

A New Multiresidue Method for Pesticides in Fruit and Vegetables Using LC-MS/MS detection. Part 1.

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Introduction

In the Swedish monitoring of pesticides, liquid chromatography coupled with UV or fluorescence detectors has been used for many years, especially for analysis of polar pesticides. These LC systems are normally easy to use, but sensitivity and selectivity are often low, and there is also a need of additional confirmation. LC-MS can be used for the analysis of most compounds, which are now analysed by LC-UV, and it also complements GC. Many pesticides, which are thermally unstable or non-volatile, and therefore difficult or impossible to analyse by GC, can be analysed directly. In addition, using LC-MS it is possible to quantify and confirm the identity of the pesticides in one single analysis with high sensitivity.

A new multiresidue method for the analysis of pesticide residues has been developed at the National Food Administration.

The method includes benzimidazoles, carbamates and N-methyl-carbamates, which traditionally have been analysed using LC-UV or LC-fluorescence. Another group of pesticides included in the method consists of organophosphorus compounds with an oxidisable sulphide group. Many of them tend to decompose under GC conditions and are therefore not GC amenable. Since the metabolites are included in the MRLs, there is a need of a method that can detect both the parent pesticides and the metabolites simultaneously.

The method has been validated for totally 57 different pesticides and metabolites. All pesticides are extracted using the NFA ethyl acetate method, the same extraction as in the GC-method, for some basic pesticides after addition of sodium hydroxide. In order to illuminate the possible contribution from matrix on recoveries, representative species from 11 different commodity groups, according to the EU commission, were chosen as matrices. The fortification levels studied were 0.01 and 0.05 mg/kg.

Experimental

Sample pre-treatment

Extraction of the pesticides is performed using ethyl acetate in the presence of sodium sulphate, and for the basic pesticides also sodium hydroxide is added for matrices with pH value below 4.5. After concentration and filtration, an aliquot of the extract is evaporated to dryness and dissolved in pure methanol. The extract is filtered prior to analysis by LC-MS/MS, and the final sample concentration is 2.5 g/ml. No further purification is performed.

The extraction method used, up to the change of solvent, is the same as in the Swedish GC multiresidue method for pesticides in fruit and vegetables.

LC-MS/MS analysis

Column: Genesis C₁₈, 100 x 3 mm, 4 µm

Mobile phase A: Methanol

Mobile phase B: 10 mM ammonium formate pH 4.1 in water/methanol (80/20)

Gradient:

time, min	%A	%B
0	0	100
15	90	10
20	90	10
23	0	100

Flow rate: 0.3 ml/min

Injection volume: 5 µl

Detection: Micromass Quattro LC with an electrospray interface in positive and negative ion mode (ES+/ES-), MS/MS

Matrix effect

Matrix effect, expressed as the signal from the pesticide in matrix compared to the signal in solvent, was tested in all matrices. To an aliquot of blank extract in methanol a pesticide mixture (3-10 % of the extract volume) was added, to a final concentration of 0.05 mg/kg of each. The LC-MS/MS signal of the standard additions was compared to the signal of standard in methanol.

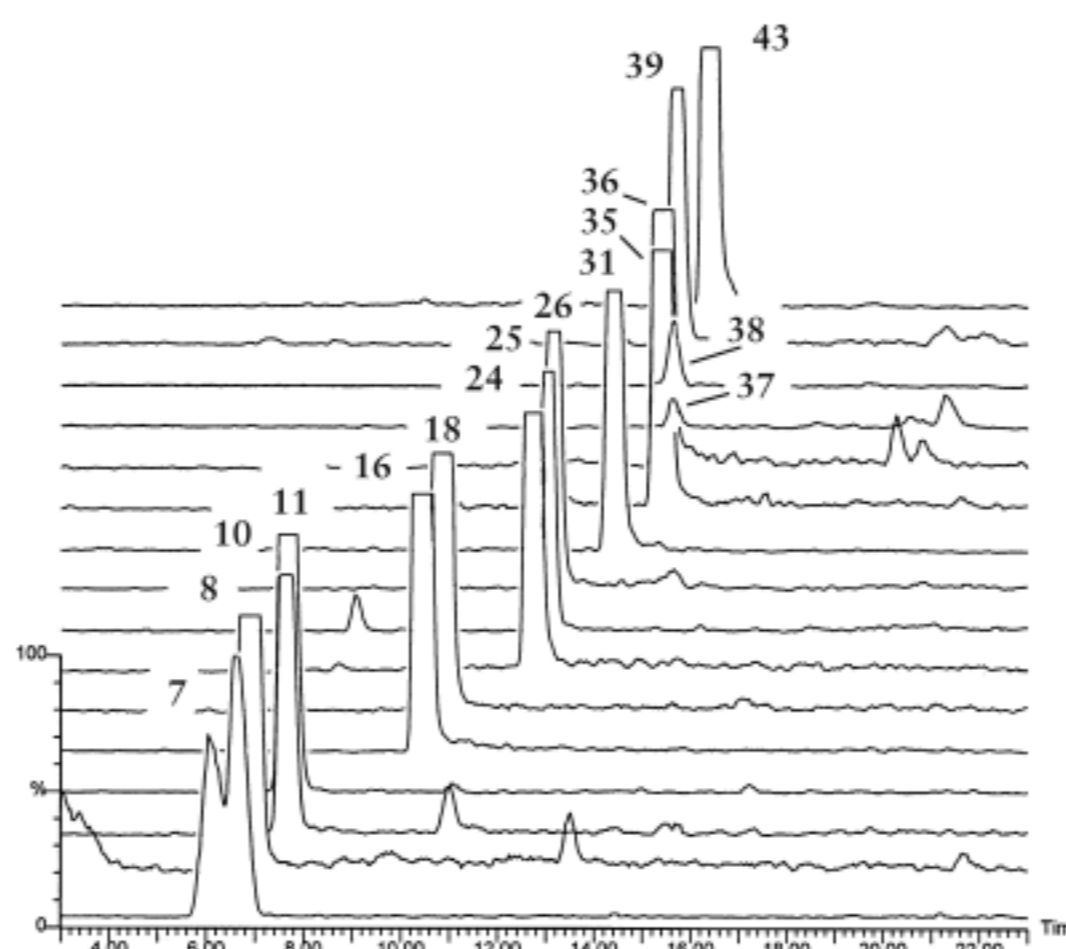
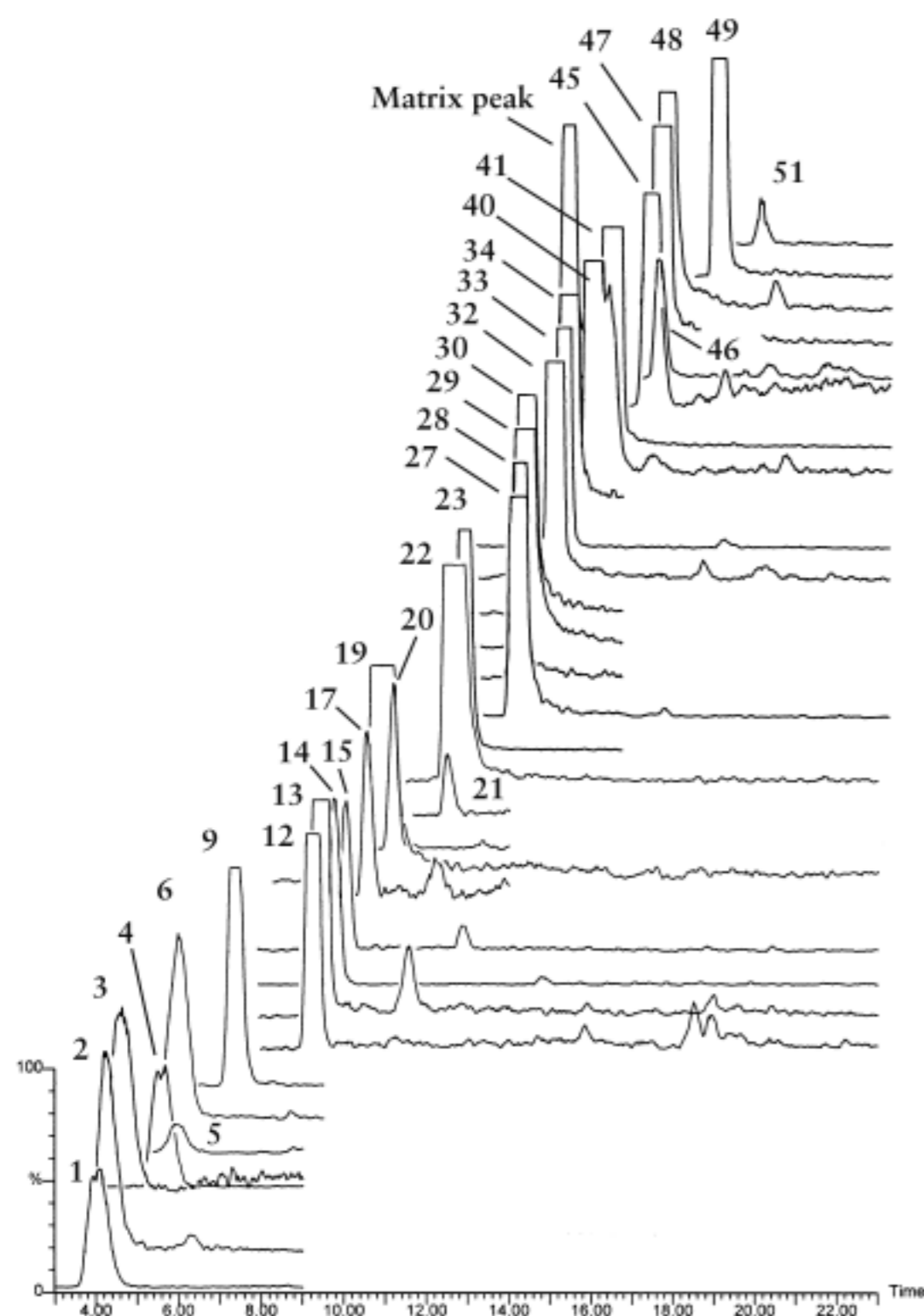


Figure 1 and 2. Chromatogram of orange spiked with studied pesticides at 0.01 mg/kg. One MS/MS-fragment for each pesticide. See table 1 for identification of peaks.

