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THE ADVANTAGES OF EXACT MASS IN TRACE ANALYSIS

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OVERVIEW

- A rapid multi-residue GC/MS method was developed for pesticides in foodstuffs.
- Plum extract was used as an example matrix.
- Analysis time was reduced from 24 minutes to 8 minutes.
- 24 pesticides were analysed with reporting levels from 10 ppb to 200 ppb.
- A GCT oaToF mass spectrometer was used.
- The benefits of exact-mass and elevated resolution are shown.

INTRODUCTION

The GCT orthogonal-acceleration Time of Flight (oaToF) mass spectrometer (**Figure 1**) provides three important advantages over the single-quadrupole type of instrument that is commonly used for GC/MS trace analyses.

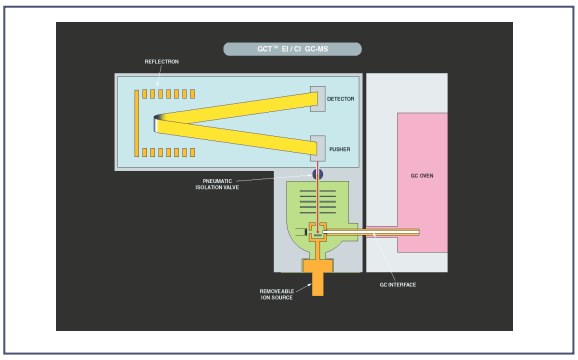

Figure 1. A schematic diagram of the GCT mass spectrometer

The first of these is that a full mass spectrum may be obtained at a sensitivity equivalent to that obtained when performing multiple SIM experiments on a quadrupole instrument. **Figure 2** shows a chromatogram obtained from 1 pg of hexachlorobenzene. A signal to noise ratio of 50:1 is obtained and such sensitivity makes the GCT an ideal instrument for analyses with a large number of target analytes, where many SIM channels would normally be required. Since complete mass spectra are obtained, all quantitative and confirmatory ions are recorded simultaneously. The complete EI spectrum for hexachlorobenzene, for example, is shown inset in **figure 2**. Whole spectra are recorded for all eluting components and library searching may be used to identify any unrecognised peaks. Such peaks would not even be observed using a SIM experiment on a quadrupole instrument.

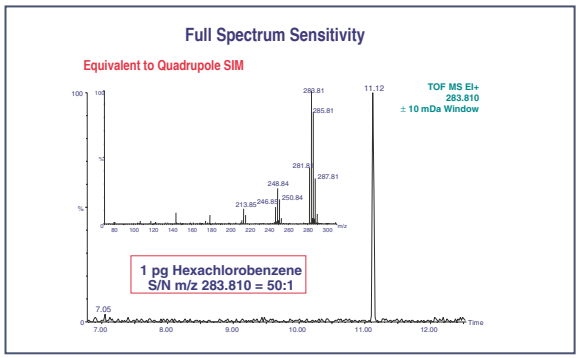

Figure 2. The mass chromatogram and spectrum of hexachlorobenzene acquired on the GCT mass spectrometer

In addition to excellent sensitivity the GCT delivers a spectral resolution of over 7,500 Full Width Half Maximum (FWHM) and mass peaks are measured to an accuracy of, on average, better than 5 ppm. The ppm error is defined as follows: -

Dppm = (observed mass - theoretical mass) / theoretical mass x 106

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For example, if the theoretical mass of an ion is m/z 400.000 and the observed mass is 400.002 then the ppm error would be: -

ppm error = (400.002 - 400.000) / 400.000 = 5 ppm

Figure 3 shows a spectrum of chlorpyrifos obtained on the GCT together with a table showing the elemental compositions and the ppm errors of the five main peaks in the spectrum. The RMS average error is only 3.5 ppm.

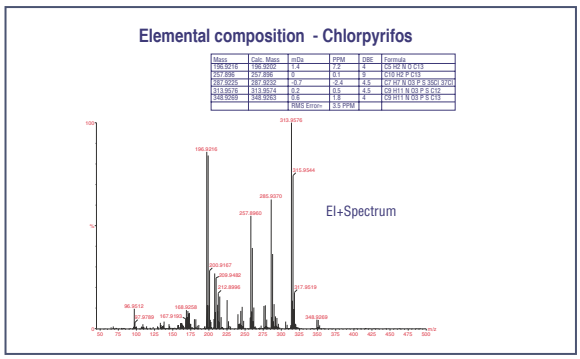

Figure 3. The exact-mass EI spectrum of chlorpyrifos with elemental compositions of ions and ppm deviations from theoretical masses

Because the GCT delivers such high resolution and mass accuracy chromatograms may be plotted using a narrow mass range, excluding a large proportion of the chemical background and significantly improving signal to noise ratios. **Figure 4** shows two chromatograms, both generated by the summation of ions at m/z 246.032 and m/z 108.992, corresponding to 2 pg of the pesticide fonofos. The upper chromatogram was generated using a 1 Da extraction window and shows three peaks, none of which has the correct retention time for fonofos. The lower chromatogram was generated using a 20 mDa window, the chemical background has been excluded and the pesticide may be seen clearly at the correct retention time.

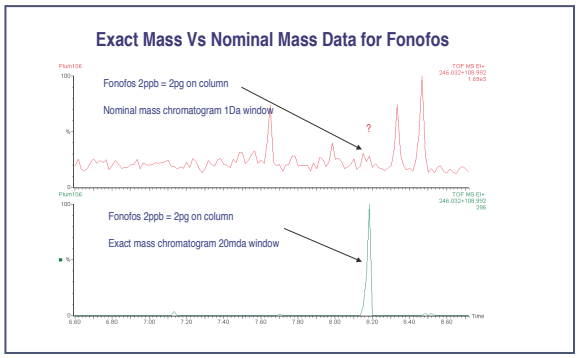

Figure 4. A comparision between 1Da and 20mDa wide chromatograms

It should be noted that the peak for fonofos is less than 4 seconds wide at the base and contains about 3 data points. The third advantage of the GCT has to do with the way in which spectra are collected by the ToF mass analyser. A quadrupole instrument acquires data, at various m/z values, sequentially. During the elution of a chromatographic peak the intensity of signal first increases rapidly and then decreases rapidly. **Figure 5** shows how this may cause variation in the observed relative abundances of ions in the spectrum. In the GCT the mass spectra are generated at a sampling rate in excess of 20,000 per second and, since all ions are sampled simultaneously, there is never any skew to the spectra. This means that, for accurate quantification, fewer points are required across the chromatographic peak.

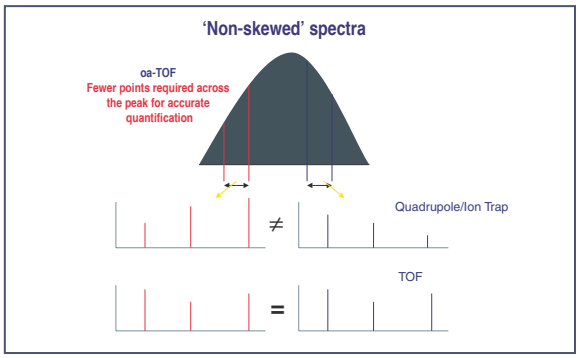

Figure 5. Showing how ToF mass spectrometers record non-skewed spectra at all times

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An existing method, for the analysis of 24 pesticide residues in fruit and vegetables, used a 24 minute GC program and an ion trap mass spectrometer as detector. The aim of this study was the development of a GC/oaToF-MS analytical method with equivalent or improved limits of determination, linearity and repeatability but with a much shorter analysis time.

EXPERIMENTAL

Existing Method

- 50 g of sample is extracted using ethyl-acetate, final volume is 250mL
- GPC cleanup, final extract equivalent to 1 g/mL
- 1 µL injection onto 30m x 0.25mm x 0.25µm column
- Detection via ion trap MS
- Analysis time of 24 min.

GCT Method 1

- Column 20m x 0.18mm x 0.18µm.
- 1µl splitless injection @ 250°C with 1ml/min He.
- Temperature Programme 70/2-200@25-250@10.
- GCT 1 spectrum/second acquiring m/z 45-650.
- EI + source @ 180°C.
- Injected matrix standards ranged 1ppb - 600ppb 1ppb=1pg
- Run time 18 min

GCT Method 2

- Column 10m x 0.1mm x 0.1µm.
- 0.2µl splitless injection @ 250°C with 1ml/min He.
- Temperature Programme 70/2-200@58-250@23.
- GCT 2 spectra/second acquiring m/z 45-650.
- EI + source @ 180°C.
- Injected matrix standards ranged 1ppb - 600ppb 1ppb=200fg
- Run time 8 min

RESULTS

GCT Method 1

The first and last eluting peaks of GCT Method 1 are shown in **figure 6**. The last peak elutes inside 18 minutes, corresponding to a saving of 6 minutes over the original analytical time of 24 minutes. Matrix-matched standards, at 10ppb, were analysed and the limit of determination (LOD) was extrapolated from the results.
Figure 7 contains a graph showing the limits of determination for the method, compared to the 10ppb level. **Figure 8** shows the difference in LODs when 1Da mass windows and 20mDa mass windows are used to generate the quantitative chromatograms. In almost every case there is a significant improvement in LOD associated with the 20mDa chromatograms.

Figure 9 shows a calibration graph for fonofos. In spite of the small number of data points across the chromatographic peak there is good linearity between the 2ppb and 120ppb levels.

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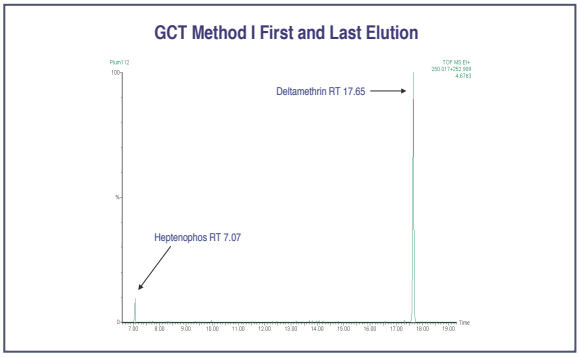

Figure 6. Showing the time window for the elution of peaks in method 1

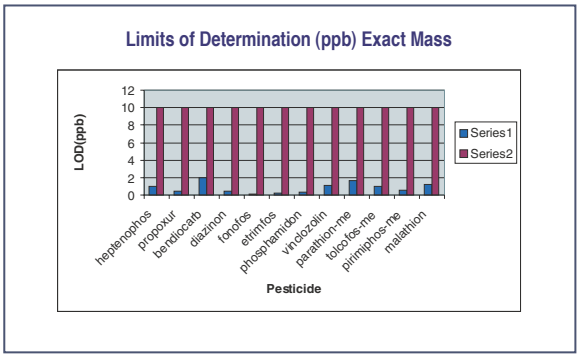

Figure 7a.

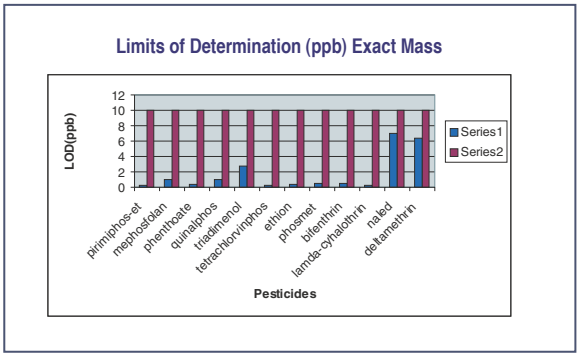

Figure 7b. The LODs achieved by method 1, extrapolated from data at the 10 ppb level

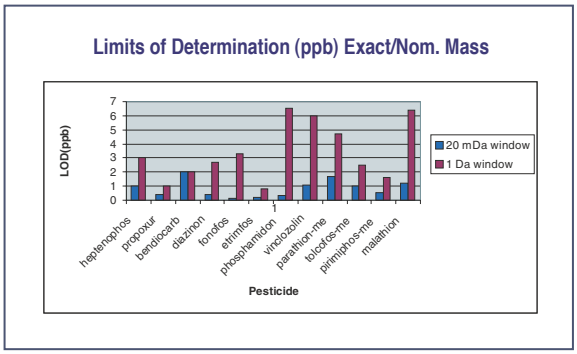

Figure 8a.

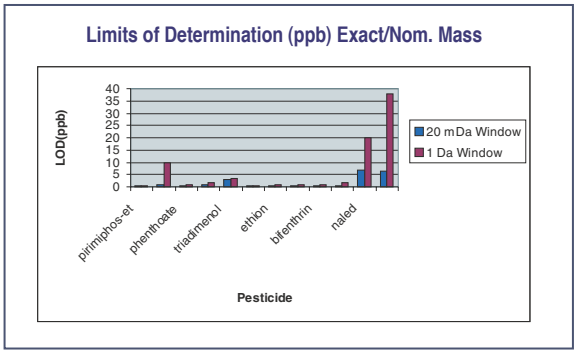

Figure 8b. Differences in LOD between 1 Da and 20 mDa window chromatograms

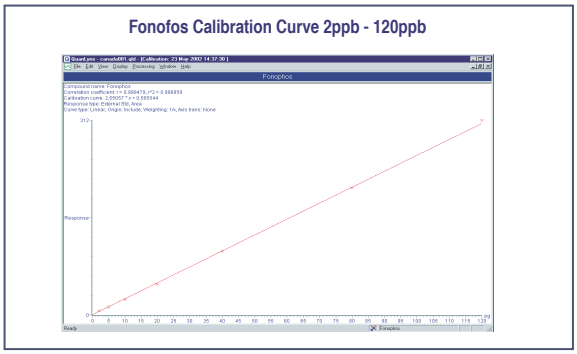

Figure 9. The calibration graph for fonofos

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GCT Method 2

Figure 10 shows the differences in LOD between methods 1 and 2. Method 1 has, on average, lower LOD values than method 2. However, method 2 has LOD levels sufficient for the purposes of the analysis whilst being only 8 minutes long, a time saving of 16 minutes per sample. In other words the analysis time has been reduced to 33% of the original value.

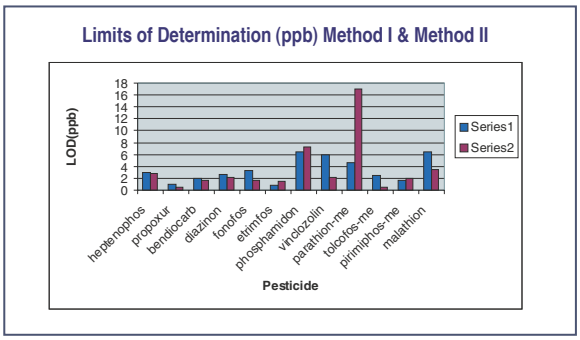

Figure 10a.

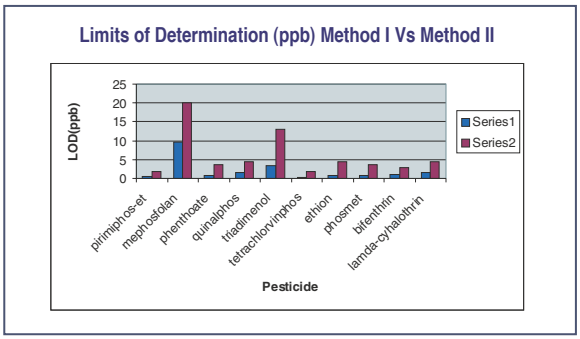

Figure 10b. Comparision of LODs between methods 1 and 2

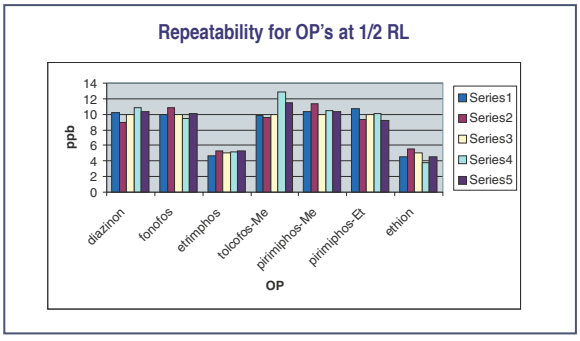

Figure 11. Repeatibility measurements

The repeatability of the method at half the reporting level is shown in **figure 11**.

CONCLUSION

- Satisfactory methods were produced using 0.18 and 0.1mm id columns. It was easily possible to achieve the required reporting levels.
- The run time was reduced to 33% of the original 0.25mm id method.
- Exact mass provided superior LODs to nominal mass data. Exact mass also gives greater specificity with respect to the confirmatory process.
- Repeatability measurements prove quantitative data may be obtained with only a small number of points over the chromatographic peak.

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