Fast Screening and Quantification of Pesticide Residues in Baby Food Using GC-Orbitrap MS Technology

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Overview

Purpose: The objective of this study was to evaluate the utility of Orbitrap-based GC-MS technology for fast pesticides screening and quantification to increase sample throughput and laboratory productivity. Specifically, the objective of the analysis was to determine the sensitivity, accuracy, and reproducibility of this new system under fast, routine analytical conditions on a challenging sample matrix.

Methods: Baby food samples were extracted following the QuEChERS protocol. The final extracts were spiked with a mixture of 132 pesticides at concentrations corresponding to 0.5–100 ng/g (ppb) for the majority of analytes and 1.0–200 for some analytes. All experiments used a Thermo Scientific™ Q Exactive™ GC hybrid quadrupole-Orbitrap mass spectrometer. Sample introduction was performed using a Thermo Scientific™ TriPlus RSH™ autosampler, and chromatographic separation was obtained using a Thermo Scientific™ TRACE™ 1310 GC and a Thermo Scientific™ TraceGOLD™ TG-5SilMS 15 m × 0.25 mm I.D. × 0.25 µm film capillary column. Chromatographic data was acquired with a minimum of 12 points/peak to ensure consistent peak integration. Data was acquired and processed using Thermo Scientific™ TraceFinder™ software.

Results: The results of this study show that the Q Exactive GC system is an ideal tool for the analysis of pesticide residues in complex matrices, offering high performance full scan analysis and fast GC separation. Routine mass resolution of 60,000 FWHM and consistent sub-ppm mass accuracy ensures selective and confident compound detection and identification. Moreover, the Q Exactive GC provides highly comparable quantitative performance to that of 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-MS is widely used in many pesticide residue laboratories. GC offers good separation efficiency and a choice of MS detectors such as single or triple quadrupoles. Quadrupole mass analyzers are selective, sensitive, and cost-effective instruments that operate at nominal mass resolution. When using quadrupole MS, the selectivity required to separate target pesticides from chemical background comes from the use of either selected ion monitoring (SIM) or selected reaction monitoring (SRM). Both SIM and SRM are targeted experiments where the analyst uses an existing database to look for a defined set of compounds. However, targeting specific compounds during acquisition limits the scope of analysis and results in the false negative results (non-detection) for unknown or untargeted compounds, which may be of concern with respect to food safety. This limitation has led to increased interest in developing methods using MS analyzers that can operate in full scan with a higher mass resolving power than quadrupoles, but provide similar levels of selectivity and quantitative performance. Until now, this requirement has not been satisfied by existing high resolution accurate mass GC-MS instruments due to limited ability to provide comparable selectivity and quantitative performance in full scan to triple quadrupole instruments operated in SRM. In this work, we demonstrate the use of GC-Orbitrap technology in the context of the SANCO guidelines[2] 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 demonstrated.

Methods

Sample Preparation

Baby food samples were extracted following a citrate buffered QuEChERS protocol.[4] The final extracts (1 g/mL in acetonitrile) were spiked with a mixture of 132 pesticides at concentrations corresponding to 0.5–100 ng/g (ppb) for the majority of analytes and 1.0–200 for some analytes.

Gas Chromatography

A sample volume of 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

Eluting peaks were transferred through an auxiliary transfer temperature of 280° C into a Q Exactive GC mass spectrometer. High resolution EI fragment 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 to maintain mass accuracy throughout the chromatogram (Table 2).

Data Analysis

Data was acquired and processed using TraceFinder software. TraceFinder software allows the analyst to build acquisition and processing methods for high throughput screening and quantitative analysis and incorporates library searching capabilities as well as easy data reviewing and data reporting.

TABLE 1. GC parameters.

TRACE 1310 GC	
Injection volume (µL)	1.0
Liner	asymmetric
Inlet (° C)	75
Inlet module and mode	PTV, splitless
Transfer delay (min)	1
Injection time (min)	0.1
Transfer rate (° C/sec)	2.5
Transfer (° C)	300
Transfer time (min)	3
Cleaning rate (° C/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. MS parameters.

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

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Results

Chromatography

Good chromatographic separation was obtained using the GC conditions described in Table 1. An example of chromatography for the matrix-matched standard spiked at 100/200 ng/g is given in 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 (deltamethrin, *m/z* 252.90451, RT = 10.33 min) eluting pesticide is shown.

MS Acquisition Speed

When using short GC run times, the analyte chromatographic peaks widths are narrow (<2.5 sec). This requires fast MS acquisition rates in order to obtain enough scans/peak. An example of the typical number of scans acquired using the Q Exactive GC system operated at 60,000 resolution is shown below for EPTC in baby food (Figure 2). Noticeably, in addition to the adequate number of scans/peak, excellent mass accuracy was obtained for every scan across the peak (<0.4 ppm RMS).

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 1. Overlay of the TIC (EI full scan) and the extracted ion chromatograms (XIC) of the first (dichlorvos, RT=4.46 min) and the last (deltamethrin, RT= 0.33 min) eluting pesticides. Relative abundance Y axis adjusted to emphasize XIC for dichlorvos and deltamethrin.

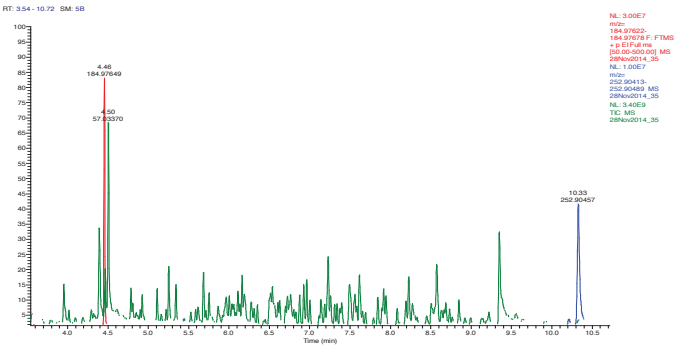


FIGURE 2. XIC of dieldrin (*m/z* 262.85642) showing 17 scans/peak (peak width 2.4 sec). Data acquired in full scan at 60,000 FWHM resolution (the exact resolution used is annotated in red). Mass accuracy/scan shown as ppm.

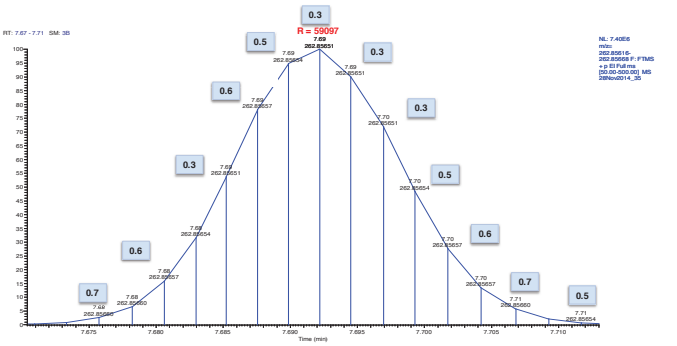
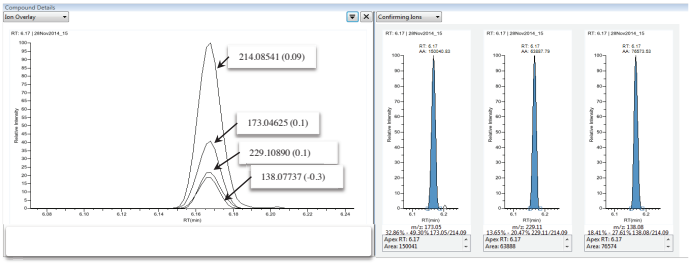


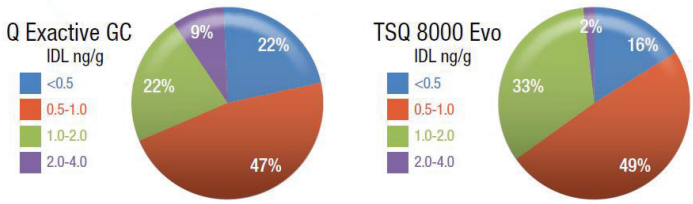
FIGURE 3. Terbuthylazine at 0.5 pg (on column concentration) showing an XIC overlay for the quantification ion and three additional confirmation ions. Annotated is the measured mass for each ion and mass error (in ppm).



Instrumental Detection Limit (IDL)

System sensitivity was assessed by calculating the IDL for each pesticide. The IDL represents the smallest signal above background noise that an instrument can consistently and reliably detect and it was determined empirically by repeatedly injecting (n = 10) the 5 ng/g (and 10 ng/g) matrix-matched standard and taking into account the Student's-*t* critical values for the corresponding degrees of freedom (99% confidence). The results of this experiment showed an average %RSD for the peak area reproducibility of 6%. All the IDLs derived from the Q Exactive GC system data were lower than the typical MRLs established by European Union for baby food samples. For most pesticides, these MRLs are currently set at <0.01 mg/kg (ng/g)[3]. Calculated IDLs were compared to the IDL values obtained for the same pesticides using the Thermo Scientific™ TSQ™ 8000 Evo triple quadrupole GC-MS/MS system [4]. The results of this experiment shows that the sensitivity of the Q Exactive GC system is comparable to that of the TSQ 8000 Evo triple quadrupole GC-MS/MS system, with 91% of pesticides having an IDL < 2 ng/g (Figure 4).

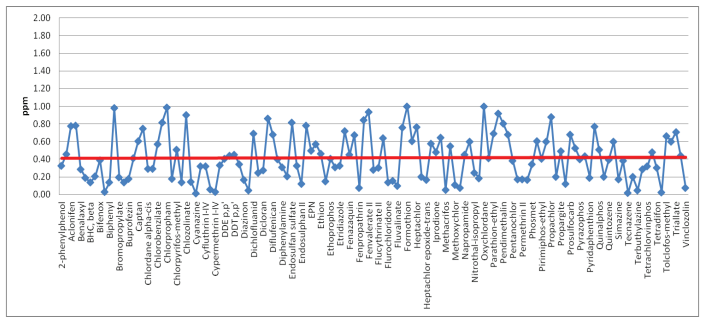
FIGURE 4. Comparison of the IDL_{99} (ng/g) calculated for 132 pesticides from a 5 ng/g matrix-matched standard from the high resolution GC-MS (left) and TSQ 8000 Evo triple quadrupole GC-MS (right). Percentage of pesticides and corresponding IDL interval relative to the total number of target compounds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



Mass Accuracy

Obtaining accurate mass information in a consistent manner is critical for determining the identity of a pesticide as well as for maintaining a high degree of discrimination against matrix interference provided by the resolving power of the instrument. The mass accuracy for all 132 pesticides was assessed at the 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).

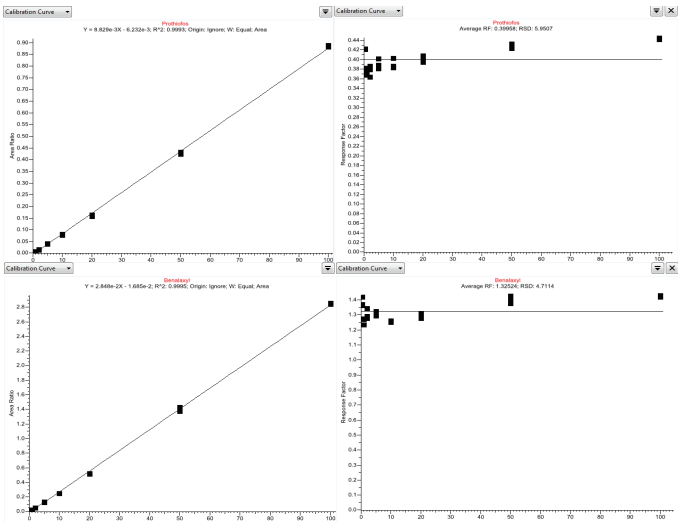
FIGURE 5. Accurate mass measurements (average value of n = 10) for the pesticides indentified in the baby food sample at 5 (or 10) ng/g level.



Linearity of Response

Quantitative linearity was assessed across a concentration range of 0.5–100 ng/g (or 1–200 ng/g for some analytes) using matrix-matched calibration standards injected 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%. Examples of compound linearity are shown in Figure 6.

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



Conclusion

- The Q Exactive GC system provides high performance quantitative analysis in full scan for broad scope pesticide residue testing, even with faster 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.
- Consistent sub-ppm mass accuracy achieved for all compounds ensures confident compound identification.
- The Q Exactive GC system provides quantitative performance that is highly comparable to that of GC triple quadrupole MS instruments.
- TraceFinder software allows the analyst to develop high throughput screening and quantitative analyses quickly and accurately.

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 Guidance document on analytical quality control and validation procedures for pesticide residues analysis in food and feed, 19.11.2013 rev. 0, 2014.
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. *Three-fold Increase in Productivity for Pesticide Residue Analysis in Baby Food Using Fast Triple Quadrupole GC-MS/MS*. Thermo Scientific Application Note 10432, January 2015. [Online] https://www.thermoscientific.com/content/dam/tfs/ATG/CMD/cmd-documents/sci-res/app/ms/GC-MS/AN-10432-GC-MS-Pesticides-Baby-Food-AN10432-EN.pdf.

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