Fast Screening And Quantification Of Pesticide Residues In Baby Food Using GC Orbitrap MS Technology

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Overview

Purpose: To evaluate the utility of Orbitrap based GC-MS technology for fast pesticides screening and quantification.

Methods: Baby food samples were extracted following QuEChERS protocol. The final extracts were spiked with a mixture of 132 pesticides at concentrations corresponding to 0.5—200 ng/g (ppb). In all experiments a Thermo Scientific™ Q Exactive™ GC hybrid quadrupole-orbitrap mass spectrometer was used. Data was acquired and processed using the Thermo Scientific™ TraceFinder™ software.

Results: The results of this study show that the Q Exactive GC is an ideal analytical tool for the analysis of pesticide residue testing in complex matrices, offering high performance full scan analysis at fast GC separation. Routine mass resolution of 60,000 FWHM and consistent sub-ppm mass accuracy ensures selective and confident compound detection and identification. The Q Exactive GC provides highly comparable quantitative performance with respect to existing state of the art GC triple quadrupole MS instruments.

Introduction

Pesticides are measured almost exclusively by liquid chromatography (LC) and gas chromatography (GC) analytical methodologies. GC offers good separation efficiency and a choice of MS detectors such as single or triple quadrupoles. However, targeting specific compounds during acquisition limits the scope of analysis. This limitation has led to increased interest in the development of methods using MS analysers that can operate in full scan with a high mass resolving power, but provide similar levels of selectivity and quantitative performance. In this work we demonstrate the use of GC-Orbitrap technology in the context of the SANCO guidelines [1-3] for fast, high throughput pesticide residues analysis in baby food samples with an almost unlimited scope in the analysis through full scan acquisition. Quantitative performance comparable to triple quadrupoles will also be presented.

Methods

Sample Preparation

Baby food samples were extracted using the citrate buffered QuEChERS protocol. The homogenized sample (10 g) was mixed with acetonitrile (10 mL) followed by the addition of MgSO4 (4 g), NaCl (1.0 g), disodium hydrogen citrate sesquihydrate (0.5 g) and trisodium citrate dehydrate (1.0 g). Dispersive solid phase extraction [MgSO4 (150 mg), C18 (50 mg), PSA (50 mg) and carbon (7.5 mg) per mL of extract] was used for sample clean-up. The final extracts were spiked with a mixture of 132 pesticides.

Gas Chromatography

1 µL was injected into a PTV injector (cold splitless) and compound separation was achieved using a Trace 1310 gas chromatograph and a TraceGOLD TG-5SILMS 30 m length × 0.25 mm inner diameter × 0.25 µm film thickness column (Table 1).

Mass Spectrometry

High resolution EI spectra were acquired using 60,000 FWHM resolution (measured at *m/z* 200) with a mass range of 50-750 *m/z*. An internal lock mass was used throughout the acquisition (Table 2).

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TABLE 1. GC parameters

TRACE 1310 GC	
Injection volume (µL)	1.0
Liner	asymmetric
Inlet (ºC)	75
Inlet module & mode	PTV, splitless
Transfer delay (min):	1
Injection time (min):	0.1
Transfer rate (ºC/sec):	2.5
Transfer (ºC):	300
Transfer time (min)	3
Cleaning rate (ºC/sec):	330
Carrier Gas, (mL/min):	He, 1.2
Oven Program:	
Temperature 1 (°C):	40
Hold Time (min):	1.5
Temperature 2 (°C):	180
Rate (°C/min)	25
Temperature 3 (°C):	300
Rate (°C/min)	100
Hold Time (min):	3

TABLE 2. Mass Spectrometer parameters

Q Exactive MS	
Transfer line (ºC)	280
Ionization type:	EI
Ion source(ºC):	230
Electron energy (eV):	70
Acquisition Mode:	Full scan
Mass range (Da):	50-500
Mass resolution (FWHM):	60,000
Lockmass (m/z):	207.03235

Data Analysis

Data was acquired and processed using the Thermo Scientific™ TraceFinder™ software. TraceFinder allows easy data reviewing and data reporting.

Results

Chromatography

Good chromatographic separation was obtained using the GC conditions (Figure 1). The total ion chromatogram as well as the extracted ion chromatograms (XIC, 2 ppm extraction mass window) of the first (dichlorvos, *m/z* 184.97650, RT = 4.46 min) and the last eluting pesticide (deltamethrin, *m/z* 252.90451, RT = 10.33 min) is shown.

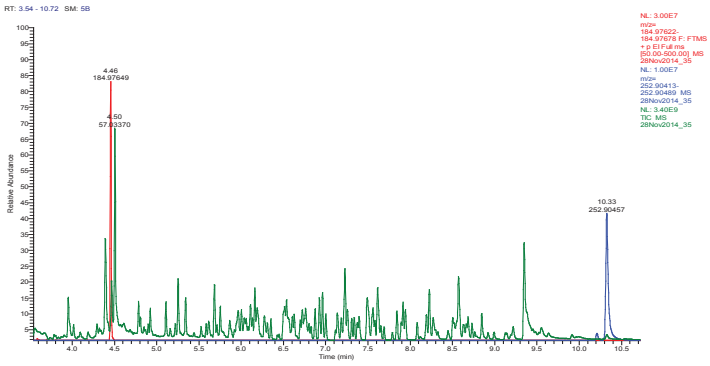

FIGURE 1. Overlay of the TIC and the extracted ion chromatograms (XIC) of the first (dichlorvos, RT=4.46 min) and the last (deltamethrin, RT= 0.33 min).

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MS Acquisition Speed

Using short GC run times requires fast MS acquisition rates in order to obtain enough scans/ peak. An example of typical number of scans acquired using the QE GC operated at 60,000 resolution is shown below (Figure 2). Noticeably, beside the adequate number of scans/peak, excellent mass accuracy for every single scan across the peak was obtained (<0.4 ppm RMS).

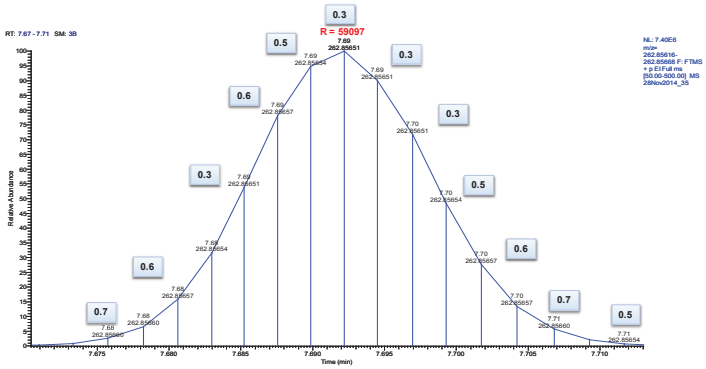

FIGURE 2. XIC of dieldrin (*m/z* 262.85642) showing 17 scans/peak (peak width 2.4 sec). Data acquired in full scan at 60,000 FWHM resolution (the exact resolution used is annotated in red). Mass accuracy/scan shown as ppm.

Sensitivity

Almost all pesticides (95%) were detected in the lowest calibration matrix-matched standard 0.5 (or 1.0) ng/g. Examples of chromatography at this concentration level are shown in Figure 3.

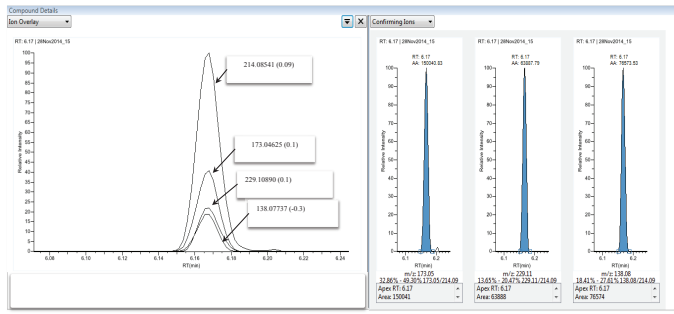

FIGURE 3 Terbuthylazine at 0.5 pg showing an XIC overlay for the quantification ion and three additional confirmation ions. Annotated is the measured mass for each ion and mass error (in ppm).

Instrumental Detection Limit (IDL)

System sensitivity was assessed by calculating the IDL for each individual pesticide. The results of this experiment show that the sensitivity is comparable to that of the TSQ 8000 Evo triple quadrupole GC-MS, with 91% of pesticides having an IDL < 2 ng/g (Figure 4).

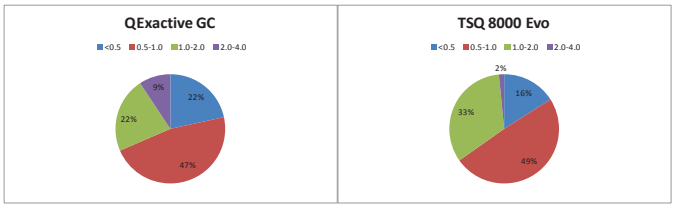

FIGURE 4. Comparison of the IDL_{99} (ng/g) calculated for 132 pesticides from a 5 ng/g matrix-matched standard from the Q Exactive GC-MS (left) and TSQ 8000 Evo triple quadrupole GC-MS (right). Percentage of pesticides and corresponding IDL interval relative to the total number of target compounds (132) is indicated.

Mass Accuracy

Obtaining accurate mass information in a consistent manner is critical for determining the identity of a pesticide. The mass accuracy for all 132 pesticides was assessed at 5 (or 10, depending on compound) ng/g level from a series of n = 10 repeat injections. The mass deviation values did not exceed 1 ppm for any of the analytes and the overall mass accuracy average value was 0.4 ppm providing the highest confidence in accurate and selective detection (Figure 5).

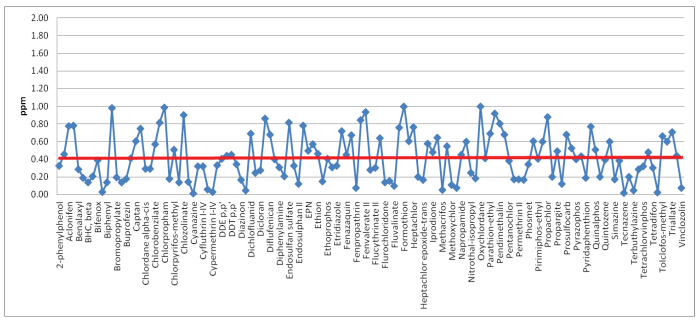

FIGURE 5. Accurate mass measurements (average value of n = 10) for the pesticides indentified in the baby food sample at 5 (or 10) ng/g level.

Linearity of response

Quantitative linearity was assessed using matrix-matched calibration standards inject in triplicate at each level. In all cases the coefficient of determination (R^2) was >0.99 with an average value of R^2 = 0.997 and with residual values from the regression line of <25%.

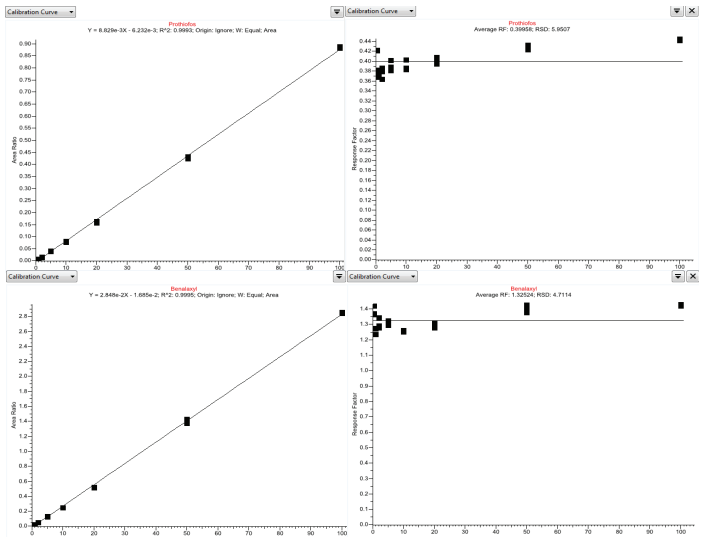

FIGURE 6. Coefficient of determination and residuals values (%RSD) for prothiofos and benalaxyl calculated for a linear range of 0.5–100 ng/g.

Conclusion

- Q Exactive GC offers the capability to perform high performance quantitative analysis in full scan for broad scope pesticide residue testing, even with fast GC separations.
- The fast scan speed, high resolution and outstanding mass accuracy together with full scan sensitivity allow reproducible and accurate pesticide quantification at very low levels.
- Routine mass resolution of 60,000 FWHM eliminates isobaric interferences, increasing confidence in results when screening pesticides in complex matrices.
- Q Exactive GC provides highly comparable quantitative performance with respect to GC triple quadrupole MS instruments.

References

1. Commission Regulation (EU) No 396/2005 on maximum residue levels of pesticides in or on food and feed of plant and animal origin and amending Council Directive 91/414/EC, 16.3.2005, p. 1–16.
2. SANCO/12571/2013 (2014), Guidance document on analytical quality control and validation procedures for pesticide residues analysis in food and feed, 19.11.2013 rev. 0.
3. Commission Directive (EU) No 2003/13/EC amending Council Directive 96/EC on processed cereal-based and baby foods for infants and young children, 14.2.2003, p. 33-36.
4. Cojocariu C., Hetmanski M., Silcock P., Fussell R. J. Three-Fold Increase in Productivity for Pesticide Residue Analysis in Baby Food Using Fast Triple Quadrupole GC-MS/MS, Thermo Scientific Application Note 10432, 2015.

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