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Multi-matrix–multi-pesticide method for agricultural products

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ABSTRACT

In an initial experiment 21 pesticides were used as test compounds to develop a method of analysis in different types of matrices for pesticides which can be analysed by gas chromatography. An attempt was made to combine a generally applicable clean-up method with a universal detection system, *i.e.* the ion trap detector. Experiments showed that potentially it should be possible to develop a quantitative method for at least 17 compounds in different matrices.

INTRODUCTION

In the Netherlands 400 pesticides are allowed for certain applications. Thirteen multi-methods exist [1] for the determination of about 220 pesticides in various foodstuffs. The presence of other pesticides may be determined by special methods, generally applicable to only one pesticide. It is impossible for controlling authorities to have all these methods available and ready for immediate analysis. Recently, due to environmental concern, the Dutch government has mandated that the quantity of pesticides used should be drecreased by at least 50% in the coming years.

There is an urgent need for a universally applicable method with a high throughput of samples. In the literature several methods based on gas chromatographic analysis are available [2,3] but the different extracts obtained need to be analysed with several specific detectors, *e.g.*, the electron-capture and nitrogen–phosphorus detector. In recent years the use of small mass spectrometers has increased rapidly.

Here we report initial results obtained with an ion trap detector for a group of pesticides generally not included in multimethods. As clean-up, gel permeation chro-

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matography (GPC) was used. The approach and applicability of a procedure using a slightly modified Luke extraction procedure and also using an ion trap detector has been tested recently with good results by Mattern *et al.* [41].

EXPERIMENTAL

Matrices

Tomato, cucumber, cauliflower, endive, chicory, capsicum, apple, wheat, potatoes and lettuce were analysed alone and with pesticide spikes.

Pesticides

Alachlor, biphenox, bromacil, crufomate, diallate, dinobuton, fenarimol, fluazifop-butyl, imazalil, lenacil, metamitron, metribuzin, nitrofen, nitrothal-isopropyl, pendimethalin, pirimicarb were analysed individually and benodanil, chlorpropham, triadimefon, triallate and trifluralin were analysed using existing multi-methods.

Gel permeation chromatography

A Bio-Beads SX3 column (45 × 1 cm), eluted with acetone–cyclohexane (1:1) at a flow-rate of 1 ml/min was used. Injection volume, 1 ml; pump, Waters M45; fraction collector, Gilson 202; fraction volume, 13.5 ml; fractionating starting 16.5 min after injection; total time of analysis, 30 min [5].

Gas chromatography–mass spectrometry (GC–MS)

A Varian 3400 gas chromatograph in combination with a Finnigan MAT ITS 40 ion trap detector was used. The gas chromatograph was equipped with a septum programmable injector and with a 30 m × 0.25 mm I.D. J&W DB-5 capillary column, film thickness 0.25 μm. Helium flow-rate 1.5 ml/min; injection volume, 1 μl. Injection temperature, 60°C for 1 min, then at a rate of 300°C/min heated to 325°C. Column temperature started isothermally at 92°C. After 1 min the column was heated up to 325°C at a rate of 20°C/min. The ITS was operated in the electron-impact mode. Each second a spectrum from mass 49 to 449 was recorded.

Extraction and clean-up

After homogenisation of the sample, 100 g were macerated with 200 ml of acetone for 3 min, filtered over glasswool and after addition of 60 ml of saturated sodium chloride solution extracted with 150 ml of hexane for 1 min. After separation the organic phase was washed twice with water, dried over sodium sulphate, concentrated to 5.0 ml, and diluted to 10.0 ml with acetone–cyclohexane (1:1). For clean-up 1.0 ml was injected into the GPC system. The appropriate fraction was collected, the internal standard PCB 153 (2,4,5,2′,4′,5′-hexachlorobiphenyl) added and the fraction concentrated to 500 μl; 1 μl of this solution was injected into the GC–MS system.

RESULTS AND DISCUSSION

In the literature, much information is available on GC behaviour of pesticides and their mass spectra. The use of GC–MS in combination with a widely applicable

TABLE I

IDENTIFICATION NUMBER OF PESTICIDES USED IN EXPERIMENTS

Number	Compound	Number	Compound
1	Chlorpropham	12	Imazalil
2	Trifluralin	13	Benodanil
3	Triallate	14	Biphenox
4	Nitrothal-isopropyl	15	Diallate
5	Crufomate	16	Metribuzin
6	Fluazifopbutyl	17	Bromacil
7	Nitrofen	18	Triadimefon
8	Fenarimol	19	Dinobuton
9	Pirimicarb	20	Metamitron
10	Alachlor	21	Lenacil
11	Pendimethalin		

extraction and clean-up technique for pesticides in all kind of matrices is rare. Though these techniques do exist [2,3] they are used mostly in combination with several other detection and/or separation techniques. We chose 21 pesticides to test a single method. Until now only five of these 21 pesticides have been incorporated in a multi-method, the other 16 are determined in individual methods [1].

The behaviour of these compounds, *e.g.* extraction with acetone from vegetable

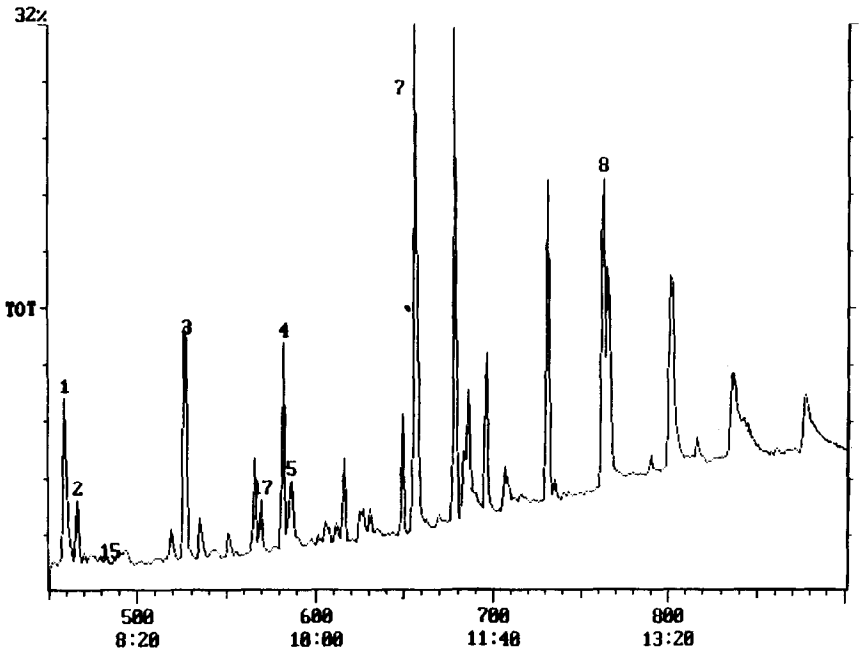

Fig. 1. Reconstructed ion chromatogram of a tomato extract spiked with a selected number of pesticides (full-scan mode). For identification see Table I. *x*-Axis: scan No. and time in min:s.

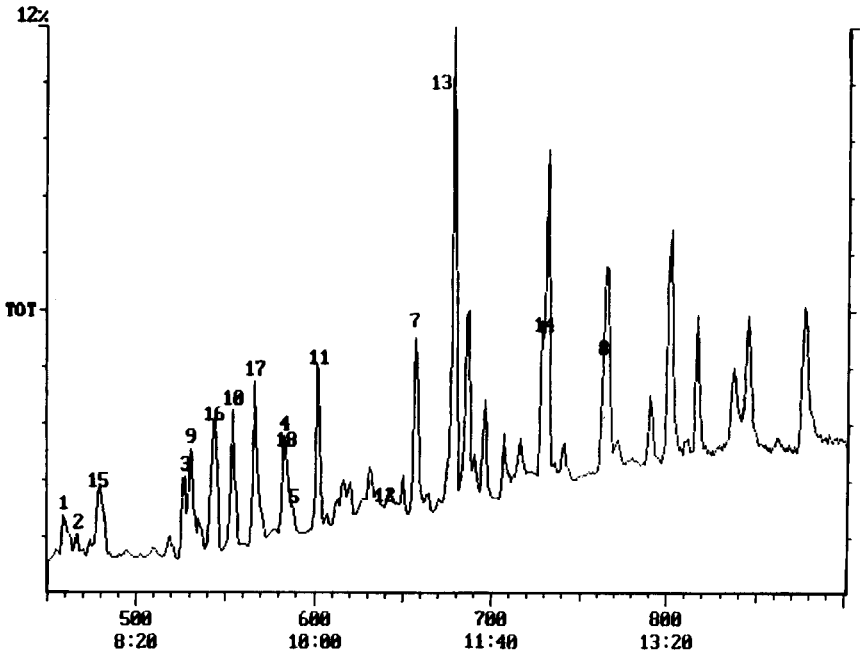

Fig. 2. Reconstructed ion chromatogram of a combined cucumber, capsicum and chicory extract spiked with pesticides (full-scan mode). For identification see Table I. *x*-Axis: scan No. and time in min:s.

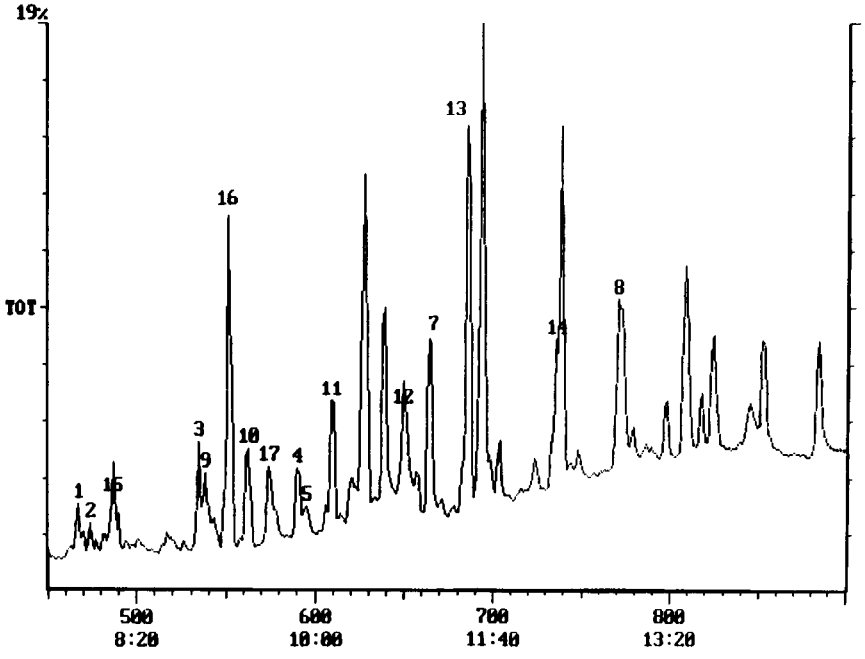

Fig. 3. Reconstructed ion chromatogram of a combined endive, cucumber and cauliflower extract spiked with pesticides (full-scan mode). For identification see Table I. *x*-Axis: scan No. and time in min:s.

matrices and clean-up by GPC is described by Specht and Tillkes [3]. They describe the behaviour of about 400 pesticides and industrial organic contaminants, as well as their recoveries. Recently Steinwandter [6] described a less time-consuming acetone extraction in combination with GPC using acetone. Good recovery data were obtained.

Since compatibility of extraction solvent with eluent is advantageous, acetone was used in our experiment as extraction solvent and acetone–cyclohexane as eluent for GPC. Initially the method was checked only with standards. Recoveries better than 75% were obtained. The above-mentioned matrices were spiked at 0.25 mg/kg pesticide and analysed both on a Hewlett-Packard mass-selective detector (HP MSD) [7] and a Finnigan MAT ITS 40.

This paper reports data obtained with the ITS 40 mass spectrometer. The sensitivity of the ion trap detector allows full-scan mass spectra to be obtained without having to resort to monitoring a few selected ions. Thus it should be possible to identify each compound on the basis of their total spectrum rather than on basis of a few selected ions. The identification procedure followed implied that in a certain retention window the chromatogram was searched for a spectrum similar to that of the compound of interest. In each case where the similarity was above a certain threshold the compound was regarded as being identified, after which quantification followed.

In Table I the identification numbers of the tested pesticides are given and in Fig. 1 the result for a tomato extract is shown. This matrix was spiked with a pesticide mixture containing eight pesticides. The data system numbers the chromatographic peaks automatically when they are identified following the above-mentioned procedure.

All the compounds except fluazifopbutyl (compound 6) could be detected. Furthermore, diallate (compound 15), present as a contaminant in the standard of triallate, was also detected, as was bromacil (compound 17). Interference of a phthalate was observed at retention time 12 min 10 s. In order to test the method for all 21 pesticides simultaneously, we combined several matrices spiked with different groups of pesticides. These combined extracts contained all pesticides mentioned in Table I. Figs. 2 and 3 are examples of the chromatograms obtained.

In addition to fluazifopbutyl (compound 6), dinobuton, metamitron and lenacil (compounds 19, 20 and 21) were also not recovered. In general, the recovery of all compounds in the matrices was lower than obtained with standards (0–80% and $<75\%$ respectively). We suspect that during the evaporation step losses occurred whereas with standards, with no evaporation step, no exceptional losses occurred. Nevertheless, of the 21 pesticides used, 17 pesticides were detectable. Of these 17 pesticides, in the past 12 had to be analysed with individual methods [1]. Therefore, according to our findings, it should be possible to develop multi-methods for the determination of pesticides in many different matrices.

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REFERENCES

1 P. A. Greve, *Analytical Methods for Residues of Pesticides*, SDU Publishers, The Hague, 5th ed., 1988.
2 M. A. Luke, J. E. Froberg, G. M. Doose and H. Masumoto, *J. Assoc. Off. Agric. Chem.*, 64 (1981) 1187–1195.
3 W. Specht and M. Tillkes, *Fresenius Z. Anal. Chem.*, 322 (1985) 433–445.
4 G. C. Mattern, G. M. Singer, J. Louis, M. Robson and J. D. Rosen, *J. Agric. Food Chem.*, 38 (1990) 402–407.
5 A. H. Roos, A. J. van Munsteren, F. M. Nab and L. G. M. Th. Tuinstra, *Anal. Chim. Acta*, 196 (1987) 95–102.
6 H. Steinwandter, *Fresenius Z. Anal. Chem.*, 331 (1988) 449–502.
7 L. G. M. Th. Tuinstra, A. H. Roos, A. M. Matser, W. A. Traag and J. A. van Rhijn, *Fresenius Z. Anal. Chem.*, 339 (1991) 384–386.