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Note

Use of the alkali-flame ionization detector for the determination of methomyl residues in plant materials*

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The rubidium sulfate alkali-flame ionization detector (Rb_2SO_4-AFID) is selectively sensitive to nitrogen-containing compounds such as the insecticide methomyl (S-methyl-N-[(methylcarbamoyl)-oxy] thioacetimidate). Methomyl may be quantitatively detected in the nanogram range by gas chromatography and the procedure was used to obtain methomyl residue data in a variety of vegetable crops.

Some investigators have hydrolyzed methomyl to the corresponding oxime (methyl N-hydroxythioacetimidate) with subsequent analysis by either a microcoulometric detector in the sulfur mode or a flame photometric detector with a 394 nm sulfur interference filter and temperature programmed[1–3]. Lee *et al.*[4] used the flame photometric detector with the sulfur filter, under isothermal conditions, but they modified the procedure of Pease and Kirkland[1] by eliminating interfering sulfur compounds in rape plants and seeds prior to analysis. Williams[5] demonstrated that methomyl could be analyzed directly on a microcoulometer gas chromatograph in the nitrogen specific mode. Reeves and Woodham[6] used the flame photometric detector in the isothermal mode and they analyzed for the parent compound in tobacco and environmental samples.

The method of Reeves and Woodham[6] performed satisfactorily for most vegetable crops. However, interference from sulfur compounds was noted in the analysis of Chinese radish greens and roots. The solution to this problem was the use of the rubidium sulfate detector. Reproducible peak heights were obtained on the chromatogram with repeated injections of a standard methomyl solution; intervals of 30 to 40 min after a sample injection may be necessary to retain the original detector sensitivity.

MATERIALS AND METHODS

A Varian Aerograph Model 1400 gas chromatograph originally equipped with a hydrogen flame ionization detector was converted to Rb_2SO_4-AFID operation with a conversion kit available from the manufacturer. The following gas chromatographic conditions were used: 6 ft. (1.82 m) × 2 mm I.D. borosilicate glass column containing

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5% Carbowax 20M on high-performance grade Chromosorb W (80–100 mesh); column temperature 160°, injection port temperature 220°, detector temperature 260°; flow-rates were nitrogen 25 ml/min, hydrogen 35 ml/min and air 220 ml/min. The flow-rates for this detector are critical and must be optimized according to the manufacturer's instructions. A methomyl reference standard was furnished by E. I. du Pont de Nemours (Wilmington, Del., U.S.A.). Standard solutions of methomyl in ethyl acetate contained 1.25–10.0 ng/μl.

Methomyl was extracted from crop samples using the procedure of Fung[3]. The ethyl acetate extract was evaporated to dryness by vacuum evaporation and purified by the coagulation and florisil column cleanup procedure of Reeves and Woodham[6]. The residue was transferred with ethyl acetate to a 5-ml centrifuge tube, the volume was adjusted to 0.5 ml, and a 2-μl aliquot was injected into the gas chromatograph. The amount of methomyl in the aliquot was determined from a calibration curve prepared on the day of analysis by injections of 2.5, 5, 10 and 20 ng of methomyl.

Representative gas chromatograms in Fig. 1 illustrate the results of the analysis of methomyl residues from 50-g Chinese radish samples. Recovery of methomyl from untreated control samples fortified with methomyl at the 0.1 ppm level averaged 72%. The limit of detectability was 0.02 ppm.

The method has also been applied to leafy vegetables and cucurbits; chromatograms of these samples exhibited some crop background peaks, but these peaks did not interfere with the resolution of methomyl.

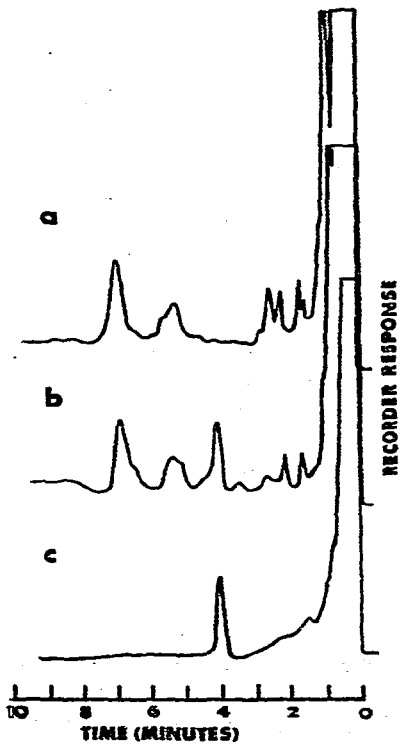

Fig. 1. Chromatograms of (a) untreated Chinese radish; (b) untreated Chinese radish fortified with 0.1 ppm methomyl; (c) methomyl standard, 10 ng.

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