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Note

Gas chromatographic determination of Metalaxyl (Ridomil®) residues in tobacco

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Metalaxyl (Ridomil®; Ciba-Geigy, Basle, Switzerland), (±)-methyl 2-[N-(2-methoxyacetyl)-2,6-xylidino]propionate, has been tested in comparison with dithiocarbamates as a fungicide against air- and soil-borne Oomycetes after foliar and soil application or seed treatment of different crops including tobacco in different climates[1–3]. It has also been used against blue mold *(Peronospora tabacina)* on tobacco in Germany[4] and Austria[5], and is applied in several countries, *e.g.*, in France in wine-growing areas.

Since up to now no method for the determination of residues of this fungicide in tobacco has been published, we have developed a method based on gas–liquid chromatography which can also be adapted to other plant materials.

METHOD AND RESULTS

Gas chromatographic conditions

The gas chromatograph used was a Hewlett-Packard Model 5710A equipped with an alkali flame ionization detector. The glass column (2 m × 2 mm I.D.) was packed with 5% OV-3 on Chromosorb W HP (80–100 mesh), and was operated at 240°C. The temperatures of the injection port and the detector were 250°C and 300°C, respectively. Helium was used as carrier gas at a flow-rate of 30 ml/min.

The retention time for Metalaxyl was 2.5 min under the conditions applied.

Extraction

Dried cut tobacco with a water content of 5% was powdered, 5.0 g transferred to a 50-ml centrifuge-tube and, after adding 25 ml methanol, homogenized for 1 min with an Ultra Turrax. After centrifugation, a 15-ml volume of the supernatant was transferred to a second 50-ml centrifuge-tube, and 13 ml distilled water, 2 ml $FeCl_3$–$CuSO_4$ solution (5% of each in water) and 0.5 g Celite® were added and shaken to precipitate interfering coextractives. After standing overnight the mixture was centrifuged, 25 ml of the supernatant transferred to a liquid–liquid extractor and extracted for 3 h with cyclohexane. The extract was evaporated to dryness on a rotary vacuum evaporator and the residue dissolved in 4 ml 20% sulphuric acid. The solution was transferred to a 25-ml centrifuge-tube, the evaporation flask rinsed with 5 ml saturated sodium sulphate solution and this washing combined with the acidic solution.

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The resulting solution was extracted on a Whirlimix for 1 min with 2 ml cyclohexane containing 2 μg/ml of the acaricide Dinobuton (mol.wt. 236.3) as an internal standard (Dinobuton is not stable in sulphuric acid). After centrifugation, 5 μl of the supernatant were injected into the gas chromatograph.

Fig. 1 shows a typical chromatogram of an extract of tobacco spiked with 0.5 mg/kg Metalaxyl, in comparison with the same unspiked tobacco.

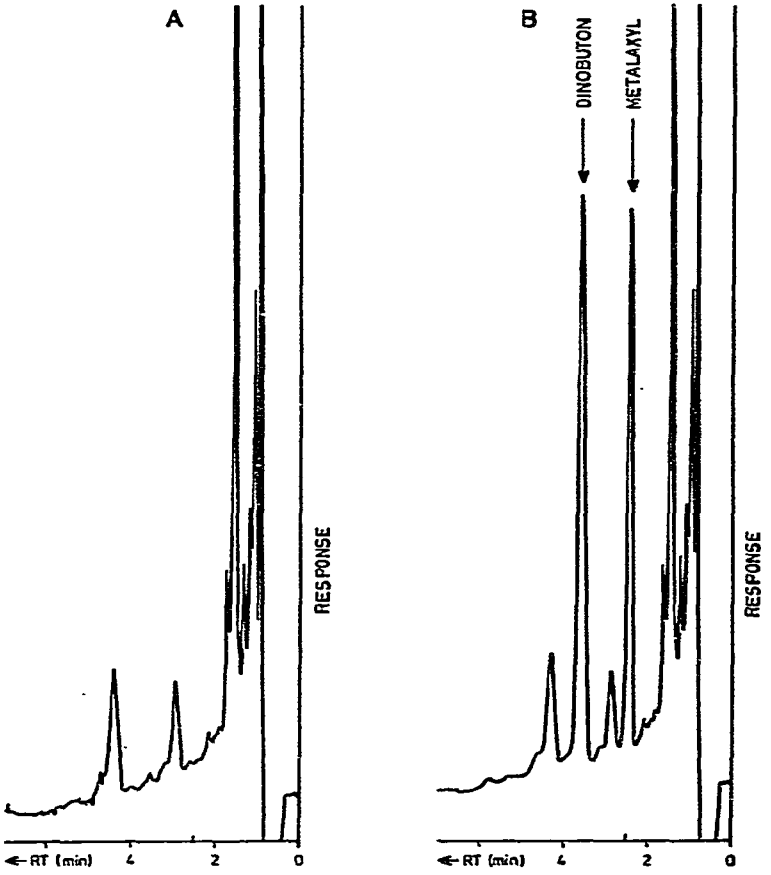

Fig. 1. Gas chromatograms of Burley (China) tobacco samples. A, Control (untreated) sample; B, sample spiked with 0.5 mg/kg Metalaxyl. RT = Retention time.

Calibration

Standard solutions of Metalaxyl in cyclohexane of concentrations between 0.3 and 5.0 μg/ml corresponding to *ca.* 0.2 and 4.0 mg/kg of Metalaxyl in tobacco were used to derive standard curves. The concentration of the internal standard Dinobuton in each standard solution was 2 μg/ml. The standard curve derived from the peak-height ratios was linear over the range 0.2–4.0 mg/kg.

Recovery and reproducibility

Untreated tobacco was spiked with Metalaxyl and assayed in duplicate samples giving the following results:

Metalaxyl added (mg/kg)	0.5	1.0	2.0
Metalaxyl found (mg/kg)	0.4	0.8	1.5
	0.4	0.8	1.5
Recovery (%)	80	80	75

Nine additional determinations were carried out with an untreated tobacco spiked with 0.5 mg/kg Metalaxyl. The mean of the results was 0.4 mg/kg and the relative standard deviation 7.4%.

Sensitivity

The method is sufficiently sensitive to determine Metalaxyl residues of less than 0.1 mg/kg in tobacco. Five untreated tobaccos, Flue cured (China), Burley (China), Burley (Malawi), Maryland (South Korea) and Orient (Turkey), were assayed. An interfering peak was only found with the Burley tobacco from Malawi, corresponding to *ca.* 0.03 mg/kg.

Residues of Metalaxyl in tobacco samples from field experiments

The described method was tested with various Metalaxyl-treated tobaccos and its applicability proved in the determination of residues of this fungicide. The results are shown in Table I.

TABLE I

RESIDUES OF METALAXYL IN TWO TYPES OF TOBACCO FIELD TREATED WITH RIDOMIL 25 WP

The tobacco samples were from the Tobacco Institute of Greece, Department of Plant Pathology, Drama, Greece. Samples 1 and 2 were harvested from different areas of one experimentally treated tobacco field.

Type	*Treatment and no. of applications*	*Rate (g/1000 m²)*	*Residue (mg/kg)*	
			Sample 1	*Sample 2*
Burley	Foliage spray			
(21 Cultivar)	6	690	5.7	6.3
	3	270	0.7	1.6
	Soil treatment			
	1	400	0.3	0.5
	1	600	0.4	0.2
	1	800	1.2	0.6
Cultivar BZ/7	Foliage spray			
(Basma)	3	170	1.6	1.6
	2	120	1.0	1.4
	Soil treatment			
	1	400	1.9	3.1
	1	600	4.5	4.0

ACKNOWLEDGEMENT

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