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Determination of Benefin and Trifluralin Residues by Quantitative Gas-Liquid Chromatography/Mass Spectrometry

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A quantitative GLC–MS procedure is described for the simultaneous determination of benefin and trifluralin residues in soil. Prior gas–liquid chromatographic separation of the two herbicides is not required due to the selective nature of the detector. Comparable soil residue levels are obtained for both the mass fragmentography (multi-ion detector, MID) procedure and an established electron-capture GLC procedure. The MID method has a similar sensitivity to the electron-capture GLC method but has a shorter analysis time.

Residue levels of trifluralin (2,6-dinitro-*N*,*N*-di-*n*-propyl-α,α,α-trifluoro-*p*-toluidine) can routinely be determined by gas–liquid chromatography (GLC) (Tepe and Scroggs, 1967). A similar procedure exists for the determination of isomeric benefin [*N*-(*n*-butyl)-*N*-ethyl-2,6-dinitro-α,α,α-trifluoro-*p*-toluidine]. As the two nitroanilines possess different herbicidal activity, a method is required which can differentiate between them at the residue level.

Simultaneous determination of trifluralin and benefin requires prior GLC separation of the two compounds. The difficult separation of these isomers has been partially achieved on a Durapak-Carbowax 400/Poracil C column (Koons and Day, 1972) and completely on a bonded monomolecular phase (Aue et al., 1973). In their work this latter phase had a very limited lifetime. Recently (Hall and Mallen, 1975) a liquid crystal phase has been used to effect a GLC separation of benefin and trifluralin. However, this phase is not suitable for use in conjunction with an electron-capture detector.

In this approach the specificity advantage of multiple ion detection mass spectrometry (MS) over electron-capture detection GLC is implemented. In consequence the prior separation of the two isomers is not required and conventional GLC columns can be used.

EXPERIMENTAL SECTION

Standard grade benefin and trifluralin were used (Eli Lilly & Co., Indianapolis, Ind.).

Extraction of Residue. Residues of benefin and trifluralin were extracted by the method of Tepe and Scroggs (1967). The extracted residues were dissolved in toluene and analyzed by quantitative GLC–MS and GLC alone.

Gas–Liquid Chromatography/Mass Spectrometry. An LKB 9000S GLC–MS equipped with a four-channel Altema AL5 multi-ion detector (MID) was used. Chromatography was performed on a 5 ft × 4 mm i.d. glass column packed with 1.2% SE30 on Gas-Chrom Q (100–120 mesh). The column temperature and injection port temperature were maintained at 190 and 200 °C, respectively; the carrier gas (helium) flow rate was 30 ml/min. The effluent from the GLC column was passed through a Ryhage jet separator (265 °C) before entering the ion source block (270 °C). The mass spectrometer settings for routine use were as follows: ionizing voltage, 20 eV; accelerating voltage, 3.5 kV; trap current, 60 μA; resolution, 1500. The required masses were brought into focus by switching the accelerating voltage with the Altema MID unit at a fixed magnetic field. Optimum precision was obtained for the method when the GLC–MS system was stabilized overnight. The signal from each ion was recorded on a four-channel Visigraph FR-3017 direct reading oscillograph. Electron-capture GLC was performed on a Pye 104 GLC equipped with a 63 Ni detector.

Calibration Procedure. In samples containing either benefin and no trifluralin or vice versa, the alternative isomer was used as an internal standard (no deuterium-labeled isotopes were available). A series of standards for benefin and trifluralin in the concentration range 0.01–0.06 μg/ml was prepared. Four microliters of each concentration solution was injected into the GLC–MS, and a standard curve prepared by plotting a ratio of selected ion (benefin, *m/e* 292; trifluralin, *m/e* 306) peak height against nanograms of the herbicide. When both herbicides were present, an external standard procedure was used. The system was calibrated daily. After the initial calibration, a standard solution was injected between every third sample solution to check that no significant drift occurred from the initial calibration. On occasions unacceptable drift after several hours work necessitated recalibration of the system. All results were corrected for an extraction recovery figure typically of about 80%.

RESULTS AND DISCUSSION

The mass spectra for trifluralin and benefin (*m/e* >250) are shown (Figure 1). Fragmentation of the molecule to give characteristic imine ions at *m/e* 292 for benefin and *m/e* 306 for trifluralin are specific to each component. A relative abundance of 100% also makes these ions very suitable for quantitation. Weaker ions at *m/e* 276 and 290 can be used to further improve method specificity.

Variation of electron voltage energies did not significantly affect the yield of these ions and hence sensitivity of the method. The detection limit of both herbicides to

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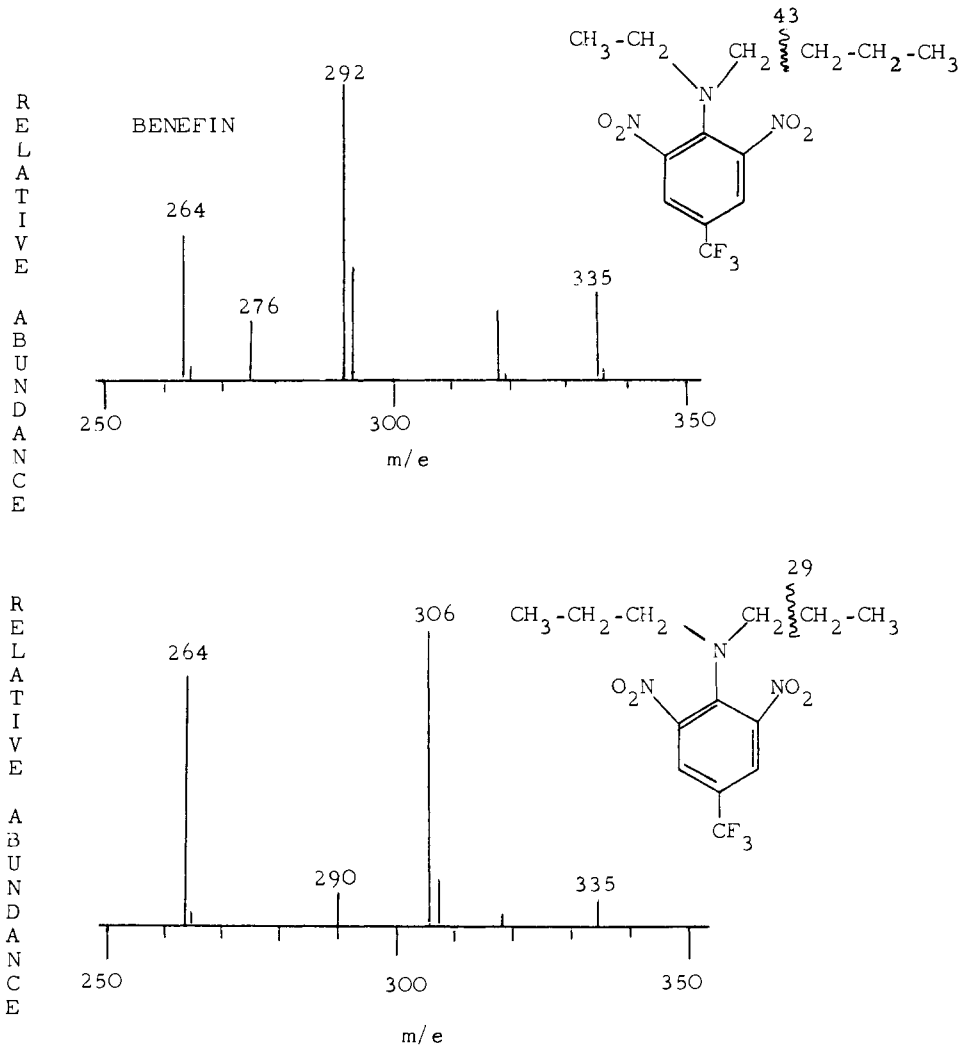

Figure 1. Spectra of trifluralin and benefin ($m/e > 250$) at 20 eV.

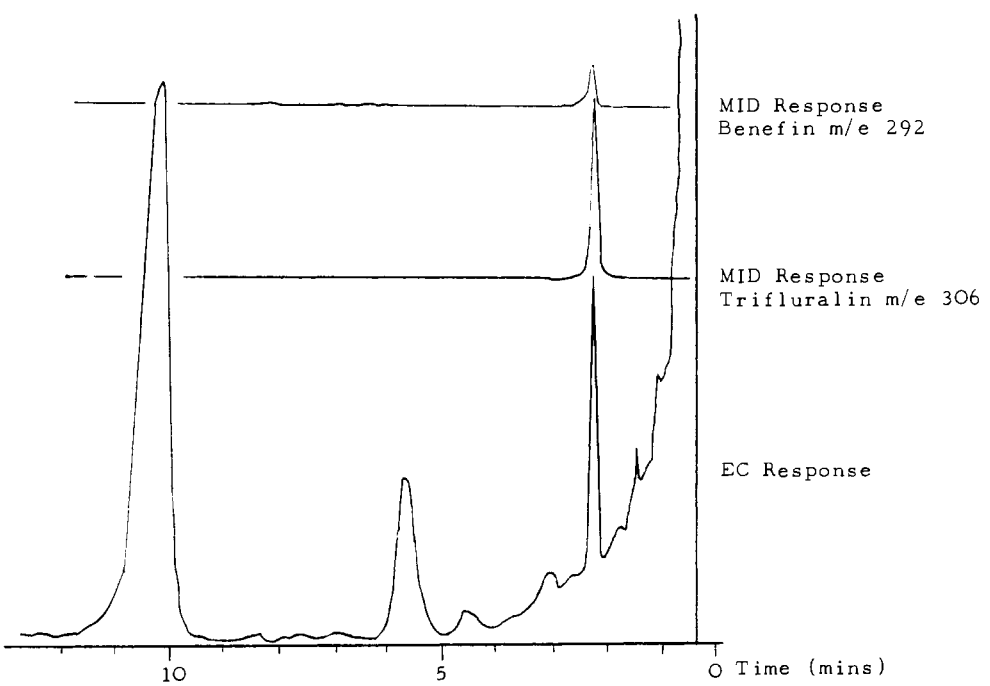

Figure 2. MID and electron capture chromatograms of samples of soil extract.

MID is 50 pg, a figure comparable with electron capture detection sensitivities.

A comparison of data for both MID and electron-capture GLC methods is shown (Table I). Good agreement for

Table I. Comparison of Results from MID and Electron Capture GLC Methods for a Series of Benefin and Trifluralin Soil Residues

Sample no.	MID assay, ppm			Electron capture-GLC,[a] ppm
	Benefin	Trifluralin	Total	Total
1	0.026	0.038	0.06	0.07
2	0.010	0.025	0.04	0.04
3	0.012	0.014	0.03	0.025
4	0.016	0.050	0.07	0.08
5	<0.01	<0.01	<0.01	<0.01
6	0.018	0.018	0.04	0.04
7	0.010	0.01	0.02	<0.01
8	<0.01	<0.01	<0.01	<0.01

[a] Not able to determine individual levels.

total benefin and trifluralin residue levels in sandy loam and sandy soil is obtained, only the MID method giving individual benefin and trifluralin residues. Although eight replicate injections of a standard solution indicate the internal standard method (coefficient of variation = 1.7%) is considerably more precise than the alternative method (benefin, coefficient of variation = 3.4%; trifluralin, coefficient of variation = 2.0%), both methods are satisfactory for the analysis of soil residues. A further indication of the selectivity of the MID approach can be seen by comparison of a GLC and MID output (Figure 2). No decrease in sensitivity or deterioration in column performance was observed during use of the assay. In consequence it can be expected that residue samples for MID analysis will need less cleanup than those for electron-capture GLC analysis and include sample extracts too impure to assay by GLC.

A more general application of quantitative mass spectrometry to crop residue analysis is limited by cost. As both chromatographic and sample workup times are reduced by the MID method, the technique is very suitable for laboratories handling large numbers of samples. In our hands the mass spectrometer is more reliable and less susceptible to contamination than is a gas chromatograph fitted with an electron-capture detector. Short retention times, minimal delay for elution of highly retentive peaks, and less sample cleanup are all factors contributing to a faster assay turnover. The assay has been used successfully over a period of several months.

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Volatilization and Photodecomposition of Plictran Miticide

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Recently, a new organic tin product, Plictran miticide containing tricyclohexyltin hydroxide, has been developed for the control of mites in apples, pears, and citrus fruits. Photodecomposition and volatility studies were conducted with this miticide. The results indicate that tricyclohexyltin hydroxide rapidly undergoes photodecomposition, the main products being inorganic tin (80%) with traces of dicyclohexyltin oxide, cyclohexylstannoic acid, and tricyclohexyltin hydroxide unchanged. The traces of tetracyclohexyltin which were present in the samples as an impurity were not affected by irradiation. The amount of tricyclohexyltin hydroxide depends on the length of exposure and the intensity of the sunlight. The longer the exposure and the more intense the light the more tricyclohexyltin hydroxide will be decomposed. Volatility studies indicate that tricyclohexyltin hydroxide is not volatile from the dry state, but that the compound can be lost from a moist surface by co-distillation. The rate at which the miticide will be lost depends on the temperature and quantity of water evaporated. The dicyclohexyltin oxide is volatile from the dry state and can co-distill with water.

Plictran miticide, a new product containing tricyclohexyltin hydroxide, recently has been introduced and found to be extremely effective for the control of plant feeding mites, yet not harmful to predacious mites. The commercial applications of this miticide are for apples, pears, and citrus fruits (Kenaga, 1966; Allison et al., 1968).

The miticide is sprayed onto the trees and thus deposited on the surfaces of the leaves and fruit. Under these conditions, the chemical is subjected to photodecomposition by the sunlight irradiation and to the environmental conditions which will influence the volatility of the compound.

Studies were undertaken to determine how rapidly this miticide would undergo photodecomposition and how rapidly it could be lost from the surfaces of leaves and fruit by volatilization. In the initial studies with this miticide, it was found that part of the products formed by photodecomposition were insoluble and could not be easily removed from various surfaces. To account for this insoluble residue, it was necessary to combust the tissue and to determine the tin by colorimetric methods. This was a very time-consuming operation and did not indicate what chemical form the tin was present in on the surface of the fruit. It was also difficult to determine the true tin blank. To overcome these difficulties, a glass slide technique was employed using radioactive tricyclohexyltin-^{119}Sn hydroxide. The ^{119}Sn isotope was used instead of the ^{113}Sn

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