Use of the Phosphorus Detector as a Confirmatory Tool for Measuring Residues of Shell Chemical's Triazine Herbicide

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With the advent of nitrogenous chemicals for pesticidal use, there is a need for selective detection of these compounds at the nanogram level, preferably through use of gas chromatography. Coulson's electrolytic conductivity (1), Cassil's microcoulometric (2) and Aue's alkali flame (3) detectors have shown utility for residue analysis of organic nitrogen compounds. Recently, Hartmann (4) described a rubidium sulfate flame detector with improved sensitivity. The alkali flame detector is a modified version of Karmen and Giuffrida's "thermionic" detector (5) for determining residues of organophosphorus pesticides. Ives and Giuffrida looked at the thermionic detector's response to nitrogen (6)

Tindle reported (7) on a GLC procedure for determining residues of s-triazine compounds in corn. Detection down to about one-half nanogram of Atrazine (2-chloro-4-ethylamino-6-isopropyl-amino-s-triazine) was accomplished through use of a GLC equipped with an alkali-flame detector with a movable electrode and rubidium sulfate as the coating material. This paper describes the use of a commercial phosphorus detector (8) for residue analysis of the triazines.

Shell Chemical Company's SD 15418 (propionitrile, 2-(4-chloro-6-ethyl-amino-s-triazine-2-ylamino)-2-methyl) is effective as a pre-emergence herbicide for controlling grass and broadleaved weeds in corn (9). The proposed analytical method for determining residues of SD 15418 prescribes the use of electron-capture GLC to detect down to about 0.05 ppm in crops. Unfortunately, the latter requires a flow rate of carrier gas which exceeds the capability of most electron capture detectors commonly used for residue analysis. As an alternative, Varian Aerograph's phosphorus detector (cesium bromide pellet) has shown selectivity for certain triazine herbicides and can be used as a confirmatory method.

Experimental

Without altering the position of the electrodes, as Aue *et al.* suggest, operating parameters of Varian's commercial instrument were optimized to measure down to about 0.5 nanogram of Atrazine and about 1.0 nanogram of SD 15418. The minimal detectable amounts are based on scale deflections of 3% of full response. GLC conditions used for this investigation are listed in Table I. Figure 1 depicts actual GLC tracings of 2 microliter injections of 5, 3, 1

Bulletin of Environmental Contamination & Toxicology,
Vol. 5, No. 1, 1970, published by Springer-Verlag New York, Inc.

and 0 microgram quantities of Atrazine per milliliter of ethyl acetate.

Table I

GLC Parameters for detecting SD 15418[a)]

Instrument	- Varian Aerograph Hy-Fl Model A-600-C equipped with a cesium bromide phosphorous detector
Column	- 17" x 1/8" stainless steel
Liquid phase	- 5% DC-710
Solid support	- Gas Chrom Q, 80/100 mesh
Carrier gas	- Helium, 110 ml/min
Column temperature	- 230°C
Hydrogen	- 12-14 ml/min to the inlet
Air	- 350-450 ml/min to the inlet
Range	- 1 E.C.
Mode	- Flame
Attenuation	- 16 X
Recorder chart speed	- 12.5 mm/min
Approx. Retention time	- 20 mm

a) Due to a number of variables between instruments, these operating conditions should serve only as a guide.

To achieve a detection level of 0.2 ppm SD 15418 in crops with the 'phosphorus detector', a final extract of 5 g/ml is required. When analyzing corn, this high ratio of crop to solvent requires prior cleanup because of the highly-polar extraction system which has been selected to remove both the parent compound and possible metabolites. Cleanup includes solvent partitioning and solid-liquid column chromatography. Extraction with solvents of decreased polarity allows less stringent cleanup. Presumably, the processing can be adjusted to accommodate 10 g/ml or even 20 g/ml extracts to effect improved sensitivity. Cleanup via the relatively rapid sweep co-distillation technique is effective for non-oily crops.

Corn samples, 50-100 grams, are extracted with methanol in Waring blenders. Blender contents are filtered quantitatively through sintered Buchner funnels to effect 4 ml per gram of kernels or 8 ml per gram of stover. An aliquot equivalent to 5 grams of crop is stripped of its methanol with a rotary evaporator, diluted with 50 ml water, then washed with 100 ml hexane. After discarding the hexane wash, the remaining aqueous portion is extracted 3 times with 70 ml of ethyl ether. The combined ether extracts are dried with anhydrous sodium sulfate, concentrated, then exchanged to hexane preparatory to column cleanup. The 5 grams of crop in hexane with trace of ether is quantitatively transferred to a miniature chromatographic column (length 130 mm and I.D. 10.5 mm) containing 2.5 g basic alumina adsorbent deactivated with 7.5% water; 10-15 ml of hexane is eluted and discarded as forecut. Following the hexane, the column is eluted with a 1:1 mixture of hexane

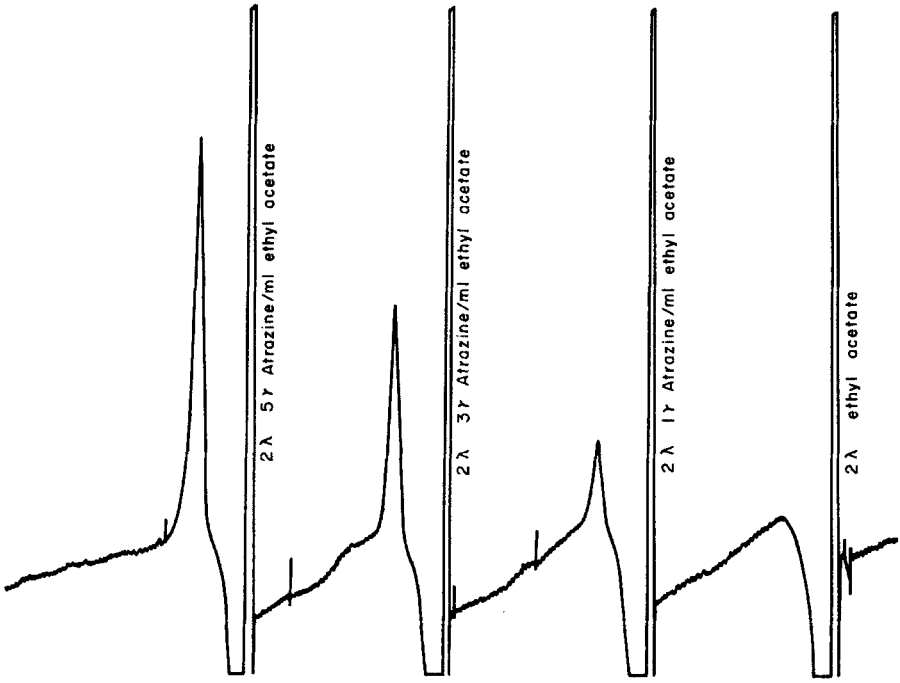

Figure 1. 10, 6, 2, and 0 nanograms of Atrazine by GLC phosphorus detector. Other than column at 190°C and helium at 14 psig, GLC conditions are as outlined in text.

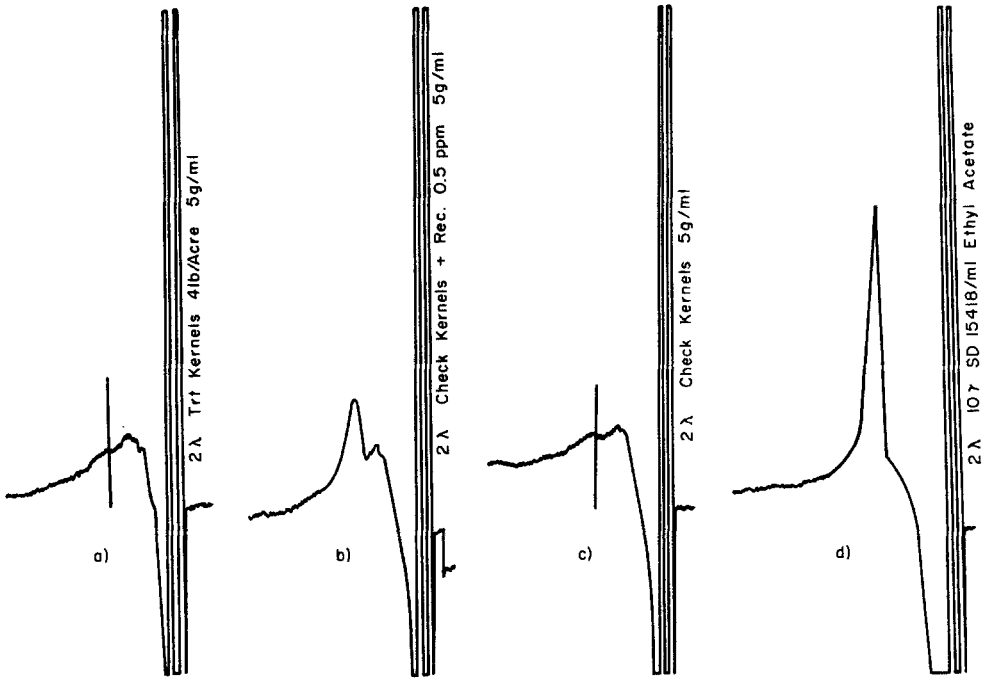

Figure 2. GLC tracings of a) kernels from treated corn, b) non-treated kernels with 0.5 ppm SD 15418 added at time of extraction, c) check kernels, and d) analytical standard.

and ethyl ether; collection of 18 ml of this eluate is typical. However, a predetermined column-profile with a standard dictates the necessary collection volume. Following concentration, the extract is brought up to 1 ml volume with ethyl acetate. Two microliters are injected into the GLC.

Results and Discussion

Several harvest samples of stover and kernels, from corn grown in soil receiving a pre-emergence treatment of 4 pounds of SD 15418 per acre, contained no detectable residue (0.2 ppm) of the parent compound when analyzed with the above method. Recoveries of 0.25, 0.50 and 1.0 ppm SD 15418 added to the corn at time of extraction generally exceed 80%. Typical GLC tracings are shown in Figure 2. An insufficient number of samples have been analyzed to date with this procedure to make a statistical evaluation of precision and accuracy. Instrument variation was slight, as shown by the uniform response of multiple injections of standards during a set of 20-30 samples. Day to day response was essentially the same.

GLC with the cesium bromide detector appears to be an ideal tool as a confirmatory method for determining residues of SD 15418. Improvements in sample processing should lower the limits of detection to approximately 0.1 ppm. The degree of interference from organophosphorus materials has not been determined. In view of the GLC conditions, organophosphates commonly used for pesticides would probably not be resolved from the solvent front.

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