Journal of Chromatography, 517 (1990) 131–142
Elsevier Science Publishers B.V., Amsterdam

CHROMSYMP. 2000

Pesticide analysis by gas chromatography with a novel atomic emission detector

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ABSTRACT

An atomic emission detector, consisting of a microwave-induced helium plasma and atomic emission spectrometer, has been used for the gas chromatographic analysis of pesticides. In principle, it is possible to detect any element in the periodic table (except helium) which can elute from a gas chromatograph. Detection limits for C, H, D, N, O, Br, Cl, F, S, Si, P, Sn and Hg were found to range from 0.1 to 75 pg/s with selectivities over carbon of 5000 or more. The gas chromatography–atomic emission detection system has been used for the detection and elemental characterization of 27 different pesticides by obtaining element-specific chromatograms for C, H, N, O, Br, Cl, F, P and S. By performing quantitative analysis for each element, it was possible to calculate the approximate empirical formulas for 20 different herbicides in two different mixtures. An extract from an apple doped with three pesticides was analyzed by gas chromatography–atomic emission detection.

INTRODUCTION

Several United States Environmental Protection Agency (EPA)-approved methods exist for the gas chromatographic (GC) analysis of pesticides including Methods 505 (ref. 1), 608 (ref. 2) and 8080 (ref. 3) (organohalide pesticides and polychlorinated biphenyls), 507 (ref. 4, 69 pesticides), 508 (ref. 5, 32 chlorinated pesticides), 515 (ref. 6, chlorinated acid herbicides), 8140 (ref. 3, organophosphorus pesticides) and 8150 (ref. 3, chlorinated herbicides). Numerous methods exist for the analysis of pesticide residues on foods. Two popular multi-residue methods are those developed by Luke[7,8] and the California Department of Food and Agriculture[9].

Four different selective detection methods are used in these methods: electron-capture detection (ECD) or electrolytic conductivity detection (ELCD) for halogenated compounds, nitrogen–phosphorus detection (NPD) for nitrogen- and phosphorus-containing pesticides, and flame photometric detection (FPD) for sulfur or phosphorus compounds.

While the above-mentioned detectors have proven to be very useful for the

0021-9673/90/$03.50

selective detection of heteroatoms in pesticides, each has certain inherent limitations. ECD is the most sensitive GC detection method for polyhalogenated compounds, but it is not very selective, responding strongly to other electronegative functional groups. Even for halogenated compounds, ECD response is not proportional to the number of halogens in a molecule and it is typically not linear beyond about two orders of magnitude. NPD sensitivity can vary over time and some types of chemical bonding can greatly reduce its sensitivity to nitrogen. For sulfur, FPD response is not linear and suffers from quenching of the signal by co-eluting compounds. Of the detection methods mentioned, ELCD is perhaps the most difficult to operate, requiring frequent maintenance and strict avoidance of contaminants.

Pesticides almost always contain heteroatoms and often have several in a single molecule. The most frequently encountered elements are C, H, O, P, S, N, Cl, Br, F and metals such as As, Hg and Zn[10]. For the analysis of complex environmental samples containing pesticides, it would be useful to have a single GC detector capable of specific element detection for any element encountered in a pesticide; indeed, a complete profile of all the elements in a pesticide molecule would greatly aid in its identification.

Detectors which combine plasma excitation with optical emission spectroscopy have been used for the selective detection of many organic and inorganic elements. Three recent reviews describe various plasma-atomic emission spectroscopy (AES) systems which have been developed as GC detectors[11–13]. Several investigators have reported analyzing pesticides using GC–plasma-AES systems[14–18].

The Hewlett-Packard (HP) 5921A atomic emission detection (AED) system used for this investigation has been described elsewhere[19–24]. The detector employs a microwave-induced helium plasma as the atomization and excitation source. This design was chosen because the energy of the helium plasma was sufficient to excite all elements in the periodic table and because it only required 100–200 ml/min of helium. In contrast, inductively coupled plasmas typically require many liters of argon or helium per minute.

This paper describes the use of this new GC–AED system for the analysis of pesticides. An objective was to show specific element detection for all of the most common elements found in pesticide formulations. Therefore a variety of insecticides and herbicides was analyzed showing specific element detection of C, H, N, O, P, F, Cl and Br. Typical detection limits and selectivities were determined for several elements.

By performing quantitative analyses on every element in an unknown molecule it should be possible to calculate its empirical formula. Several researchers have reported the results of such calculations with mixed results[24–26]. This work represents an initial investigation into the feasibility of determining complete empirical formulas for pesticides using this commercially available GC–AED system.

EXPERIMENTAL

GC–AED system

A prototype of the HP 5921A atomic emission detector was coupled to an HP 5890A gas chromatograph. Papers detailing the design and performance of the GC–AED system have appeared elsewhere[19,20].

The HP 5890A GC system was equipped with a HP 7673A automatic injector and split–splitless capillary injection port which was operated at 200–300°C, depending on the sample. Three HP columns were employed: (A) 25 m × 0.32 mm I.D. × 0.17 μm film HP-1 operated at a helium flow-rate of 1.05 ml/min (21.8 cm/s), (B) 50 m × 0.2 mm I.D. × 0.5 μm film HP-5; helium flow-rate 0.39 ml/min (21 cm/s) and (C) 25 m × 0.32 mm I.D. × 0.17 μm film HP-5; helium flow-rate 0.95 ml/min (19.7 cm/s).

Samples

Diazinon (VAP Special Products), alachlor (Monsanto), metolachlor (Ciba-Geigy), chlorpyrifos (Dow), and prometon (Ciba-Geigy) were all obtained as commercial pesticide preparations from local suppliers. They were received as 25, 45.1, 86.4, 40.7 and 25% solutions, respectively, which were diluted 1:100 in hexane or methanol. Capillary GC was performed with a 100:1 split ratio. Two herbicide mixtures containing nine and thirteen compounds, respectively, were obtained from Supelco (Bellefonte, PA, U.S.A.) as solutions of 100 μg/ml each in ethyl acetate. The herbicide mixtures were analyzed as received using a 55:1 split ratio for the detection of C, H, N, Cl, Br and S and a 12:1 split ratio for the F and O analyses.

The analysis of pesticides spiked into an apple was conducted as follows. A solution of chlorpyrifos, endosulfan I and endosulfan II was injected into a 20-g wedge-shaped apple slice so that the pesticides would be present at 680, 337 and 330 ppb[a], respectively. The apple was chopped up and blended for 3 min with 40 ml of acetonitrile in a Sorvall Omni Mixer. The solution was filtered rapidly by suction into a flask containing about 10 g of sodium chloride and the layers were allowed to separate. A 4-ml aliquot of the organic layer was evaporated to near-dryness with a stream of nitrogen and the residue was taken up in 2 ml of acetone. Analysis of the acetone solution was performed by GC-AED using 1-μl splitless injections.

RESULTS AND DISCUSSION

When extracted from water, soil or plant material, pesticides are often isolated together with numerous other synthetic and natural organic compounds. Contamination from laboratory ware (especially phthalates from plastics) and solvents is another source of concern. Element-selective detection methods such as ECD, FPD, NPD and ELCD are used for GC analysis as a way of "isolating" the halogen-, sulfur-, nitrogen- or phosphorus-containing pesticides from these contaminants. Of course, when a contaminant contains the monitored heteroatom or when the detection method (particularly ECD) is not sufficiently selective, spurious peaks arise.

Pesticides are usually very rich in heteroatoms with most having two to four elements present in addition to C and H. Using GC–AED it is possible to monitor every element in a pesticide (albeit, with varying sensitivities) providing multiple channels of corroborative data.

Table I lists several elements by groups which could be observed simultaneously along with detection limits (MDL) and selectivities which have been obtained with this system. As is commonly done for plasma detectors, the MDL values are expressed as pg/s of the element which gives a signal-to-noise ratio of 2. These values

[a] Throughout this article, the American billion (10^9) is meant.

TABLE I

TYPICAL DETECTION LIMITS AND SELECTIVITIES OBTAINED USING GC–MIP–AES

Group	*Element*	*Wavelength (nm)*	*MDL (pg/s)*	*Selectivity*
I	N	174.2	7.0	6 000
	S	180.7	1.7	150 000
	Hg	184.9	0.1	>1 000 000
	C	193.1	0.5	
II	P	177.5	1.5	25 000
III	C	247.9	2.6	
	Si	251.6	7.0	90 000
	Hg	253.7	0.1	>1 000 000
IV	Br	478.6	75	19 000
	Cl	479.5	39	25 000
	H	486.1	2.2	
	C	247.9 (2^{nd} order)	12	
V	D	656.1	2.5	600 *vs.* H
	H	656.3	3.0	
VI	F	685.6	40	30 000
VII	O	777.2	75	25 000

can be easily converted to the detection limit for a compound (in pg). The detection limit for a given element from Table I is multiplied by the GC peak width and the compound's molecular weight divided by the gram atoms of the element in the analyte. Selectivities are with respect to C except for deuterium which is relative to H.

Fig. 1 shows a multi-element-specific chromatogram of diazinon ($C_{12}H_{21}N_2O_3PS$). Three sequential chromatographic runs were required to obtain chromatograms for C, S, N, P and H. The chromatograms for C, S and N were obtained simultaneously using oxygen and hydrogen scavenger gases. While the emission line for P falls in the same region (177.5 nm), it required hydrogen as the only

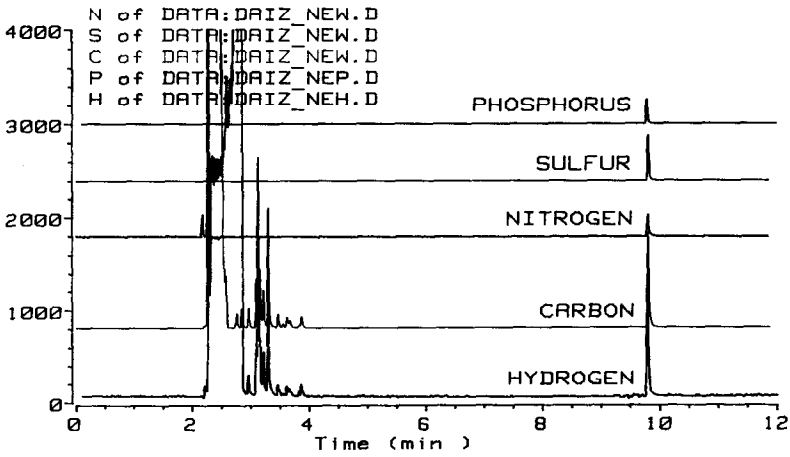

Fig. 1. GC–AED analysis of diazinon using column A. Oven temperature program: 100°C (1 min), 10°C/min to 250°C; inlet and transfer line/cavity temperatures 200°C.

scavenger gas and, therefore, had to be determined separately. The H chromatogram was obtained in a third run at 486.1 nm using only oxygen as scavenger. The three sequential runs were fully automated from the GC–AED system's controller.

Current procedures for the analysis of pesticides typically obtain only one element-specific chromatogram providing two-dimensional data (presence of the element plus retention time). In addition to the retention time, the presence of five constituent elements was confirmed using AED. Of particular interest are the chromatograms for S, N and P. Their presence combined with the retention time would usually be sufficient to identify the pesticide. Quantitation could be done using any (or all) of the elements present. This flexibility can be very useful if interfering compounds appear in one element channel but not in another.

Fig. 2 shows four element-specific traces for alachlor ($C_{14}H_{20}ClNO_2$); C, H and Cl were obtained simultaneously in a single run and N from a second run. The controller's software automatically combined data from these two injections into a single file for integration, plotting or for incorporation into a report.

At the time that diazinon and alachlor were analyzed, the experimental software did not allow the collection of oxygen-specific chromatograms. Using software modified to include oxygen detection, a mixture of prometon ($C_{10}H_{19}N_5O$), chlorpyrifos ($C_9H_{11}Cl_3NO_3PS$) and metolachlor ($C_{15}H_{22}ClNO_2$) was analyzed. A complete elemental profile was obtained in four sequential analyses; seven element-specific chromatograms (C, H, N, O, Cl, P and S) are shown in Fig. 3.

Chlorpyrifos and metolachlor were not separated on an HP-1 column (column A; *cf.* Experimental) but could be partially resolved with a 50-m HP-5 column (column B). Since the three pesticides contain different atoms, it is a trivial matter to distinguish between them. In addition to C and H prometon has N and O while metolachlor has Cl, N and O. Chlorpyrifos has all seven elements.

With less than perfect resolution, quantitation of metolachlor and chlorpyrifos would be difficult using a universal, nitrogen-specific or halogen-specific detector since both compounds would respond. However, using GC–AED, chlorpyrifos could

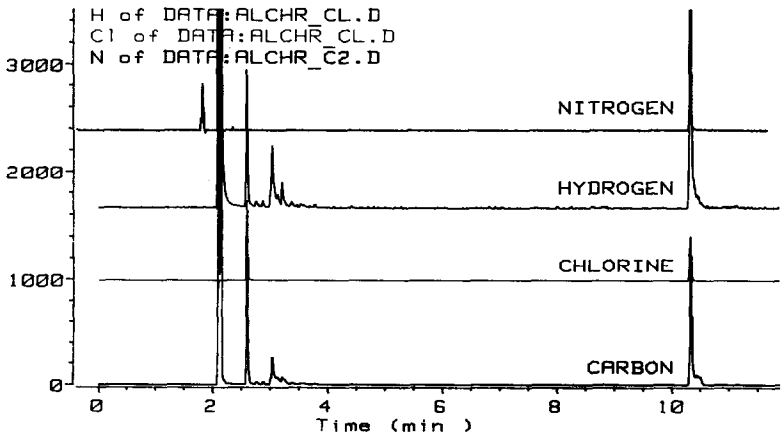

Fig. 2. GC–AED analysis of alachlor using column A. Oven temperature program: 100°C (1 min), 10°C/min to 250°C; inlet and transfer line/cavity temperatures 200°C.

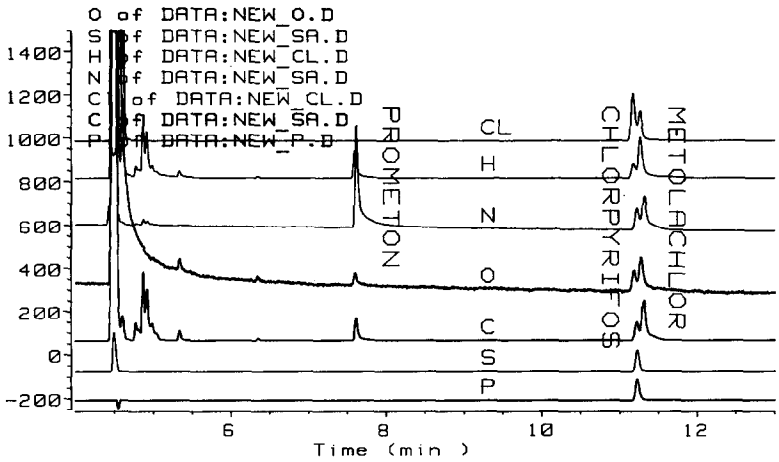

Fig. 3. GC–AED analysis of prometon, chlorpyrifos and metolachlor using column B. Oven temperature: 270°C isothermal; inlet and transfer line/cavity temperatures: 270°C and 300°C, respectively.

be quantitated using the S- or P-specific chromatograms since metolachlor gives no response on those channels. Metolachlor could then be determined by difference using the summation of the chlorpyrifos and metolachlor N signal. (Any of the five channels on which they both respond could be used.) Subtracting the known amount of chlorpyrifos would give the metolachlor amount by difference. In principle, it would not be necessary to separate the compounds at all.

A more complex mixture of 13 known herbicides (herbicide mix 1) is shown in Fig. 4 and in Table II. Eight elements are present in this mixture, including C, H, N, O, S, F, Cl and Br. The last eight peaks could easily be correlated to the known constituents by inspection. The presence or absence of peaks along with approximate peak ratios were all the information that was needed. The molecular formulas of the first five pesticides were quite similar, varying only slightly in C and H content; for these, comparison with standards was required.

Each compound was present at the 100-ng/μl level. F and O analyses were run with a 12:1 split so that 8.3 ng of each compound reached the detector. All other elements were run at a 55:1 split, delivering 1.8 ng/component to the plasma. Since AED responds to elements, not compounds, detection limits such as those in Table I are expressed in terms of the mass of an element (not molecule) which can be detected. While the amount of each herbicide reaching the detector was 1.8 ng, the amount of H detected in each of the compounds ranged from 56 pg for oxyfluorfen to 191 pg for butylate.

With a single GC detector it was possible to obtain eight different element-selective chromatograms. Of particular interest is the ability to distinguish between the halogens; neither ECD nor ELCD can do this. Since a significant number of pesticides contain either F or Br, it is helpful to detect them selectively rather than lump them together with the chlorinated pesticides.

Accurate quantitative analysis of each element should allow the analyst to calculate an empirical formula for each molecule in a mixture. Several reports have

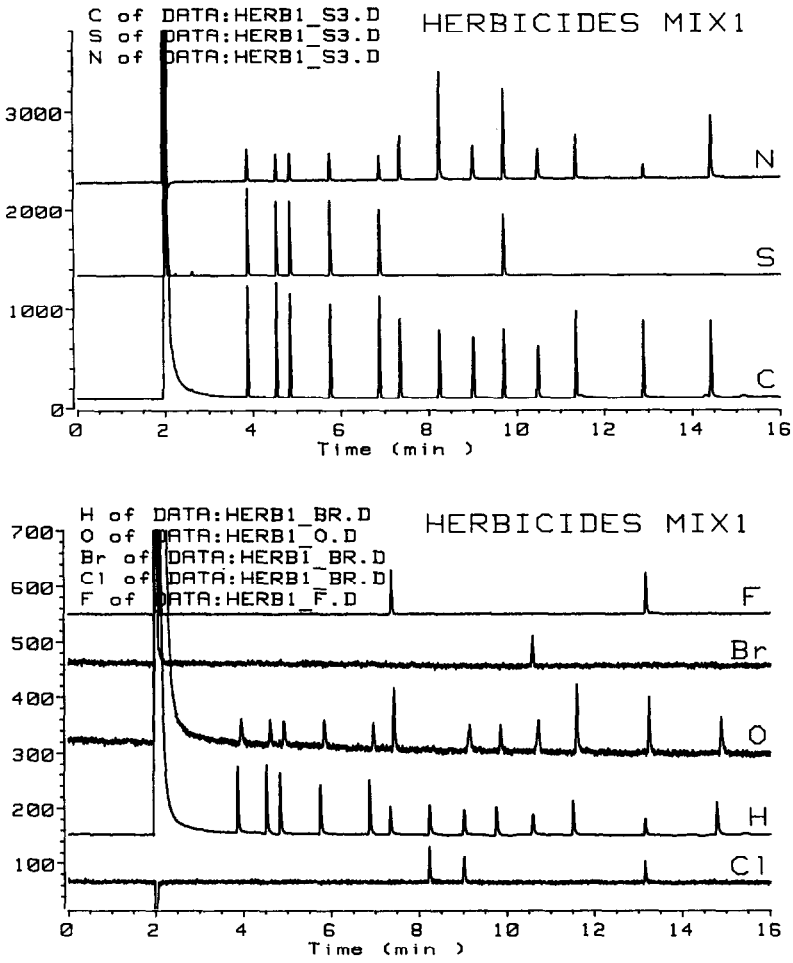

Fig. 4. GC–AED analysis of a mixture containing 13 herbicides using column C. Two plots were required to show all eight element-specific chromatograms. Compound identities and calculated elemental ratios are given in Table II. Oven temperature program: 150°C (3 min), 10°C/min to 300°C; inlet and transfer line/cavity temperatures: 280°C and 300°C, respectively.

appeared in the literature in which this has been accomplished for a limited number of elements with varying degrees of success.

Recent reports by Widmer[24] and by Sullivan and Quimby[22] have shown examples using the Hewlett-Packard GC–AED system. Widmer discussed an example for which the approximate empirical formula was generated for a compound containing C, H, O and Cl. Sullivan and Quimby used 15 different C-, H-, N- and O-containing compounds and found that approximate empirical formulas could be determined for unknowns when heteroatoms were present and certain assumptions were made about the size of the molecule. It was of interest to see if empirical formulas could be generated for the herbicides in this mixture, since between them, they contained eight different elements.

TABLE II

ELEMENTAL RATIOS CALCULATED FOR HERBICIDE MIX 1 ON THE BASIS OF GC-AED DATA (DATA WERE NORMALIZED TO KNOWN VALUES FOR C)

No.	*Herbicide molecular formula*	*Calculated elemental ratios*						
		C	*H*	*N*	*O*	*S*	*Cl*	*F*
1	EPTC $C_9H_{19}NOS$	9	15.7	0.8	1.1	0.9		
2	Butylate $C_{11}H_{23}NOS$	11	20.8	0.8	1.1	0.9		
3	Pebulate $C_{10}H_{21}NOS$	10	18.4	0.8	1.1	0.9		
4	Molinate $C_9H_{17}NOS$	9	15.1	0.9	1.0	0.9		
5	Cycloate $C_{11}H_{21}NOS$	11	17.6	0.8	1.0	0.9		
6	Trifluralin $C_{13}H_{16}N_3O_4F_3$	13	15.7	2.2	4.1			2.5
7	Atrazine $C_8H_{14}N_5Cl$	8	10.7	4.2			1.3	
8	Terbacil $C_9H_{13}N_2O_2Cl$	9	10.9	1.5	2.1		1.1	
9	Metribuzin $C_8H_{14}N_4OS$	8	11.8	3.3	1.4	I.S.		
10	Bromacil[a] $C_9H_{13}N_2O_2Br$	9	11.4	1.6	3.1			
11	Isopropalin $C_{15}H_{23}N_3O_4$	15	21.9	2.4	4.5			
12	Oxyfluorfen $C_{15}H_{11}NO_4F_3Cl$	Internal standard						
13	Hexazinone $C_{12}H_{20}N_4O_2$	12	17.7	3.0	2.4			

[a] Br was not determined.

Using oxyfluorfen as the internal standard (I.S.) (metribuzin for S), elemental ratios were calculated for the other twelve herbicides. These are summarized in Table II. No calibration was done for Br as only one Br-containing compound was present. All of the results were normalized to the known values for C.

A second mixture of 9 herbicides (herbicide mix 2; 100 ng/μl each) was analyzed under the same conditions (a minor difference is noted below) as that shown in Fig. 4. Fig. 5 shows the seven element-specific chromatograms which were obtained. Using metolachlor as the internal standard (profluralin for F), elemental ratios were calculated for each of the other herbicides. Since only one sulfur-containing compound was present, this element does not appear in the calculations. The results (normalized to carbon) are given in Table III.

The data presented in Tables II and III do not allow the determination of a precise empirical formula for most of the compounds. However, the numbers were often very close to the correct values and in every case the presence or absence of an element in an herbicide was correctly determined. It is believed that this is the first discussion of elemental ratios calculated for seven elements on the basis of GC–microwave-induced helium plasma (MIP)-AES data. These preliminary results are, in fact, very encouraging.

There are several changes in the experiment's conditions which are likely to result in even better elemental ratios. First, the herbicide mixtures were injected in the split mode which could lead to some discrimination between molecules of differing volatilities. Only one injection was made for each element group of the sample; averaging carefully integrated peak areas from multiple injections should lead to more accurate results. Second, the injection port was held at 280°C for herbicide mix 1 and 260°C for mix 2. Many pesticides are thermally labile and are known to decompose in hot injection ports. Degradation of the internal standard could lead to inaccuracies in

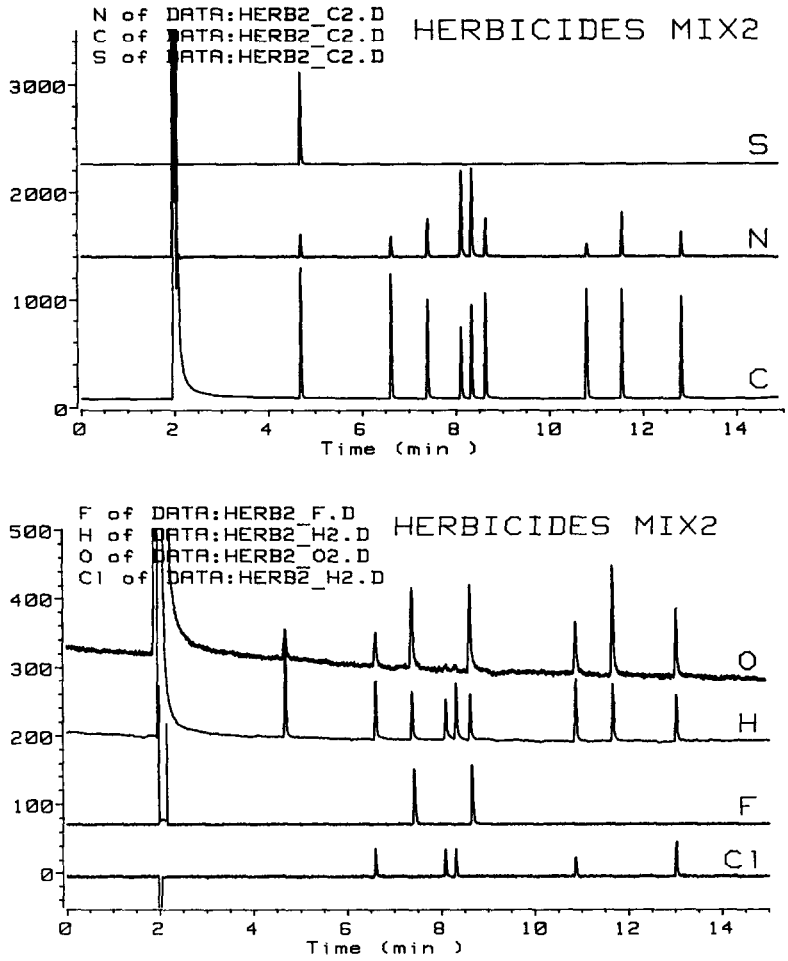

Fig. 5. GC–AED analysis of a mixture containing 9 herbicides using column C. Two plots were required to show all seven element-specific chromatograms. Compound identities and calculated elemental ratios are given in Table III. Oven temperature program: 150°C (3 min), 10°C/min to 300°C; inlet and transfer line/cavity temperatures: 260°C and 300°C, respectively.

the calculations, especially when more than one internal standard is used or if there are overlapping peaks. A possible solution for both of these potential problems is to use cool on-column injection. Calculated values for H, N and S were most often low for the 13-herbicide sample, suggesting that a different internal standard for these elements could improve the values. Widmer[24] has used multiple standards to get a closer estimation of an unknown's empirical formula.

Residue extraction experiment

In order to simulate the conditions of a real pesticide residue analysis, an apple was doped with two pesticides below the EPA action level. A solution containing chlorpyrifos ($C_9H_{11}Cl_3NO_3PS$) and endosulfan ($C_9H_6Cl_6O_3S$) was injected into a

TABLE III

ELEMENTAL RATIOS CALCULATED FOR HERBICIDE MIX 2 ON THE BASIS OF GC-AED DATA (DATA WERE NORMALIZED TO KNOWN VALUES FOR C)

No.	*Herbicide molecular formula*	*Calculated elemental ratios*					
		C	*H*	*N*	*O*	*Cl*	*F*
14	Vernolate $C_{10}H_{21}NOS$[a]	10	19.5	1.0	1.1		
15	Propachlor $C_{11}H_{14}NOCl$	11	13.3	1.0	1.0		
16	Benfluralin $C_{13}H_{16}N_3O_4F_3$	13	17.1	2.8	3.6		2.8
17	Simazine $C_7H_{12}N_5Cl$	7	11.1	4.7		0.9	
18	Propazine $C_9H_{16}N_5Cl$	9	15.0	4.6		0.9	
19	Profluralin $C_{14}H_{16}N_3O_4F_3$	14	17.7	2.8	4.4		I.S.
20	Metolachlor $C_{15}H_{22}NO_2Cl$	Internal standard					
21	Pendimethalin $C_{13}H_{19}N_3O_4$	13	19.7	3.0	4.6		
22	Oxadiazon $C_{15}H_{18}N_2O_3Cl_2$	15	18.5	2.0	3.2	1.8	

[a] Sulfur was not determined.

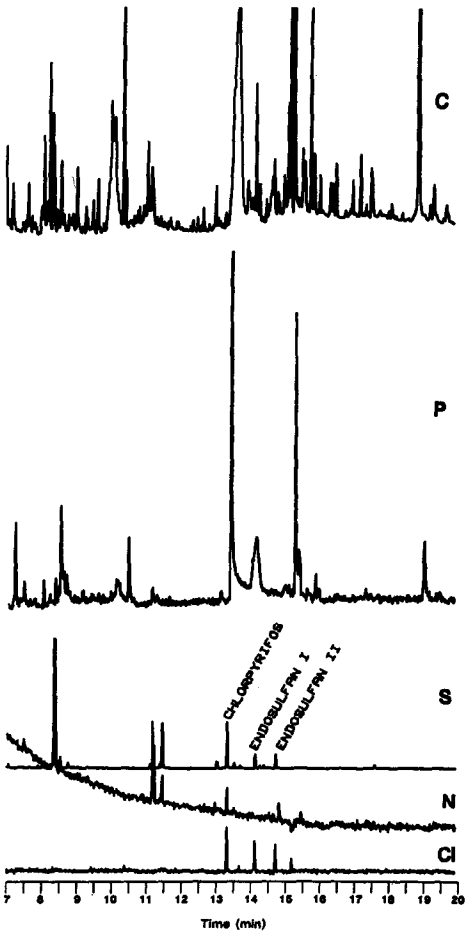

Fig. 6. GC–AED analysis of an extract from an apple doped with chlorpyrifos, endosulfan I and endosulfan II using column C. Oven temperature program: 50°C (3 min), 20°C/min to 300°C, 300°C (20 min); inlet and transfer line/cavity temperatures 300°C.

20-g wedge-shaped slice of an apple to give concentrations of 0.68 and 0.67 ppm, respectively. In apples, the EPA allows a maximum residue limit of 1.5 ppm for chlorpyrifos and 2.0 ppm for endosulfan[27]. Endosulfan was obtained as a 51:49 mixture of isomers endosulfan I and endosulfan II. In the apple their respective concentrations were 0.34 and 0.33 ppm.

Pesticides were extracted from the apple employing a slight modification of procedures used by the California Department of Food and Agriculture[9]. The carbon-selective chromatogram of the extract shown in Fig. 6 is similar to that which would be obtained from a flame ionization detector. The complexity of this chromatogram makes it clear why selective detectors are necessary for residue analyses in the absence of extensive clean-up steps.

Also shown in Fig. 6 are the element-selective chromatograms for S, N, Cl and P which were obtained from three successive injections. All of these elements are present in the chlorpyrifos peak while the endosulfan isomers show only S and Cl as expected. Oxygen was not run on this sample. In spite of the complexity of the dirty extract, these pesticides are readily seen on each of the appropriate element channels of the AED system. Coupled with the retention time, this elemental information may often be sufficient to confirm the presence of a pesticide. In other cases where similar compounds elute close together, confirmation by GC–mass spectrometry would still be required.

CONCLUSIONS

GC detectors most commonly used for pesticide methods are limited to the detection of halogens, S, N and P. ECD and ELCD cannot differentiate between F, Cl and Br. These detection methods may lack selectivity (ECD), suffer from quenching (FPD) and lack linearity (ECD and FPD). In contrast, GC–AED can, in principle, selectively detect any element in the periodic table so long as it can be analyzed by GC.

Pesticides are particularly good candidates for GC–AED analysis since they are rich in heteroatoms. Using a GC–AED system, the analyst has the choice of detecting any individual element in a molecule or of obtaining a multi-element profile.

It was possible to determine the approximate elemental composition at the low-ng level for molecules containing up to seven different elements.

The GC–AED technique shows potential as a sensitive, element-selective detector, applicable to the analysis of pesticides and many other organic and organometallic molecules. Additional work is in progress to evaluate the system for quantitative analysis and for residue analysis using a variety of pesticides doped into various fruits and vegetables. Methods for obtaining more accurate empirical formulas are also being investigated.

ACKNOWLEDGEMENT

The authors wish to thank Bruce Quimby for providing the data shown in Table I and for helpful discussions.

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