Gas–Liquid Chromatographic Analysis of the Herbicide Dinoterb (2,4-Dinitro-6-*tert*-butylphenol) in Soil

Dinoterb (2,4-dinitro-6-*tert*-butylphenol), recovered from soil, was analyzed by gas chromatography after methylation with diazomethane. A minimum detection limit of 1 μg/kg of soil could be reached. Therefore, it was essential to remove the excess diazomethane before analysis.

Dinoterb (2,4-dinitro-6-*tert*-butylphenol) is a preemergence herbicide used for the protection of cereals and cotton. The environmental regulations imposed by the Dutch government required an investigation of the fate of dinoterb in soil. In particular, knowledge about the extent of leaching from the soil by rain into the ground water was prerequisite for the admission of the compound. In view of the relatively low spraying concentrations in the field (5 kg/ha) a sensitive detection method had to be developed.

For the extraction of dinoterb the methods of Hurle (1968, DNOC in soil) and of McKellar (1971, dinoseb in milk) were modified. In both methods the dinitrophenol is ultimately obtained in a small amount of an organic solvent. McKellar analyzed the extract by gas–liquid chromatography (GLC) after treatment with an excess of diazomethane (giving the dinitrophenyl methyl ether); Hurle applied a colorimetric method. Both reached a detection limit of 10 μg/kg. When applying this GLC analysis we found the detector response to decline sharply at the lower dinoterb concentrations.

From GLC experiments with the synthetically prepared 2,4-dinitro-6-*tert*-butylphenyl methyl ether it appeared that even trace amounts of diazomethane are capable of causing this decline. Probably a reaction occurs between the dinitrophenyl methyl ether and excess diazomethane in the hot injection port of the gas chromatograph. Indeed, the decline was found to start at higher concentrations as the temperature of the injection port was raised. In this connection the reported substitution of 1,3,5-trinitrobenzene by diazomethane to yield cyclopropane derivatives should be mentioned (Van Velzen et al., 1971, 1972). The problem could be solved by destroying the excess diazomethane with a slight excess of acetic acid, giving a detection limit of 1 μg of dinoterb/kg of soil (corresponding to a final minimum detectable amount of 25 pg of dinoterb on the gas chromatograph).

EXPERIMENTAL SECTION

Soil was obtained from a wheat-growing area in the Haarlemmermeer-polder, south-west of Amsterdam. According to data obtained from the Institute for Biological and Chemical Research on Field Crops and Herbage at Wageningen, this soil contains: organic matter, 1.6%; sand, 71%; clay particles <16 μm, 20%; lime, 7.1%.

The gas chromatograph used was a Hewlett-Packard Model 5750 with electron capture detector, glass column 1.80 m × 4 mm i.d., packed with 4% SE 30 on Gas-Chrom Q (60–80 mesh); temperature of the injection port, 220 °C; of the column, 160 °C; carrier gas, argon with 5% methane at 60 ml/min.

Extraction of Dinoterb from Soil. Soil (50 g) was shaken with 75 ml of 96% ethanol. In a filter centrifuge the ethanol was filtered off and the soil was washed with another 250 ml of 96% ethanol. The ethanolic extract was evaporated to dryness in a rotary evaporator, using a water bath at <35 °C. The residue was shaken with a mixture of 70 ml of 0.1 *N* NaOH and 100 ml of hexane. The NaOH layer was separated and the hexane layer three times extracted with 25 ml of 0.1 *N* NaOH. The NaOH layers were combined, acidified with 10 ml of 4 *N* H_2SO_4, and extracted three times with 70 ml of hexane.

Analysis of the Extracts. The hexane extracts were dried over anhydrous sodium sulfate, concentrated to a volume of about 0.5 ml, and transferred to a 10-ml volumetric flask, using about 2 ml of benzene. A 7% diazomethane solution (0.5 ml) in hexane was added to each sample (*caution:* diazomethane is toxic and explosive under the influence of light or in contact with sharp edges). After standing for 30 min at room temperature, small amounts of acetic acid were added until no further change in color was seen and the mixtures were diluted with benzene to 10 ml. Aliquots (5 μl) were injected into the gas chromatograph and the difference between the resulting peak height and that of a blank was compared with the standard curve.

Standard Curve. Aqueous solutions of dinoterb were added to soil samples so as to reach concentrations covering the range 10–3000 μg/kg. These samples containing known concentrations of dinoterb were extracted and analyzed as described above. The resulting peak heights were plotted against the concentration after correction for a blank.

Recoveries were determined by comparison with corresponding solutions of dinoterb in benzene, methylated as described above. The average recovery was 72 ± 17% (19 samples).

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