. Pesticides found in fruits, vegetables, and milk

Sample No. and commodity	Pesticides found	Amount, ppm	
		Selective detector	MS/MS
913 green bean	Methamidophos	0.012	0.011
	Acephate	0.026	ND
914 green bean	Methamidophos	0.008	0.014
	Acephate	0.013	ND
	Trifluralin	ND[a]	0.00004
	Demeton-s-sulfone	ND	0.15
915 green bean	Demeton-s-sulfone	0.38	0.35
	Methamidophos	0.053	0.024
	Acephate	0.015	ND
923 peaches	Iprodione	<0.05[b]	0.003
	Permethrin-t	<0.016	0.0002
925 peaches	Permethrin-t	<0.016	0.0007
	THPA (captan breakdown)	<0.030	0.009
930 peaches	Iprodione	0.006	0.006
	Permethrin-t	<0.016	0.001
	Permethrin-c	<0.024	0.001
313 sweet potato	Chlorpyrifos	<0.010	0.0006
	Dichloran	0.23	0.24
	Esfenvalerate	ND	0.00021
	Fenvalerate	ND	0.00021
	Piperonyl butoxide	ND	0.00017
	Trifluralin	ND	0.000094
569 sweet potato	Chlorpyrifos	<0.003	0.0007
	Dichloran	1.3	0.77
	Piperonyl butoxide	<0.04	0.007
565 pear	Azinphos-m	0.21	ND
	Methoxychlor olefin	ND	0.0005
	Permethrin-c	ND	0.006
	Permethrin-t	ND	0.0004
	Endosulfan II	<0.003	ND
	Endosulfan sulfate	ND	0.001
	Parathion-m	<0.003	0.002
	Thiabendazole	1.1	0.79
	Chlorpyrifos	ND	0.0004
512 spinach	Permethrin-c	1.2	1.3
	Permethrin-t	1.3	1.4
	Trifluralin	ND	0.0002
622 green bean	Dacthal	ND	0.0006
	DDE-*p,p*	ND	0.002
	Metalaxyl	0.017	0.025
	Permethrin-c	0.58	0.73
	Permethrin-t	0.56	0.68
	Trifluralin	ND	0.004
653 sweet potato	Chlorpyrifos	0.008	0.011

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Table 2. (*continued*)

Sample No. and commodity	Pesticides found	Amount, ppm	
		Selective detector	MS/MS
	Dichloran	ND	0.0006
	Endosulfan I	<0.006	0.002
	Endosulfan sulfate	<0.010	0.002
655 sweet potato	Chlorpyrifos	0.008	0.005
	Dichloran	ND	0.002
	Dieldrin	<0.004	0.004
	Trifluralin	ND	0.0001
658 sweet potato	Chlorpyrifos	ND	0.0003
	Dichloran	0.45	0.31
	Piperonyl butoxide	0.022	0.035
557 tomato	Endosulfan I	<0.006	0.001
	Endosulfan II	<0.008	0.009
	Endosulfan sulfate	ND	0.004
	Cyfluthrin	ND	0.004
722 strawberry	THPA	ND	0.38
	Iprodione	0.53	0.75
	Malathion	0.009	0.01
	Metalaxyl	0.049	0.045
	Myclobutanil	ND	0.002
731 strawberry	Iprodione	0.58	0.83
	Malathion	0.018	0.017
	Bifenthrin	0.034	0.054

[a] ND = not detected.

[b] < = between 3 and 10 times noise.

alternate scanning with each of the 2 sets of parameters. These alternating parameters are saved and executed as one IPM file. When data acquisition is complete, 2 chromatograms can be constructed by connecting the data point that corresponds to each analyte.

IPMs are created by first running each pesticide in full scan and collecting data to about 10 atomic mass units (amu) above the molecular weight. Next, a structurally significant ion is chosen as the parent or precursor ion. This ion should be the highest mass present in good abundance. The parameters of the IPM can now be varied to obtain the desired product spectrum. Ideally the spectrum would contain at least 2 product ions at an abundance of at least 50% of the base peak (12).

With conventional MS of relatively dirty extracts, masses below 100 amu are avoided because of the large amount of interference. Many matrix coextractives have masses under 100 amu, and they cause such heavy interference that analyte fragments cannot be distinguished from those of the matrix. In MS/MS, the only masses in the product spectrum are those resulting from fragmentation of the precursor ion. As a result, lower mass ions are not interfered with and are more useful. For example, when an IPM was built for acephate, the ion with *m/z* 42 proved to be the quantification ion because no interference was observed even at this low mass. Listed in Table 1 are the IPM parameters for each pesticide.

To obtain sensitive and reproducible results, scan rate is set to at least 1 scan/s in each IPM. Spectra are then entered into a database, and the target ion is chosen as the quantification ion.

A standard was made up for each of the 2 groups and run in full scan to make sure that the run time windows in which the IPMs function corresponds to the retention times of the appropriate compounds. To prevent changes in retention time, the guard column (old piece of matched analytical column) is replaced with a new one of the same length each time maintenance work is done on the injection port.

For maximum sensitivity, the ion trap is optimized for MS/MS. The trap is first tuned for full-scan work. The electron multiplier is then increased by 200, the target is set to 10 000, and the emission current set to 80 μA (10). Each set of standards is run with the acquisition method associated with each injection group. To cover all the compounds in the method, all samples are injected twice: once for each acquisition method. Calibration curves are then created for each compound, and as each sample is run, the spectra are queried with the database made by the standards.

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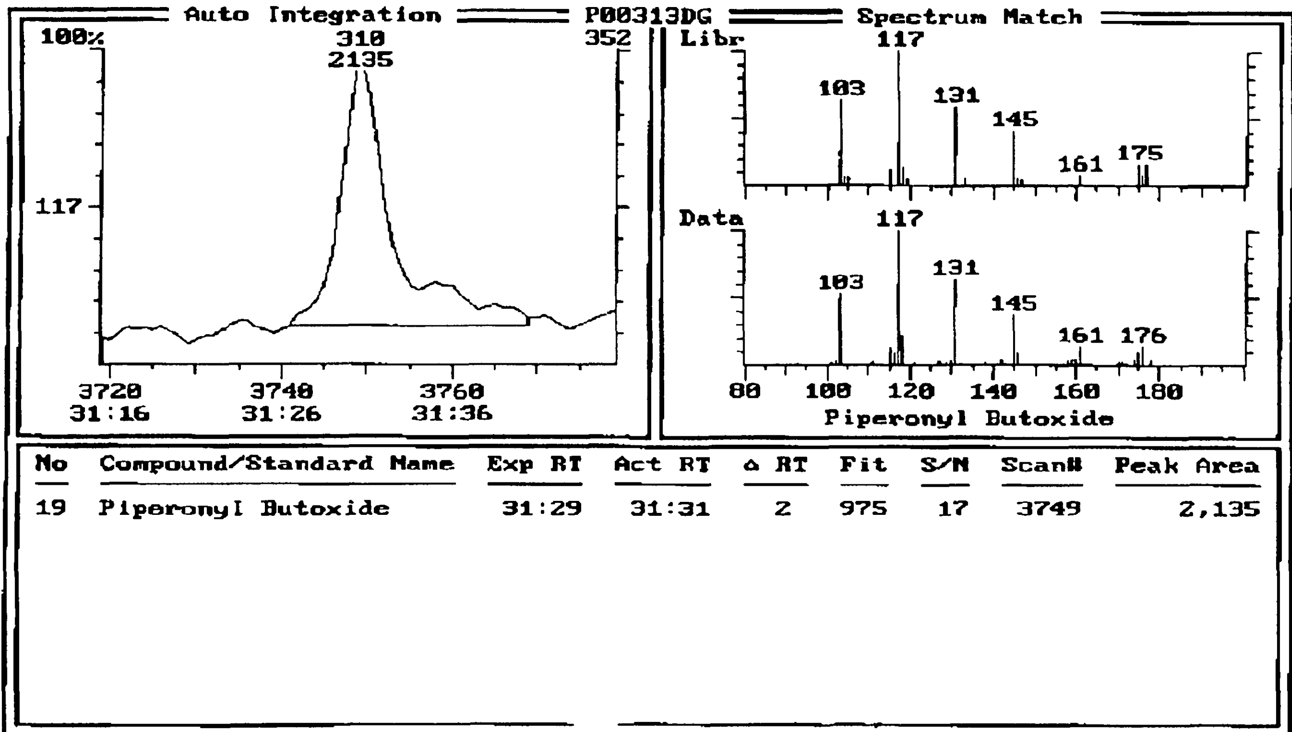

Figure 1. Sweet potato <1 ppb piperonyl butoxide.

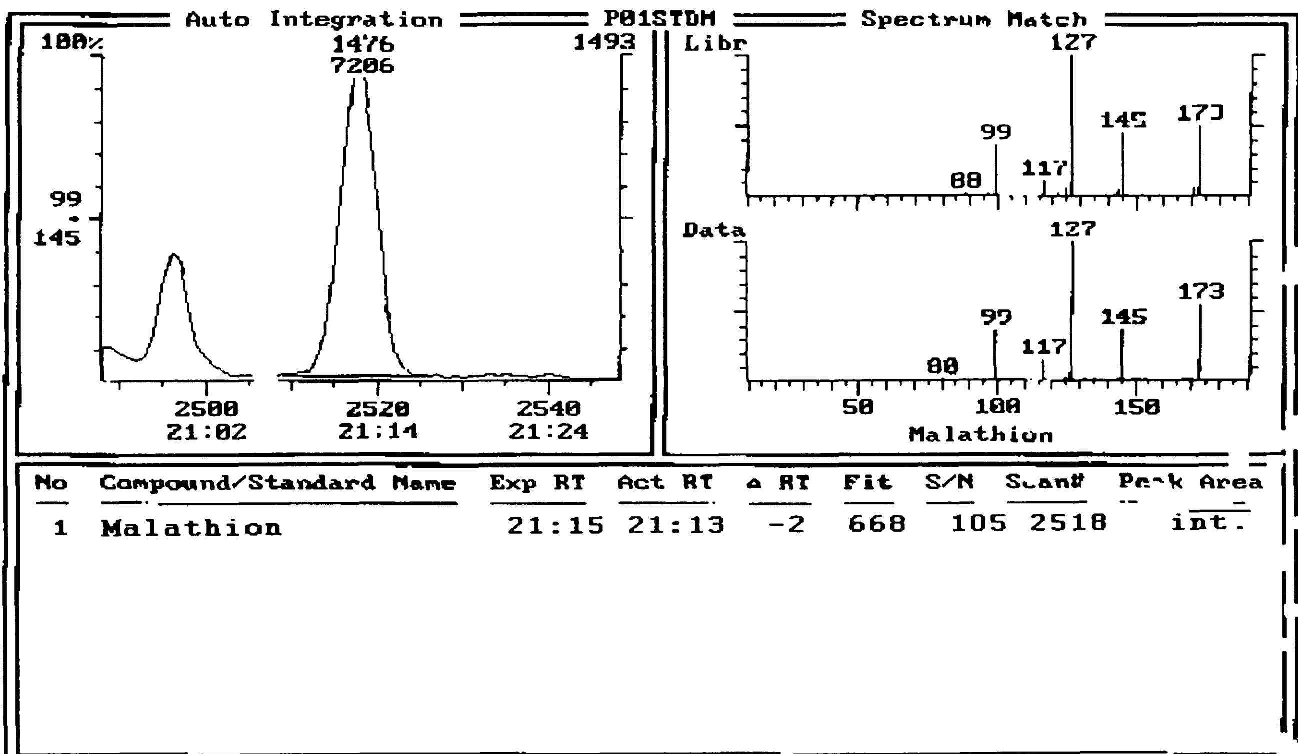

Figure 2. Strawberry 17 ppb malathion.

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Detection of pesticides in real samples has been successful even when the pesticides were present in various concentrations. The spectra of pesticides found in samples have been stable enough, regardless of concentration, for the software to match it correctly to that in the spectrum database. This matching is possible, because only a narrow band of masses are kept in the trap and the population of ions in the trap remains low at all times during MS/MS. This low population of ions in the trap reduces ion–ion interactions, and few changes in the spectra with variations in concentrations are observed.

Some obstacles exist, however, in routine analysis of a large number of samples. Sensitivity for acephate and methamidophos, 2 popular pesticides, has been a problem. This poor sensitivity has been seen with other mass spectrometers and may be due to active sites in capillary columns, because sensitivity improves briefly when the column is changed. These 2 pesticides recently have been eliminated from the screen method because responses are not stable. Phosmet and m-azinphos also have been observed to not respond linearly or consistently from injection to injection, and it is unclear why.

Another problem is with lab contamination. When sensitivity is greatly increased, as it is with this method, we routinely see several compounds such as o-phenylphenol (OPP) and diphenylamine (DPA) in extraction reagent and matrix blanks. OPP and DPA are thought to adhere to metal parts of blenders, and may be eliminated as contaminants with better washing. However, other compounds may be retained on other surfaces, and it is not yet clear whether extraction carryover can be completely eliminated.

These obstacles make a determination of detection limits difficult. However, an indication of sensitivity can be obtained by analyzing samples with the MS/MS spectrometer as well as with the routine selective detector screen. Listed in Table 2 are data for real samples screened by both MS/MS and selective detectors. A Q indicates that quantitation was estimated because the integrated peak area was below that of the lowest standard.

Several compounds are detected more successfully than others by the selective detectors, such as acephate, m-azinphos, methamidophos, and phosmet. Many other compounds, however, are as or more easily detected by the MS/MS instrument, and some analytes may have much lower limits of detection with MS/MS.

Piperonyl butoxide in sample 313 (sweet potato) was detected by MS/MS but not by mass-selective detection (MSD). Piperonyl butoxide is routinely detected by MSD instead of other GC detectors because it contains no phosphorus or chlorine. Figure 1 shows the chromatogram of piperonyl butoxide in the sample with all major product ions present and the good peak shape of the quantitation ion. Because the amount found was far below the level of the lowest standard, we reported the amount as below 1 ppb. In sample 731 (strawberry), malathion was found by FPD and MS/MS in comparable quantitated amounts: 0.018 and 0.017 μg/g, respectively (Figure 2).

Conclusion

Even when trace analysis is performed and low detection limits are achieved with traditional GC detectors, an MS confirmation usually is required. The limit to any laboratory's ability to detect compounds at trace level is therefore restricted by the sensitivity of the MS method. SIM has been used to lower detection limits. However, collecting data on a few ions will not give as much information as full scan data and cannot be considered as an equal confirmation. This MS/MS method allows quantitation and true confirmation at detection limits that are, in most cases, equal to or lower than those of GC detectors.

Acknowledgments

We thank the USDA-PDP, New York State Department of Agriculture and Markets, laboratory personnel including Kurt Mangione, Virginia Greene, Lucy Desjardins, Priscilla Sweet, Debbie Oglesby, and Terry Taylor.

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