DEPISTAGE ET QUANTIFICATION DE RESIDUS DE PESTICIDES DANS LES ALIMENTS PAR UTILISATION D'UN COUPLAGE GC-TOF

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Jean-Marc Joumier[a], Cristiana C. Leandro[bcd], Peter Hancock[b], Richard J. Fussell[c], Brendan J. Keely[d]

[a]Waters EHQ, BP 608, St Quentin en Yvelines Cedex, France [b]Waters Corporation, Manchester M225PP, UK.

[c]Central Science Laboratory, Sand Hutton, York YO41 1LZ, UK. [d]University of York, Heslington, York YO10 5DD, UK.

THE UNIVERSITY of York

RESUME

- Une méthode GCMS à temps de vol a été développée pour la quantification d'une centaine de pesticides dans des échantillons de poire et de laitue. Les extraits ont été dopés avec 100 et 10 µg/kg, les recouvrements moyens sont de 70 à 109% avec des RSDs inférieurs à 26%, et une bonne linéarité.
- Une approche ciblée et non ciblée ont été utilisées pour le screening. Les pesticides recherchés ont été identifiés dans les échantillons de poire et de laitue à des concentrations de l'ordre de 10 µg/kg. L'approche non ciblée avec recherche en bibliothèque et calcul de la composition élémentaire a permis la détection et l'identification d'un résidu non ciblé, (le chlorthal-diméthyle) dans un échantillon de laitue à une concentration de 70 µg/kg.

INTRODUCTION

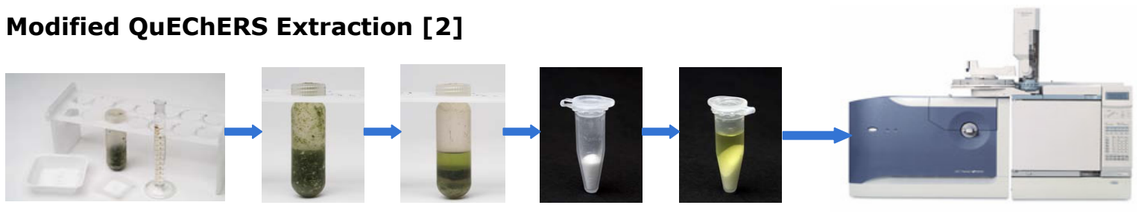
- Comprehensive analysis of pesticide residues by GC and LC coupled with TOF-MS allow coverage of a much larger number of pesticides, since TOF-MS instruments provide high performance across the full mass range.
- TOF-MS instruments measure the time an ion takes to travel through a field-free region. The ions generated in the ion source are accelerated as discrete packages into the field-free flight tube by using a pulsed electrical field. The duty cycle of a TOF-MS is 20 - 30% as against 0.1 - 1% for a scanning instrument, leading to better response for TOF-MS than for the other instruments when operated in the scanning mode [1].
- The GC-exact mass TOF-MS, also called elevated resolution TOF-MS, provides accurate mass measurement (sub 5 ppm) with moderate scan speed (20 Hz in the more recent instruments), .
- Recently, a new technology was introduced to the GCT Premier: dynamic range enhancement (DRE). This allows the working dynamic range of the instrument to be extended by an order of magnitude both for exact mass measurement and for quantitative studies, maximizing the information obtained from a single analysis.

AIMS

- Here we report application of the most recent GC-TOF-MS, with exact mass measurement, in the quantification and confirmation of pesticide residues in food at 0.01 mg kg^{-1}, and in the identification of pesticide residues using the deconvolution and library searching software routines.

METHODS

Modified QuEChERS Extraction [2]



GCT Premier

GC-TOF-MS Conditions

- Analyses were performed on a GC system 6890 series (Agilent Technologies, Palo Alto, CA, USA) using a GCT Premier TOF mass spectrometer (Waters, Manchester, UK). A Rxi-5ms (30 m x 0.25 mm i.d., 0.25 µm) capillary column (Restek, Bellefonte, PA, USA) was used for separation. GC was temperature programmed from 50 to 150ºC at 20ºC min^{-1}, and then to 280ºC at 6ºC min^{-1} followed by an isothermal hold for 7 min (total run time of 34 min). Helium (99.997% purity; flow rate of 1 ml min^{-1}) was used as a carrier gas. Large volume injections (5 µl) were performed using a cryo-cooled PTV injector in solvent vent mode with a vent pressure of 5 kPa and vent flow of 20 ml min^{-1} for 0.5 min. The TOF-MS was equipped with a 4.0 GHz TDC. It was operated with a MCP voltage of 2900 V, acquisition rate 2 spectra s^{-1} (with DRE on), pusher interval of 35 µs (resulting in 28571 raw spectra s^{-1}), inhibit push value of 4, scan range of 50 – 500 Th, ion source temperature 200ºC and transfer line temperature 260ºC.
- Manual tuning was performed using 2,4,6-tris-trifluoromethyl-[1,3,5]-triazine as internal standard. During analysis, the internal standard (lock mass) was continuously introduced into the ion source. MassLynx 4.0, TargetLynx and ChromaLynx were used for data processing.

CONCLUSIONS

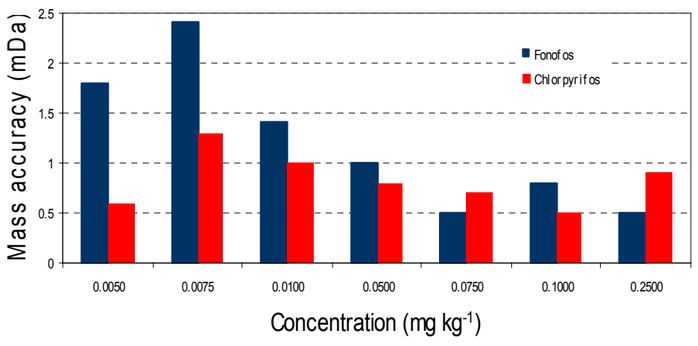
- A GC-exact mass TOF-MS method has been developed for the quantification of approximately one hundred pesticides and transformation products at 0.01 and 0.1 mg kg^{-1} in fruit-based baby food, pear and lettuce samples and has been applied to screening of pear and lettuce samples containing incurred residues. Good linearity and satisfactory recoveries were obtained for the majority of pesticides in fruit-based baby food, pear and lettuce.
- The mass accuracy improved with the concentration of the analytes of interest and was more critical for analytes with low *m/z* values (*m/z* < 200).
- The TOF instrument provided an improvement in selectivity for the pesticides by narrowing the *m/z* window, giving better separation of the target compounds from co-eluting compounds, which is very important when analysing complex matrices.
- A targeted approach (using TargetLynx) and an untargeted approach (using ChromaLynx and a library search to detect and identify incurred residues) were used for screening, successfully identifying incurred pesticides in pear and lettuce samples at concentrations above 0.01 mg kg^{-1}, and with a good agreement with previous results obtained from GC-single quadrupole analysis. The targeted approach with TargetLynx is essential for successful identification and confirmation of the analytes and ChromaLynx is a valuable tool for additional analysis, enabling untargeted analytes to be recognised.

References

1. J. Dallüge, P. Roose, U.A.Th. Brinkman, J. Chromatogr. A 970 (2002) 213.
2. S.J. Lehotay, K. Mastovska, A.R. Lightfield, J. AOAC Int. 88 (2005) 615.
3. T. Čajka, J. Hajšlová, J. Chromatogr. A 1058 (2004) 251.
4. C. Leandro, P. Hancock, R. Fussell, B. Keely, J. Chromatogr. A (2007) accepted.

RESULTS AND DISCUSSION

- **Mass accuracy**



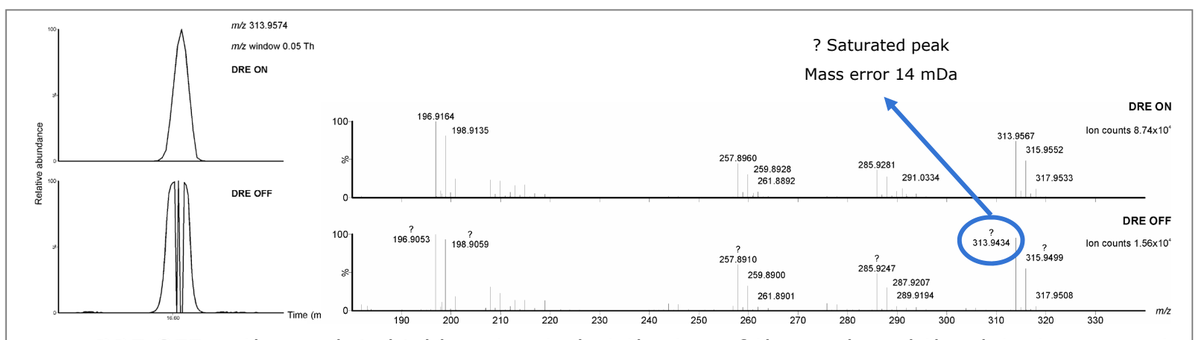
⇒ Mass accuracy < 1.5 mDa

⇒ At lower concentrations, the signal for fonofos was too weak to allow exact mass measurement, corroborating with Čajka report [3].

⇒ No saturation of the TDC was observed.

Figure 1. Mass accuracy (mDa) of fonofos (m/z 108.9877) and chlorpyrifos (m/z 313.9574) in dependence of concentration (mg kg^{-1}) of analyte in fruit-based baby food matrix-matched standards.

- **DRE ON vs. DRE OFF**

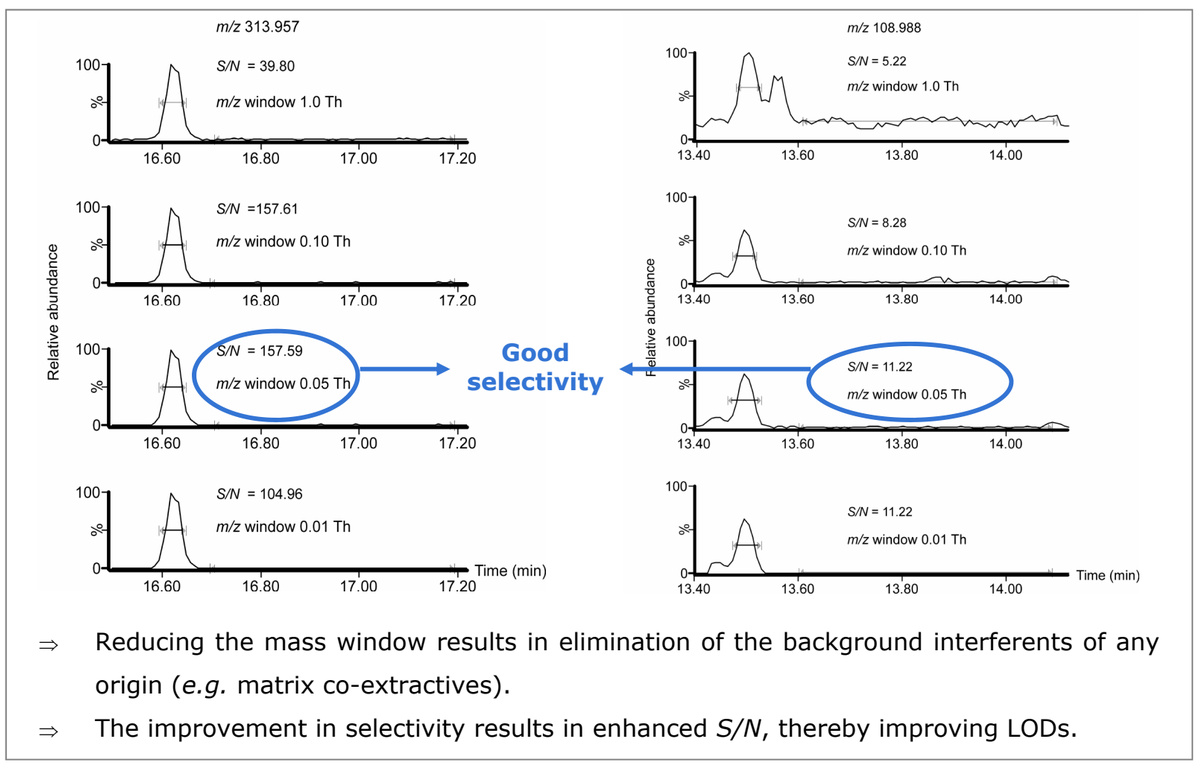


⇒ DRE OFF — the peak is highly saturated at the top of the peak and the detector can not deal with such a large number of ions and the response falls outside the extracted mass chromatogram window (0.05 Th).

⇒ DRE ON — the instrument is capable of managing the large number of ions by switching to low sensitivity mode and then applying the DRE magnification factors to correct the response, generating the peak representative of chlorpyrifos.

Figure 2. Extracted ion chromatograms of chlorpyrifos (m/z 313.9574) with DRE ON and OFF and its spectra, in a lettuce matrix-matched standard at 1.0 mg kg^{-1}.

- **Mass windows vs. *S/N***



⇒ Reducing the mass window results in elimination of the background interferents of any origin (*e.g.* matrix co-extractives).

⇒ The improvement in selectivity results in enhanced *S/N*, thereby improving LODs.

Figure 3. Influence of width of the m/z window in the signal to noise ratio (S/N) for chlorpyrifos (m/z 313.9574) and fonofos (m/z 108.9877), in fruit-based baby food .

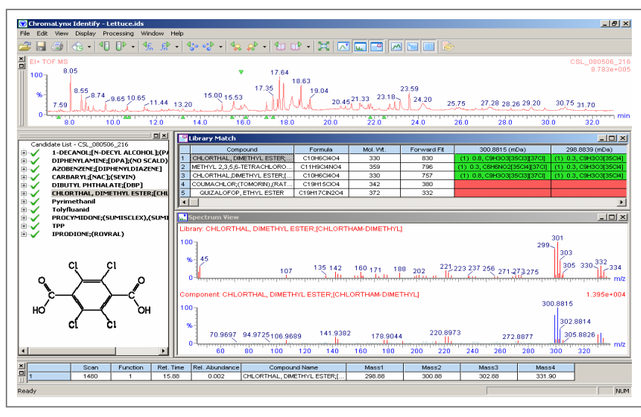
- **Recoveries and selectivity**

⇒ Satisfactory method recoveries were obtained for the majority of the pesticides spiked at concentrations of 0.10 and 0.01 mg kg^{-1} in fruit-based baby food (70 – 108%, RSD < 22%), pear (72 – 108%, RSD < 25%) and lettuce (70 – 109%, RSD < 26%).

Table 1. Examples of recoveries (RSDs, %) obtained by GC-TOF-MS analysis of fruit-based baby food fortified with a standard solution containing 108 pesticides, at two spiking levels (*n*=5).

Pesticide	t_R (min)	*m/z*	Recovery (RSD, %) 0.01 mg kg^{-1}	0.1 mg kg^{-1}
Tecnazene	10.89	202.8803; 214.8803; 260.8732	90 (4)	85 (6)
Buprofezin	19.8	172.1034; 175.0871; 305.1562	100 (9)	99 (5)
Azoxystrobin	32.3	344.1035; 388.0933; 403.1168	103 (5)	106 (3)

- **Screening of samples**



⇒ Chlorthal-dimethyl (DCPA), a non-targeted pesticide in the MS screen method, was detected and identified by ChromaLynx.

⇒ Re-extraction of the lettuce sample, where it was detected DCPA, and its analysis using the GC-single quadrupole MS method confirmed the presence of this pesticide at 0.07 mg kg^{-1}.

Figure 4. Identification of an incurred residue (chlorthal-dimethyl) using ChromaLynx in lettuce.

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