Results and Discussion

In this study, we demonstrate a novel GC/Q-TOF based workflow to screen pesticides in lipid-rich food matrices. This application requires untargeted acquisition of full scan mass spectra of all GC amenable commodities is considered as one of the most demanding laboratory. The screening of a broad scope of pesticides in various food commodities is considered as one of the most demanding laboratories. This application requires untargeted acquisition of full scan mass spectra of all GC amenable commodities. The screening of pesticides in lipid-rich food matrices is also important in meet regulatory requirements on maximum residue levels (MRL).

High resolution accurate mass GC/Q-TOF serves as a fit-for-purpose tool in pesticide screening as it improves compound identification and reduces screening detection limits. In this study, we demonstrate a novel GC/Q-TOF based workflow to screen pesticides in lipid-rich food matrices with added confidence.

Experimental

Preparation

Organic phase oil, avocado and salmon were extracted using SAXEASY (5:1,5) and followed by a clean up with SDE on a Lipid AP2.5 and polish with dry steps. A mixture of 120 pesticide standards were then spiked at 5 and 10 ng/mL in the extract. Avocado extract was also spiked with 5-200 ng/mL (Figure 4). Most pesticides showed single digit %RSD, suggesting that the majority of screened pesticides can be detected at even lower concentrations. The RTL backflushing method ensured retention time and curated mass spectrum of each compound was identified compound information can also be easily accessed and curated mass spectrum of each compound was identified compound information can also be easily accessed. An accurate mass pesticide library containing retention times and curated mass spectra of each compound was used to perform the screening analysis. Over 110 spiked pesticide categories, including carbamate, nitroaniline, triazine, insulinomycin, organophosphorous, and pyrethroid pesticides at concentrations of 5 ng/mL and 115 spiked pesticides at 10 ng/mL were verified by standard data analysis (Find by Fragment) in all three investigated matrices. The detailed detectability and data analysis parameters are tabulated in Table 2.

Figure 2. Configuration using MEA column backflushing.

Table 1. GC/Q-TOF Operational Conditions.

Table 2. Number of Pesticides (out of 128) Detected in Matrices

Pesticide Detectability

The 128 applied pesticides represent a large variety of pesticide categories, including carbamates, insecticides, organophosphorous, organochlorines, and pyrethroids. An accurate mass pesticide library containing retention times and curated mass spectra of each compound was used to perform the screening analysis. Over 110 spiked pesticide categories, including carbamate, nitroaniline, triazine, insulinomycin, organophosphorous, and pyrethroid pesticides at concentrations of 5 ng/mL and 115 spiked pesticides at 10 ng/mL were verified by standard data analysis (Find by Fragment) in all three investigated matrices. The detailed detectability and data analysis parameters are tabulated in Table 2.

Figure 3. Standard Deviation of Retention Time.

Retention Time and Response Repeatability

The RTL backflushing method ensured retention time stability, was validated compliance (S:5:0.5 ppm) measured for all identified pesticides even at 5 ng/mL in all three matrices (Figure 3). The instrument precision is illustrated by RSD distribution of identified pesticides at both 5 and 10 ng/mL (Figure 4). Most pesticides showed single digit %RSD, suggesting that the majority of screened pesticides can be detected at even lower concentrations. The RTL backflushing method ensured retention time stability, was validated compliance (S:5:0.5 ppm) measured for all identified pesticides even at 5 ng/mL in all three matrices (Figure 3). The instrument precision is illustrated by RSD distribution of identified pesticides at both 5 and 10 ng/mL (Figure 4). Most pesticides showed single digit %RSD, suggesting that the majority of screened pesticides can be detected at even lower concentrations.

Figure 4. Response RSD of Pesticides in Food Matrices.

Long Term Stability

The long term system stability has also been evaluated by a sequence of alternate injecting 5 and 10 ng/mL pesticides in matrices, with 20 injections in total. Figure 5 shows the long term response stability of four example pesticides.

Figure 5. Long Term Stability in Avocado and Salmon

Conclusions

• High resolution accurate mass GC/Q-TOF and an accurate mass library has been combined to accelerate screening in lipid-rich complex food matrices.
• The confirmatory identification is enhanced by stable MS/MS fragmentation and confirmed by reference spectra. Novel detection enhancement criteria in major guidelines.

Figure 6. Calibration Graph Examples in Avocado

Increased Dynamic Range

An innovative algorithm was used to calibrate the identified pesticides in whole dynamic range in matrices. The calibration of 5-200 ng/mL (triplicates) yielded good linearity (r^2=0.997) for 115 pesticides in this matrix, with results of two example compounds shown in Figure 7.

Figure 7. Calibration Graph Examples in Avocado

Discussion

The analysis of these pesticides by GC/Q-TOF provided excellent mass accuracy for molecules of medium to high complexity (Figure 5). The mass accuracy of each pesticide was calculated as the average spectrum extracted over the entire compound peak. For these pesticides with MA > 5 ppm, the majority had at least 2 ions identified with S/N >3 for the corresponding EICs and had relative IR variance <30% compared to the reference spectrum, thus meeting identification criteria in major guidelines.

Table 3. Mass Accuracy at 10 ng/mL in Food Matrices

<table>
<thead>
<tr>
<th>Pesticide</th>
<th>Mass Accuracy (MA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosalone</td>
<td>5 ppm</td>
</tr>
<tr>
<td>Aldrin - 6 Levels</td>
<td>5 ppm</td>
</tr>
<tr>
<td>Butralin - 6 Levels</td>
<td>5 ppm</td>
</tr>
</tbody>
</table>
| Long Term Stability in Avocado

Long Term Stability

The long term system stability has also been evaluated by a sequence of alternate injecting 5 and 10 ng/mL pesticides in matrices, with 20 injections in total. Figure 5 shows the long term response stability of four example pesticides.

Aldrin – 6 Levels

Butralin – 6 Levels

Phosalone

Results and Discussion

The screening of a broad scope of pesticides in various food commodities is considered as one of the most demanding laboratories. This application requires untargeted acquisition of full scan mass spectra of all GC amenable commodities. The screening of pesticides in lipid-rich food matrices is also important in meet regulatory requirements on maximum residue levels (MRL). In this study, we demonstrate a novel GC/Q-TOF based workflow to screen pesticides in lipid-rich food matrices with added confidence.