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GAS CHROMATOGRAPHIC DETERMINATION OF AZOXYSTROBIN AND TIFLOXYSTROBIN RESIDUES IN APPLES

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SUMMARY

Azoxystrobin and trifloxystrobin have been determined in apples by a gas chromatographic method with micro-electron capture detection (μ-ECD). Pesticides were isolated by matrix solid-phase dispersion. Recoveries from fortified samples ranged from 70 to 100%. Limits of determination were 0.02 mg kg^{-1} for azoxystrobin and 0.01 mg kg^{-1} for trifloxystrobin.

INTRODUCTION

Azoxystrobin and trifloxystrobin are strobilurin fungicides. They are synthetic analogues of naturally occurring fungal metabolites the strobilurins and oudemansins [1–4]. Pesticides that contain these substances are recommended for protection of garden and greenhouse vegetables against powdery and downy mildew and grey mould. They can be also used to protect cereals against fungal diseases such as powdery mildew, stem rust, leaf rust, and black stem rust, and to protect apple and pear orchards against scub and mildew [5,6]. The fungicides thus have a wide range of applications and are commonly used in agriculture; it is, therefore, necessary to determine levels of azoxystrobin and trifloxystrobin residues in plant material.

EXPERIMENTAL

The aim of this work was to include determination of azoxystrobin in the procedure used for analysis of trifloxystrobin in apples [7], using MSPD (matrix solid phase dispersion) [8]. For analysis of the fungicides homogenised apple pulp was mixed with silica gel 60 (0.063–0.2 μm;

Merck) and the mixture was introduced into a glass column. The analytes were then eluted with 9:1 dichloromethane–acetone, the eluate was evaporated to dryness, and the residue was dissolved in acetone. The acetone solution obtained was analysed by gas chromatography with an Agilent 6890 instrument equipped with a 30 m × 0.32 mm i.d. HP-1 capillary column and μ-ECD detector. The injector temperature was operated at 250°C and the detector temperature at 300°C. Nitrogen at the flow rate of 5.3 mL min^{-1} was used as carrier gas. The column was held at 140°C for 1 minute after injection, then programmed at 30° min^{-1} to 195°C and then at 40° min^{-1} to 260°C, which was held for 8 min. The retention times of trifloxystrobin and azoxystrobin were 4.4 and 9.1 min, respectively. The time required for chromatographic analysis was 15 min.

The operating ranges of the chromatographic analysis were determined. Fig. 1 shows the calibration plots for trifloxystrobin between 0.01 and 1 ng and for azoxystrobin between 0.02 and 1 ng. The correlation coefficients were 0.9995 and 0.9998, respectively.

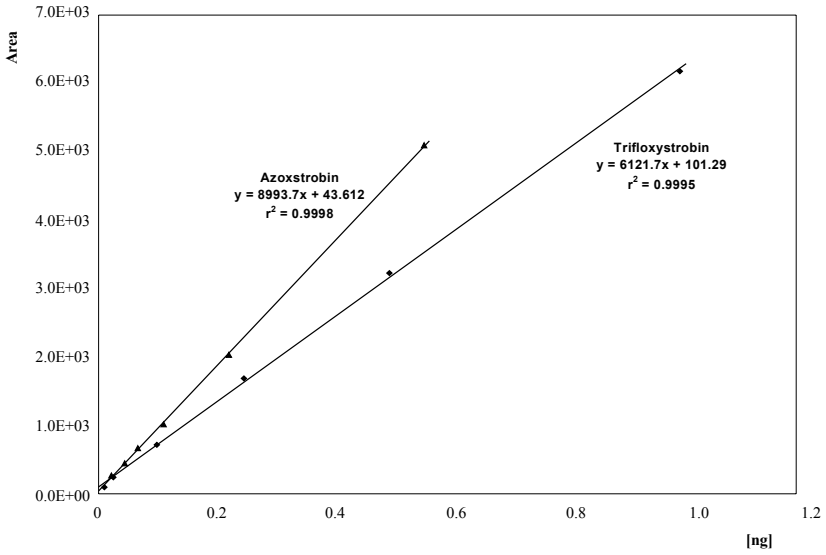

Fig. 1

Calibration plots for trifloxystrobin and azoxystrobin

RESULTS AND DISCUSSION

This method for separation of azoxystrobin and trifloxystrobin is easy to set up and reproduce and can be used for effective determination of the analytes in apples. Our experiment used gas chromatography with EC detection, but residue determination can also be confirmed by use of nitrogen–phosphorus detection [9]. Table I lists recoveries obtained from samples fortified with azoxystrobin and trifloxystrobin; values were between 70 and 110%; limits of determination were 0.01 mg kg^{-1} for trifloxystrobin and 0.02 mg kg^{-1} for azoxystrobin.

Table I

Recovery of trifloxystrobin and azoxystrobin from apples, and the statistical data obtained

	Fortification level, $n = 3$ (μg g^{-1})	Mean recovery (%)	Relative standard deviation, *RSD* (%)
Trifloxystrobin	0.01	76.0	7.44
	0.02	90.0	7.86
	0.05	72.0	4.94
	0.10	76.3	5.91
	0.20	106.1	2.87
Azoxystrobin	0.02	87.7	2.34
	0.04	87.2	9.82
	0.06	82.6	6.78
	0.08	101.7	2.43
	0.10	79.3	4.32

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