Comparison of the Atomic Emission Detector to Other Element-Selective Detectors for the Gas Chromatographic Analysis of Pesticide Residues

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Gas chromatography with an atomic emission detector (GC-AED) was compared to GC with other element-selective detectors for the analysis of pesticide residues in agricultural products. The objective was to compare the selectivity of the AED to other GC detectors most commonly used for pesticide analysis. Twelve different agricultural commodities were fortified with 10 commonly used pesticides (mostly at 0.2 ppm). The pesticides were extracted according to procedures of the California Department of Food and Agriculture; no cleanup steps were used. The crude extracts were then analyzed by capillary GC using the following detectors: AED, electron capture detector (ECD), electrolytic conductivity detector (ELCD), nitrogen–phosphorus detector (NPD), and flame photometric detector (FPD) in the sulfur and phosphorus modes. The AED was used for carbon-, phosphorus-, chlorine-, fluorine-, nitrogen-, and sulfur-selective analyses. The AED was found to have much better selectivity than the other detectors and could be used to determine organochlorine, organofluorine, and organophosphorus pesticides in all 12 extracts. Because of interferences, the ECD was only useful for 5 commodities and the ELCD in the halogen mode for 8; the FPD (P mode) and the NPD had adequate selectivity for 9 of the 12 samples.

INTRODUCTION

For efficiency in a regulatory setting, multiresidue methods (MRMs) are preferred to single-residue methods (SRMs) for the analysis of pesticides in agricultural products, since many pesticides can be determined in a single analysis. Several widely used MRMs have been published by the U.S. Food and Drug Administration (Luke et al., 1981; Krause, 1980; Storherr et al., 1971; Mills et al., 1963) and by the California Department of Food and Agriculture (CDFA) (Lee et al., 1991; Joe, 1988).

Typical procedures require organic solvent extraction, possible cleanup steps, and chromatographic analysis. Extracts of many commodities include indigenous compounds that can interfere with the chromatography, so most modern GC methods employ high-resolution capillary columns with selective detectors.

An ideal selective detector for residue analysis would respond only to the target pesticides, while other coextracted compounds remain transparent. Pesticides almost always contain heteroatoms and often have several in a single molecule. The most frequently encountered heteroatoms are O, P, S, N, Cl, Br, F, and metals such as Ag, Hg, Sn, and Zn (Worthing and Walker, 1987). Therefore, most GC methods employ element-selective detectors. Most commonly used are the electron capture (ECD) and electrolytic conductivity detectors (ELCD) for halogenated compounds, the nitrogen–phosphorus detector (NPD) for nitrogen- and phosphorus-containing pesticides, and the flame photometric detector (FPD) for sulfur or phosphorus compounds.

In many cases, these detectors are not sufficiently selective, and cleanup steps are required to remove interfering coextracted compounds. However, it is advantageous to avoid cleanup steps whenever possible, since they can be tedious, time-consuming, and expensive; in addition, residues may be lost in the process. If a detector could be found with sufficient selectivity that these interferences could be eliminated, cleanup steps might be avoided, saving time and expense while eliminating steps where residues may be lost.

Detectors that combine plasma excitation with optical emission spectroscopy have been used for the selective detection of many organic and inorganic elements. Three comprehensive reviews describe various plasma–atomic emission spectroscopy systems that have been developed as GC detectors (Uden, 1986; Ebdon et al., 1986; Matousek et al., 1984).

Recently described was a GC with a new atomic emission detector (GC-AED) that is selective for 23 elements (and 4 isotopes), including all those commonly found in pesticides (Quimby and Sullivan, 1990; Sullivan and Quimby, 1990; Wylie and Quimby, 1989; Wylie et al., 1990). Wylie and Oguchi have demonstrated its use for the multielement detection of pesticides and the calculation of their approximate empirical formulas (Wylie and Oguchi, 1990). Therefore, an investigation was initiated to compare the AED to other widely used element-selective detectors with an emphasis on their relative selectivities for pesticides.

EXPERIMENTAL PROCEDURES

Reagents. All solvents were of pesticide grade or better. Analytical pesticide standards were obtained from the U.S. Environmental Protection Agency (U.S. EPA) repository. Stock solutions of the 10 pesticides in Table I were prepared at milligram per milliliter concentrations in acetonitrile. Fortification standards were prepared in acetonitrile from these stock solutions.

Plant Materials. The 12 commodities (Table II) used in this study were collected as part of a routine market-basket survey

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Table I. Organophosphorus and Organohalide Pesticides Used To Spike Samples of Agricultural Commodities

	pesticide	molecular formula	spike level, ppm
1	ethalfluralin	$C_{13}H_{14}F_3N_3O_4$	1.0
2	dimethoate	$C_5H_{12}NO_3PS_2$	0.2
3	diazinon	$C_{12}H_{21}N_2O_3PS$	0.2
4	chlorothalonil	$C_8Cl_4N_2$	0.2
5	chlorpyrifos	$C_9H_{11}Cl_3NO_3PS$	0.2
6	parathion	$C_{10}H_{14}NO_5PS$	0.2
7	chlorthal-dimethyl	$C_{10}H_6Cl_4O_4$	0.2
8	folpet	$C_9H_4Cl_3NO_2S$	5.0
9	dieldrin	$C_{12}H_8Cl_6O$	0.2
10	azinphos-methyl	$C_{10}H_{12}N_3O_3PS_2$	0.2

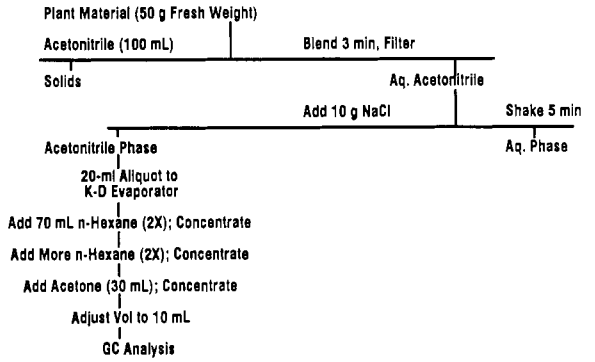

Figure 1. Procedure for extracting pesticide residues from agricultural products. One microliter of the final solution is equivalent to 1 mg of the original commodity.

program conducted by the CDFA. Samples were collected from both wholesale and retail market places on the same day as the samples were prepared for analysis.

Sample Preparation. The 12 commodities were extracted using the procedure outlined in Figure 1 (Lee et al., 1988). After chopping and mixing, samples were split into two portions; one was fortified with pesticides, while the other was used as a blank. Prior to blending with acetonitrile, 100 μL of a solution containing 10 organohalide and organophosphorus pesticides was added to one of the samples so as to fortify it at the levels shown in Table I. Both fortified and blank sample extracts were divided into several 2-mL autosampler vials for GC analysis on the instruments described below.

Instrumentation. All extracts were analyzed on each of four GC systems. One system consisted of an HP 5890 Series II GC equipped with an HP 5921A atomic emission detector (AED), an HP 7673A automatic sampler, and split/spitless capillary injection port (Hewlett-Packard Co., Avondale, PA). Element-selective chromatograms were obtained for C, Cl, F, N, P, and S at the wavelengths 193.03, 480.19, 690.47, 174.20, 178.08, and 181.40 nm, respectively. The inlet was held at 250 °C, the transfer line at 280 °C, and the cavity of 290 °C.

To maximize the AED's sensitivity, a peak width value of 0.14 min was used and the makeup gas flow rate (measured with reagent gases off) was reduced to 10 mL/min for Cl-selective runs. For P-selective analyses, the makeup gas flow rate was increased automatically by the AED to 150 mL/min. Quimby and Sullivan have shown that these makeup gas flow rates give optimum sensitivity for Cl and P (Quimby and Sullivan, 1990).

A second system consisted of an HP 5890A GC equipped with a packed column inlet modified for 0.53 mm i.d. capillary columns (held at 250 °C), an HP 7673A automatic sampler, a flame photometric detector (FPD), and an electrolytic conductivity detector (ELCD) operated in the halogen mode (OI Corp., College Station, TX).

The third system was an HP 5880A GC equipped with a packed column inlet modified for 0.53 mm i.d. capillary columns (held at 250 °C), an HP 7673A automatic sampler, and an electron capture detector (ECD) operated at 320 °C.

The last GC was an HP 5880A equipped with an HP 7672A automatic injector, packed column inlet modified for 0.53-mm capillary columns (held at 220 °C), and a nitrogen–phosphorus detector (NPD) operated at 250 °C.

To minimize differences between the GC systems, most analyses were obtained using a 30 m × 0.53 mm × 0.88 μm 5% phenylmethyl silicone fused silica capillary column (Hewlett-Packard) with a helium flow of 7.3 mL/min. Exceptions were as follows: (1) ECD analyses were obtained with a 25 m × 0.2 mm × 0.33 μm 5% phenylmethyl silicone column (Hewlett-Packard). (2) NPD analyses were run using a 10 m × 0.53 mm × 0.88 μm film methyl silicone column (Hewlett-Packard) with a helium flow of 16.5 mL/min. (3) The AED analyses shown in Figure 12a were obtained using a 25 m × 0.32 mm × 0.52 μm film HP-5 column coupled directly to the cavity and operated with a helium flow of 1.62 mL/min. In all other GC-AED runs, the analytical column was coupled in the GC oven to a 1 m × 0.32 mm × 0.11 μm film HP-1 column that was passed through the transfer line and coupled to the cavity. Instead of using higher bleed 0.53-mm columns for the ECD and NPD analyses, columns were chosen that would optimize the analytical results; these columns are routinely used by the CDFA for residue analysis. Splitless or direct injections of 1 μL were made using the following oven temperature program: 100 °C for 2 min, 20 °C/min to 280 °C, 280 °C for 10 min.

RESULTS AND DISCUSSION

The 12 commodities used for this study (Table II) were obtained as part of a routine pesticide residue monitoring program focusing on fresh fruits, vegetables, and nuts. Commodities were selected to represent sample types with varying contents of moisture, sugars, organic acids, pigments, oils, and other secondary metabolites. Combinations of these indigenous phytochemicals present arrays of matrix interference problems for conventional element-selective detectors normally used for trace level residue analysis. Extracts of carrots and iceberg lettuce are rather clean and present little problem, while others, such as broccoli, onions, strawberries, and alfalfa, include indigenous compounds that interfere with analysis by conventional detectors.

The 10 organohalide and organophosphorus pesticides were chosen from the list of pesticides known to be recovered using the CDFA MRM (Joe, 1988; Lee et al., 1988), and except for dieldrin, they are commonly found residues. In addition, they contained a variety of heteroatoms, which could be detected selectively by the AED (P, S, N, Cl, F, and O). Chlorpyrifos was chosen in particular because it could be detected by all of the element-selective detectors used. The closely eluting trio consisting of chlorpyrifos, parathion, and chlorthal-dimethyl were purposely chosen to evaluate the selectivity of different element channels of the AED relative to the other selective detectors. Ethalfluralin was chosen to demonstrate the AED's fluorine-selective detection and because both the ECD and ELCD respond poorly to fluorinated compounds. Chlorothalonil was selected because it is commonly found as a residue on these commodities, but its analysis is problematic, with results that seem to vary depending upon the sample matrix and the chromatographic conditions.

The commodities were fortified with the 10 pesticides at trace levels near the U.S. EPA tolerance limits.

Analysis Using Conventional Element-Selective Detectors. Twenty-four extracts were obtained from the 12 fortified and 12 nonfortified samples. Each extract was analyzed under similar GC conditions, with the main difference being that four different element-selective detectors were used: ECD, ELCD, NPD, and FPD in both the P and S modes. Minor differences in inlet and detector temperatures or column choice have been noted under Experimental Procedures. Rather than operate every GC with absolutely identical parameters, minor differences were allowed when previous experience showed that the

Table II. Levels of interference caused by coextracted compounds when analyzing crude plant extracts for pesticides by GC with different element-selective detectors.

Plant Material	FPD(P)	FPD(S)	NPD	ECD	ELCD(X)	AED
Alfalfa	●	●	●	●	●	●
Almonds	●	●	●	●	●	●
Broccoli	●	●	●	●	●	●
Carrot	●	●	●	●	●	●
Cauliflower	●	●	●	●	●	●
Green Onion	●	●	●	●	●	●
Iceberg Lettuce	●	●	●	●	●	●
Orange	●	●	●	●	●	●
Romaine Lettuce	●	●	●	●	●	●
Strawberry	●	●	●	●	●	●
Sweet Onion	●	●	●	●	●	●
Zucchini	●	●	●	●	●	●
	Worst ●	●	●	●	●	Best

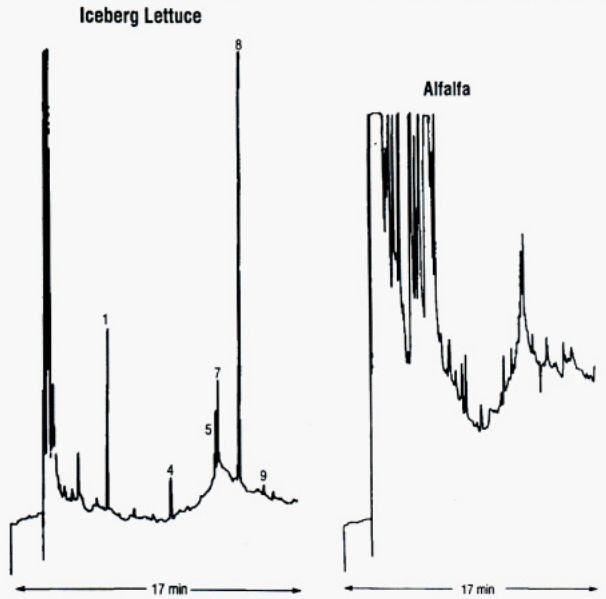

Figure 2. GC-ECD analysis of iceberg lettuce and alfalfa extracts. Both samples were fortified with pesticides at levels indicated in Table I; peak numbers correspond to pesticides listed in that table. Interference from coextracted materials made detection of pesticides in the alfalfa chromatogram virtually impossible.

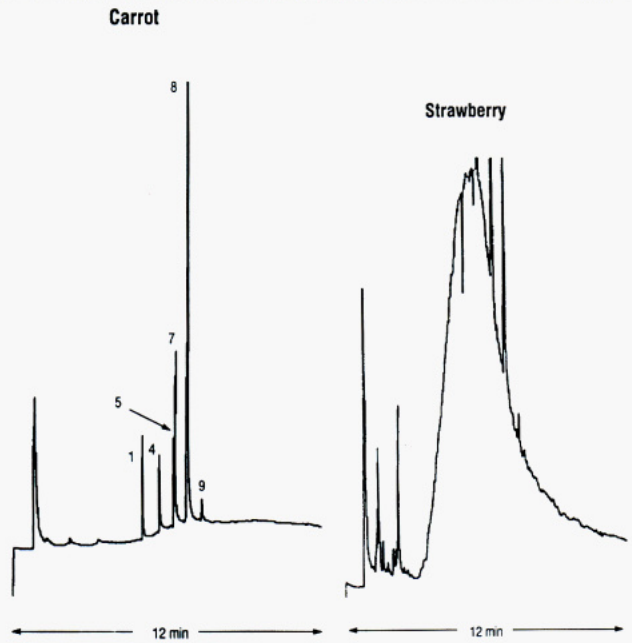

Figure 3. GC-ELCD analysis of carrot and strawberry extracts. Both samples were fortified with pesticides at levels indicated in Table I; peak numbers correspond to pesticides listed in that table. Interference from coextracted materials made detection of pesticides in the strawberry chromatogram virtually impossible.

conditions used had been optimized for this analysis. In all, 120 different chromatograms were obtained. For presentation here, representative results have been chosen that illustrate both easy and difficult analyses.

Figure 2 shows two chromatograms that illustrate typical ECD results. The five halogenated pesticides could be detected in the relatively clean lettuce extract. However, the alfalfa sample contained so much coextracted material that analysis by ECD was impossible. While the ECD is easily the most sensitive detector for polyhalogenated compounds, it is not very selective and detection limits are seriously eroded by interferences. For this reason, the ECD is used for pesticide analysis only when the extracts are very clean.

The ELCD is used more commonly for organochlorine pesticide analysis because it is relatively sensitive and more selective than the ECD. Figure 3 shows a good analysis for the five chlorinated pesticides in carrot; however, ethalfluralin, which contains F but no Cl, cannot be detected by the ELCD. Large interferences were observed with strawberries (Figure 3), alfalfa, almonds, and oranges. The cause of these interferences is not well understood, but neutralizing the extracts before analysis or cleanup with gel permeation, Florisil, or C-18 solid-phase extraction seems to remove them.

Organophosphorus (OP) pesticides are commonly an-

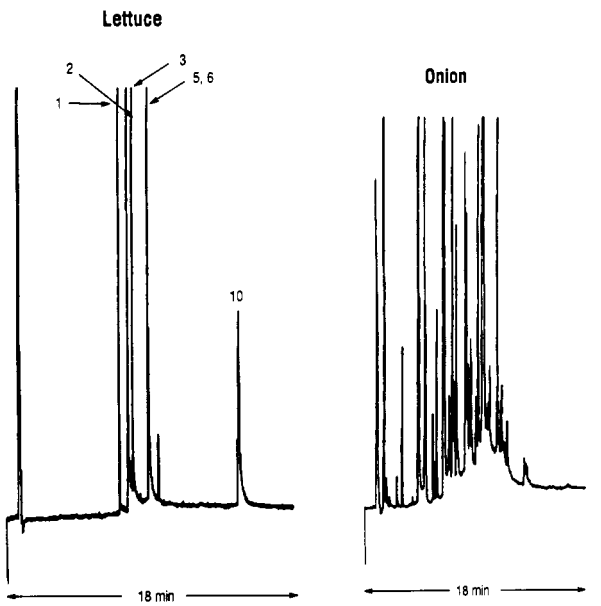

Figure 4. GC analysis of iceberg lettuce and mature onion extracts with an FPD detector operated in the phosphorus mode. Both samples were fortified with pesticides at levels indicated in Table I; peak numbers correspond to pesticides listed in that table. FPD response from coextracted sulfur-containing compounds made it impossible to detect the phosphorus pesticides selectively in the onion extract.

alyzed by FPD with a phosphorus filter. Unfortunately, the FPD's selectivity for P over S varies greatly, depending upon detector flow rates and temperature, but is never very high (Dressler, 1986). Therefore, commodities with a high sulfur content, such as onions and broccoli, give a high background in the FPD phosphorus chromatogram. Figure 4 shows a comparison of lettuce, which has no discernible sulfur, with onion, where the high background of sulfur compounds prevents analysis for the OP pesticides.

OP and nitrogen-containing pesticides could be determined, in principle, by GC with an NPD, but serious interferences were encountered with alfalfa (Figure 5), broccoli, and cauliflower. All of the other commodities exhibited at least some interferences. The zucchini chromatogram in Figure 5 is typical of these. Since the NPD is selective for both N and P, it is impossible to tell if an analyte contains N or P or both. For these reasons, there is no widely accepted MRM specific for N-containing pesticides.

Six of the pesticides contained sulfur and could be detected by GC-FPD when indigenous sulfur compounds were not present. As expected, high sulfur commodities such as onion, broccoli, and cauliflower could not be analyzed by this method. Figure 6 shows typical results.

While there are advantages to analyzing crude extracts, the above results illustrate why many MRMs employ cleanup steps. Table II summarizes in a qualitative way the level of interferences found from the 12 commodities analyzed by the four conventional detectors as well as the AED. The table can be read like a modified stoplight, where green means there is no problem in doing the analysis of a given commodity with the indicated detector. Yellow suggests that modest interferences exist and analysis should proceed with caution. Pink and red suggest increasing levels of interferences, making analysis very difficult or impossible. The ECD could be used to analyze only 5 of the 12 fortified extracts, while the ELCD was useful for 8. The FPD (P mode) and NPD each gave usable results for 9 samples.

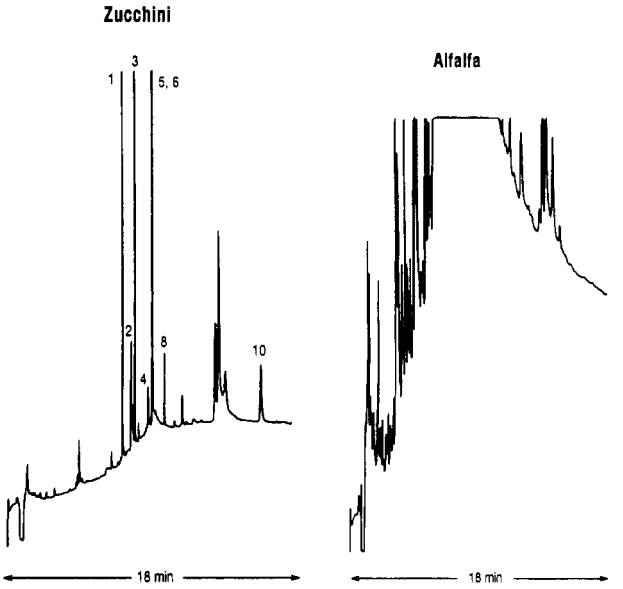

Figure 5. GC-NPD analysis of zucchini and alfalfa extracts. Both samples were fortified with pesticides at levels indicated in Table I. Interference from coextracted materials made detection of pesticides in the alfalfa chromatogram virtually impossible. Assignment of peaks 4 and 8 in the zucchini chromatogram is tentative.

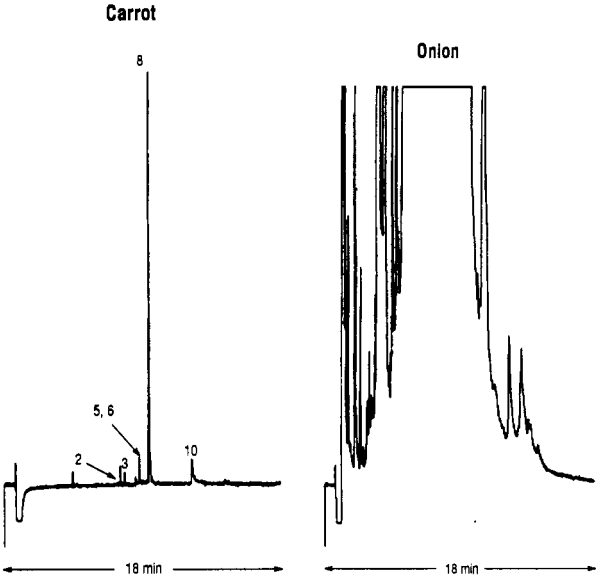

Figure 6. GC analysis of carrot and mature onion extracts with an FPD detector operated in the sulfur mode. Both samples were fortified with pesticides at levels indicated in Table I; peak numbers correspond to pesticides listed in that table. FPD response from coextracted sulfur-containing compounds made it impossible to detect the sulfur pesticides selectively in the onion extract.

GC-AED Analysis. To compare the AED to the other detectors, similar GC conditions were used as much as possible. One deviation was to use direct injection (0.53-mm fused silica column fitted to a packed inlet) for runs with the conventional detectors, while the AED runs were done with splitless injection. Another difference was to use a 1 m × 0.32 mm × 0.17 μm HP-1 column to connect the 0.53-mm analytical column between the oven and the cavity. Not only did this simplify column changing, but having a thinly coated column in the continuously heated transfer line minimizes column bleed into the cavity. Column bleed from silicone stationary phases can be oxidized to SiO_2 in the plasma, which causes peak tailing.

The AED is capable of accumulating up to eight element-

specific chromatograms which are placed in a single data file for analysis. The instrument's design makes it possible to collect certain groups of element-selective chromatograms, such as C, S, and N, or C, H, Cl, and Br, in a single GC run. Elements such as F and P are usually run individually. Although it may require multiple injections to accumulate data for the desired set of elements, the entire process is automated. Element-specific chromatograms were collected for C, Cl, S, N, P, and F for each of the 12 fortified samples and the 12 blanks. This required four injections per sample. One injection of an acetone blank was made between each sample to ensure that carryover was not observed.

The six element-specific chromatograms obtained for iceberg lettuce are shown in Figure 7. The five organochlorine pesticides are readily seen and can be distinguished from ethalfluralin, the only fluorine-containing pesticide in the spiking solution. The five OP pesticides can be seen in P chromatogram. While parathion and chlorpyrifos were not resolved chromatographically, the latter one contains Cl, while the former one does not. Because of their different elemental content, analysis is still possible with the AED. An additional peak at 8.1 min is probably from a pesticide found in the original lettuce sample. The commodities used for these experiments were not known to be pesticide-free.

C-, S-, and N-selective chromatograms are shown for iceberg lettuce in Figure 7. For sulfur the AED is highly selective, linear, and free of quenching (Quimby and Sullivan, 1990); it would seem to be an ideal detector for organosulfur pesticides so long as the commodity is free of indigenous sulfur compounds.

The eight nitrogen pesticides are detectable in the crude lettuce extract, but interferences are clearly present. These may be due to coextracted N-containing compounds or to C-containing compounds, which exceed the selectivity of the AED's N channel. At the wavelength used (174.2 nm) the AED's selectivity for N over C is about 6000; for comparison, the selectivity of the Cl and P channels (with respect to carbon) is reported to be 25 000 (Quimby and Sullivan, 1990). Recently, Quimby et al. reported a new "recipe" for N using the second order of the 174.2 line; they observed increased sensitivity and a selectivity greater than 12 000 (Quimby et al., 1990; Quimby, Hewlett-Packard Co., Avondale, PA, personal communication, 1990). This new method should be tried when one is scanning specifically for N-containing pesticides. Nevertheless, cleanup steps would be required whenever interfering nitrogen compounds are present.

Figures 8–11 show the GC-AED results for mature onions, green onions, strawberries, and alfalfa, the four commodities that caused the most problems with other element-selective detectors. Only the Cl, P, and F chromatograms are shown; these are diagnostic for the pesticides used. Both onion samples (Figures 8 and 9) were easily analyzed with no interferences from coextracted compounds. In particular, the phosphorus channel shows no background interferences from indigenous sulfur compounds. Clearly, the AED's selectivity for P is much greater than that of the FPD.

Peaks in the green onion P chromatogram at ca. 6.5 and 11.6 min are due, most likely, to OP pesticides in the original sample. The selectivity of the phosphorus channel is sufficiently high to exclude even the very high background of coextracted materials found in the alfalfa sample (Figure 11). When the selectivity of the AED is in doubt, spectra (called snapshots) can be used to prove the presence or absence of an element (Sullivan and Quimby, 1990; Wylie and Quimby, 1989; Sullivan, 1991). In this respect, the AED has a clear advantage over other element-selective detectors. Spectral proof for elements is discussed in more detail below.

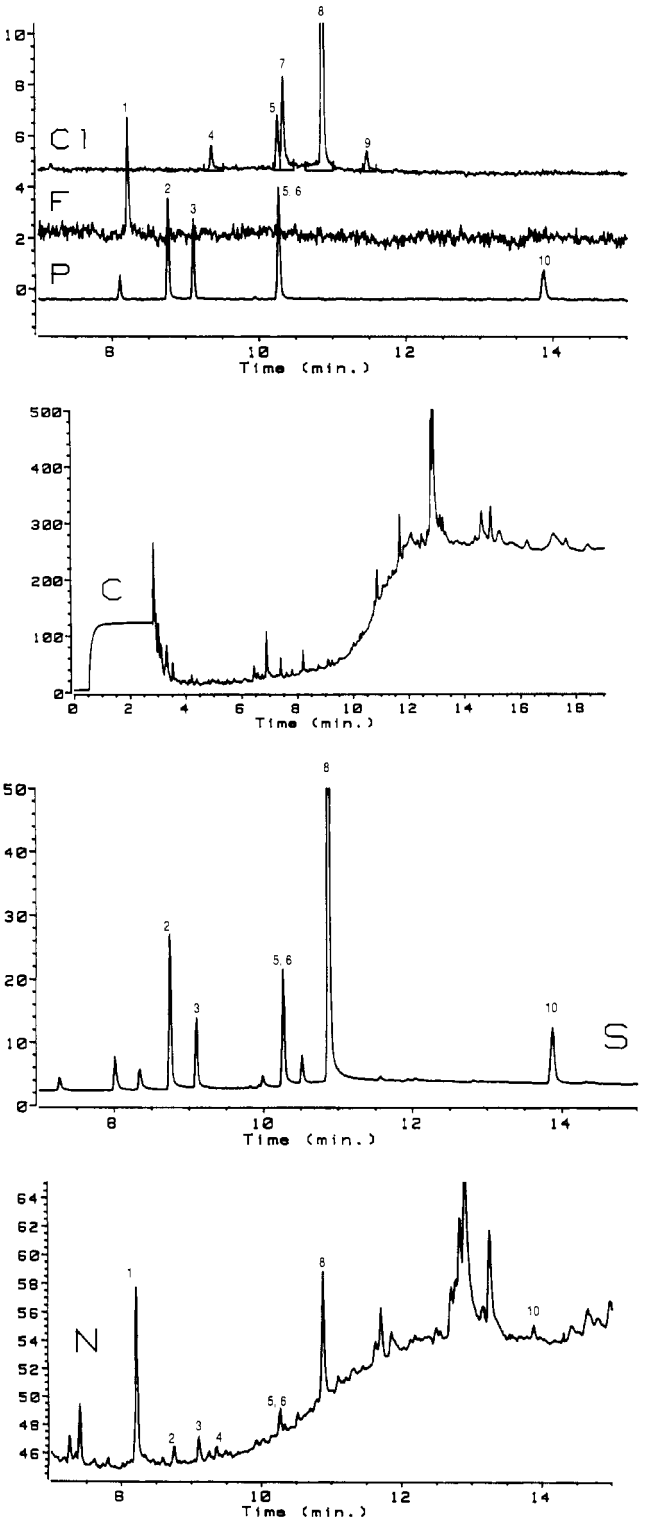

Figure 7. C-, Cl-, F-, P-, N-, and S-selective chromatograms obtained from GC-AED analysis of an iceberg lettuce extract fortified with pesticides at levels indicated in Table I. Four sequential automated GC injections were required to obtain all six chromatograms. Peak numbers correspond to pesticides listed in Table I.

The strawberry sample (Figure 10) showed none of the interferences that prevented analysis by ELCD. The small Cl-containing peaks in the 3–6-min range were not identified. It is certain that these peaks did not arise from

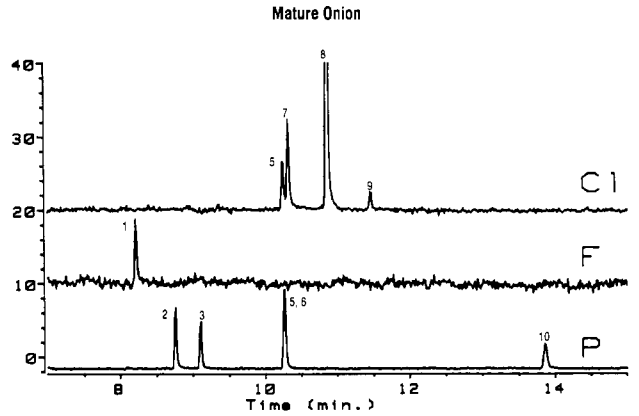

Figure 8. Cl-, F-, and P-selective chromatograms obtained from GC-AED analysis of a mature onion extract fortified with pesticides at levels indicated in Table I. No interferences were observed from coextracted compounds. Peak numbers correspond to pesticides listed in Table I.

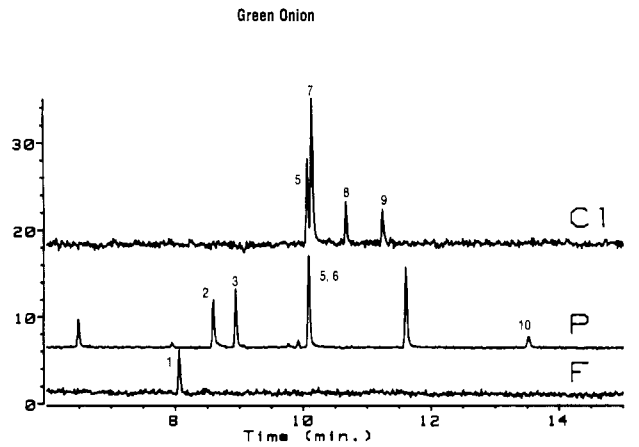

Figure 9. Cl-, F-, and P-selective chromatograms obtained from GC-AED analysis of a green onion extract fortified with pesticides at levels indicated in Table I. No interferences were observed from coextracted compounds. Peak numbers correspond to pesticides listed in Table I.

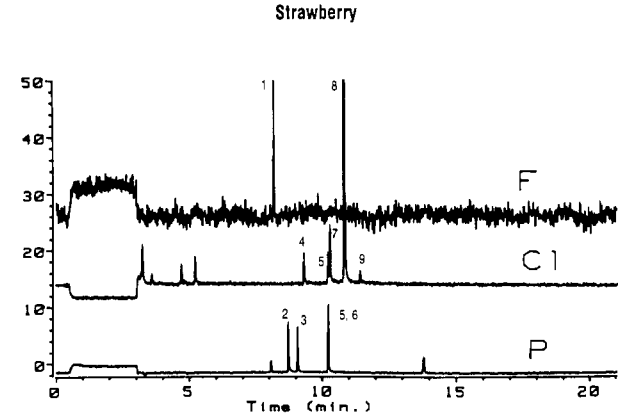

Figure 10. Cl-, F-, and P-selective chromatograms obtained from GC-AED analysis of a strawberry extract fortified with pesticides at levels indicated in Table I. No interferences were observed from coextracted compounds. Peak numbers correspond to pesticides listed in Table I.

poor Cl selectivity with respect to C because several very large peaks in the carbon chromatogram do not show up in the Cl analysis.

In only one case did the AED show interferences from coextracted compounds. The Cl-specific chromatogram of alfalfa in Figure 11 has a noisy baseline due to imperfect selectivity of the AED's Cl channel. Nevertheless, each

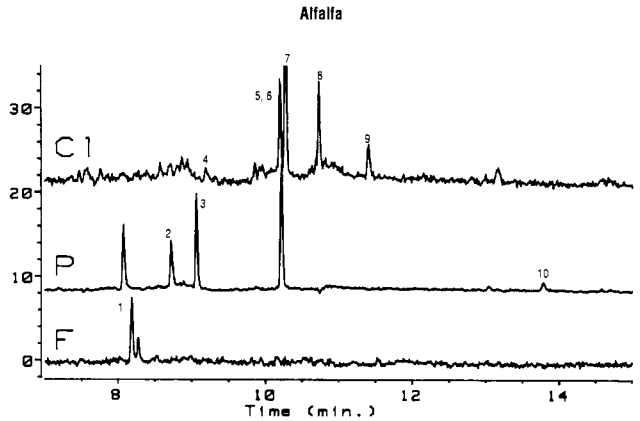

Figure 11. Cl-, F-, and P-selective chromatograms obtained from GC-AED analysis of an alfalfa extract fortified with pesticides at levels indicated in Table I. No interferences were observed from coextracted compounds in the P and F chromatograms. The very high background of coextracted compounds causes modest interferences in the Cl chromatogram. Peak numbers correspond to pesticides listed in Table I.

of the five organochlorine pesticides could be detected by the AED. Crude alfalfa extracts are an especially difficult challenge for any MRM. The extract was dark green and nearly opaque. The alfalfa carbon chromatogram showed levels of coextracted compounds that were at least 10-fold greater than those of any of the other commodities analyzed.

The level of folpet in green onions (Figure 9) and alfalfa (Figure 11) appears to be much less than it is in mature onions (Figure 8) or strawberries, in spite of the fact that the samples were fortified identically. While some differences in recovery could be expected, this may not explain the rather large differences here. Green onions and alfalfa were the last samples analyzed in a sequence that involved 96 splitless injections of the crude extracts. There appeared to be a trend toward lower folpet levels as the sequence progressed, suggesting that an increasingly dirty injection port liner may have contributed to loss of this fungicide.

There was also some difficulty in the analysis of chlorothalonil (2,4,5,6-tetrachloro-1,3-benzenedicarbonitrile) with the GC-AED system. This compound was not detected in extracts of cauliflower, broccoli, green onion, and mature onion; however, it was found in the other eight extracts. Moreover, it was detected in all 12 commodities by GC-ELCD. Interestingly, only vegetables with high sulfur content had no chlorothalonil by GC-AED.

The fact that chlorothalonil was seen by GC-ELCD rules out poor extraction recovery as an explanation. The sample splits analyzed by AED were kept at room temperature for about 2 days during shipping, while those analyzed by other detectors were refrigerated immediately. However, chlorothalonil is reported to be stable to heat and light and to both acidic and basic aqueous solutions (Worthing and Walker, 1987). No satisfactory explanation has been found that would implicate the AED. No examples of one element quenching the response of another have ever been reported.

A possible explanation may lie in the different injection techniques used. The AED analyses were performed by splitless injection at 250 °C, while the others were done by direct injection into a packed inlet adapted for 0.53 mm i.d. columns operated at 220 °C. Active surfaces in the inlet, perhaps in combination with some sulfur compounds, may have led to the demise of chlorothalonil. Cool on-column injection with AED analysis could be used

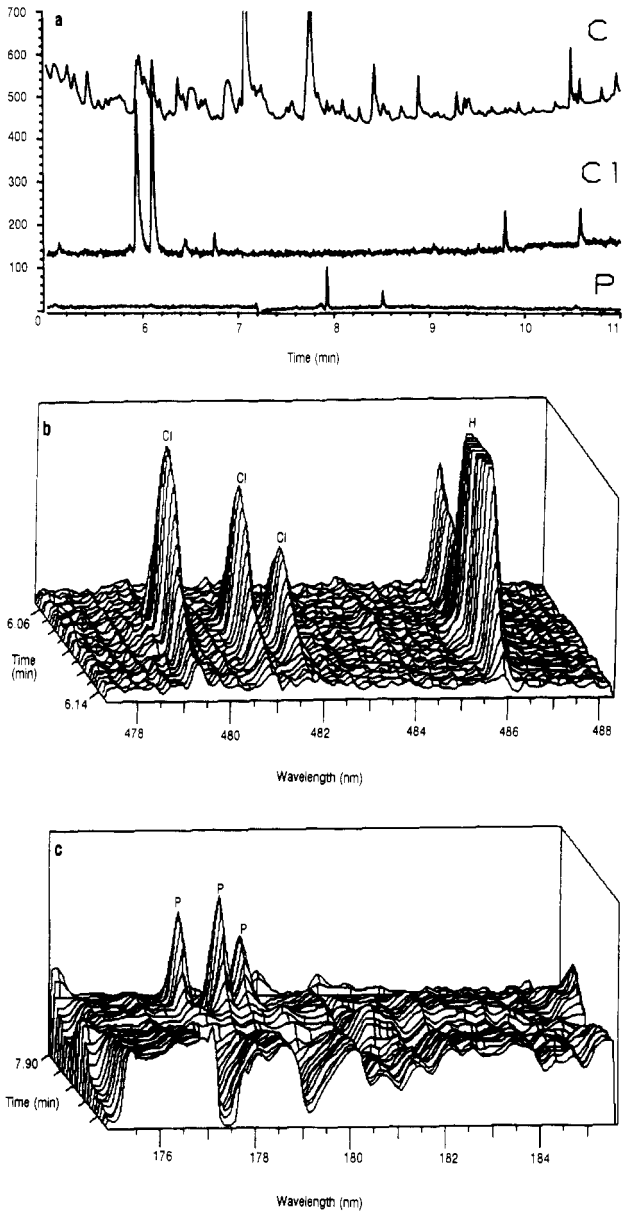

Figure 12. (a) C-, Cl-, and P-selective chromatograms obtained from GC-AED analysis of an orange extract that was not fortified with pesticides. (b) Three-dimensional plot of the AED spectral output (in the 478–488-nm range) vs time. The emission lines centered at 479.45, 481.00, and 481.95 nm, with the relative intensities shown, are proof that the chromatographic peak at 6.1 min contains Cl. The emission line at 486.1 nm is characteristic of H. (c) Three-dimensional plot of the AED spectral output (in the 175–185-nm range) vs time. The three emission lines centered near 178 nm, with the relative intensities shown, are proof that the chromatographic peak at 7.93 min contains P.

to test this theory; however, on-column injections are inappropriate for routine analysis of such dirty samples.

The AED results are juxtaposed with those from the other detectors in Table II. The AED was the only detector that could be used for analyzing all 10 pesticides in all 12 commodities; moreover, a single fully automated method was used to collect all of these data.

Spectral Proof for Elements. Figure 12a shows the C-, Cl-, and P-specific chromatograms of the unfortified orange extract. Several Cl peaks and two P peaks are observed. It is easy to see that these peaks do not result from poor selectivity with respect to carbon because large peaks in the carbon chromatogram (e.g., 7.1 and 7.8 min) do not give corresponding peaks in the Cl and P chromatograms. While these compounds were not identified, it is likely that they are pesticide residues contained in the original sample of oranges.

Table III. Method Detection Limits for Three Pesticides in Two Commodities Representing Three Different Element-Selective Channels of the GC-AED[a]

	AED channel used	method detection limits, ppm: almonds	mature onion
chlorpyrifos	Cl	0.031	0.030
diazinon	P	0.015	0.015
ethalfluralin	F	0.300	0.390

[a] A 2:1 signal-to-noise ratio is assumed at the detection limit.

The AED takes optical emission spectra continually over a wavelength range of about 25 nm during a chromatographic run. These snapshots can be used to prove that a chromatographic peak actually contains the element in question. Figure 12b shows a plot of snapshots spanning the range 478–488 nm. Spectra collected from 6.06 to 6.14 min are plotted, giving a three-dimensional picture of the spectral changes over the time range that includes the Cl peak at 6.1 min. The three spectral lines centered at 479.45, 481.00, and 481.95 nm, with the relative intensities shown, are proof that the chromatographic peak at 6.1 min actually contains chlorine. The emission at 486.1 nm is characteristic of H.

A similar plot is shown in Figure 12c; in this case the three emission lines centered near 178 nm are characteristic for P, thus proving that the GC peak at 7.93 min actually contains P. With nonspectral element-selective detectors, there is no certainty that a GC peak is caused by a specific element, unless the selectivity with respect to all other elements is known to be infinite. The selectivity of the detectors used in this study varies, but in no case is it infinite. The AED's ability to prove the existence of an element in a GC peak should provide more reliable pesticide residue analyses.

Detection Limits Using GC-AED. While the main focus of this work was to compare the AED's selectivity to that of other common element-selective detectors, method detection limits were determined for representative pesticides in almonds and onions using the GC-AED system, and these are shown in Table III. These values include the entire procedure from extraction through GC-AED analysis and assume a 2:1 signal-to-noise ratio at the detection limit. Lower detection limits probably could be achieved in many instances by making larger injections or by concentrating the extracts prior to analysis. Because of its high selectivity, the AED should be able to detect pesticides in spite of higher background levels of coextracted materials.

CONCLUSION

To analyze a broad range of volatile pesticides using conventional element-selective detectors, several different GC configurations are needed. As illustrated in this work, interferences from many commodities makes analysis of crude extracts virtually impossible; as a result, cleanup steps are required. However, cleanup procedures, such as Florisil chromatography, reduce the range of pesticides that can be analyzed (Storherr et al., 1971; Mills et al., 1963).

Analysis by GC-AED could obviate the need for cleanup in most cases and lead to more reliable identifications because confusing interferences are absent. In addition, other elements in a pesticide can be used for confirmation, since the AED can detect all of the elements commonly found in pesticides (albeit with different sensitivities). Unlike the ECD and ELCD, the AED can distinguish

between the halogens. Since a significant number of pesticides contain either bromine or fluorine, this should be a distinct advantage for an MRM. Since HF is a weak electrolyte, the ELCD cannot be used for F detection. Fluorine response in the ECD is quite unpredictable and much weaker than that of the other halogens. Analysis of crude extracts caused no degradation of the AED's performance over several hundred injections; however, inlets are less forgiving, and liners needed to be changed periodically.

GC-AED analysis of pesticide residues appears to offer significant improvements in selectivity and convenience over other element-selective detectors. A single system could be used for the screening or confirmation of most volatile pesticides. Indeed, pesticides are particularly good candidates for GC-AED analysis, since they often contain several heteroatoms. Using this system, the analyst has the choice of detecting any individual element in the pesticide or of obtaining a multielement profile. In most cases, the AED's sensitivity should be adequate, and, because of its high selectivity, some concentration of the crude extracts should be possible if increased sensitivity is needed. The AED's sensitivity and selectivity for N is less than for the other elements of interest; therefore, the AED may not be a useful detector for the trace analysis of pesticides that have N as the only heteroatom.

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Received for review February 6, 1991. Revised manuscript received July 29, 1991. Accepted August 13, 1991.

Registry No. Ethalfluralin, 55283-68-6; dimethoate, 60-51-5; diazinon, 333-41-5; chlorothalonil, 1897-45-6; chlorpyrifos, 2921-88-2; parathion, 56-38-2; chlorthal-dimethyl, 1861-32-1; folpet, 133-07-3; dieldrin, 60-57-1; azinphos-methyl, 86-50-0.