A New Method for the Quantitation of a Large Number of Pesticides Residues in Food by Gas Chromatography Mass Spectrometry

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Introduction

There is a requirement within the European Union (EU) and elsewhere to measure the levels of certain pesticide residues in food. The United Kingdom government has issued a series of statutory instruments that specify maximum pesticide residue levels in crops, food and animal feeding stuffs. This legislation incorporates FAO/WHO CODEX Alimentarius commission methods of analysis and sampling. In practice some 92 pesticide residues are routinely measured down to MRL's of 0.01 mg/kg. This normally is carried out by a number of GC runs with specific detectors. We have been able to condense the analysis time by developing a single GC-MS method that determines all the target compounds and allows semiquantitative analysis of other residues that may be present.

Method

The analysis was performed on extracts taken from homogenised foodstuffs. The extraction method was based on the FDA Pesticide Analytical Manual section 302 and consists of taking a 100g representative sample which was spiked with an internal standard mixture at a level of 0.1 mg/kg and then extracted at room temperature with 100ml of acetone. This mixture was then filtered and the acetone/water phase back extracted with 200ml of 50:50 DCM/petroleum ether. The liquid/liquid extraction was then repeated a further two times with DCM, the resulting combined extracts were then reduced in volume to 1ml. A 1ul aliquot was injected onto a 30m 0.25u DB5-ms. The GC is connected to a VG 70S mass spectrometer fitted with an electron ionisation source. Full mass spectra were collected and recorded over a mass range of 65-450 Daltons.

Results

The results show that a wide range of pesticide residues can be analysed in a single GC-MS run, avoiding the need to carry out multiple injection on instruments with selective detectors. Table 1 shows the list of targeted pesticides and internal standards used for the analysis. In figure 1 we can see the complexity of the standard mixture. Figure 2 gives a good illustration of the power of this technique on a grape extract. Note the peak at a retention time of 26.5 min, identified as iprodione, which is present well below the MRL of 5 mg/kg and quantified at 0.02 mg/kg. Note that there is no significant peak in the total ion chromatogram but the mass chromatogram used to target this analyte is clear. The spectrum for this target is shown in Figure 3 and indicates the dynamic range of the system given the excellent spectral quality of this component at this level. A second sample of grapes shows a component Figure 4 that is not in the target database but is a pesticide, carbaril, this component's spectrum and its library match are shown in Figure 5.

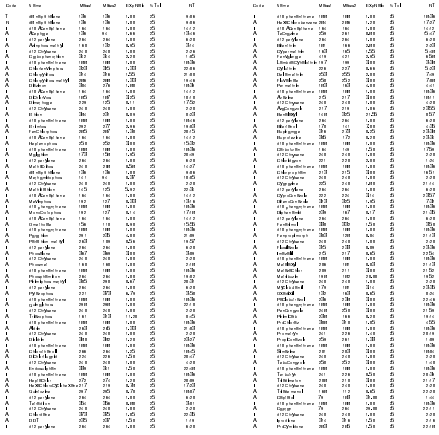

Table 1 List of target compounds and internal standards

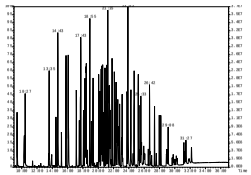

Figure 1 TIC Chromatogram of a Standard mixture

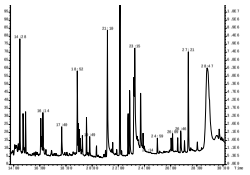

Figure 2 Chromatogram of a grape sample showing low level components.

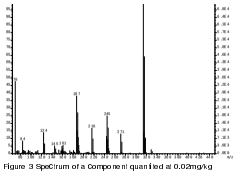

Figure 3 Spectrum of a Component quantified at 0.02mg/kg

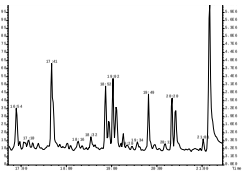

Figure 4 Chromatogram of expanded section showing low level components

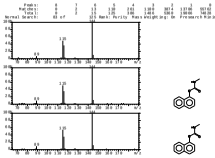

Figure 5 Library fit of the non-targeted compound

Conclusion

This method of screening for target pesticides has been shown to both rapid and sensitive when compared to other published methods using a range of selective detectors. The use of a magnetic sector mass spectrometer for this application over a lower cost quadrupole or ion trap was necessary to achieve the detection limits required within a single experiment. The ability to detect low concentrations whilst capturing full spectra is essential if targets not in the list are to be reported. The authors feel that this application would be well suited to time of flight instrumentation that would be capable of obtaining full mass spectra whilst not compromising sensitivity. There is great interest in reducing GC run times using new minibore GC columns, an advance that cannot be utilised using the existing sector mass spectrometer, but is well suited to the new fast 'scanning' GC-TOF instruments. The dynamic range of such a system must however be at least equivalent to the current instrumentation.

References

1. CODEX Alimentarius Volume 2A Part1
2. Statuary Instrument 1999 N0 3483 Pesticide Residue Levels in Crops, food and feeding stuffs