Using PeakView™ Software with the XIC Manager for Screening and Identification with High Confidence based on High Resolution and Accurate Mass LC-MS/MS

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Overview

The high resolution and accurate mass AB SCIEX TripleTOF™ 5600 LC/MS/MS system was used to screen extracts of fruit and vegetable samples for pesticide residues. Automatically acquired MS/MS spectra were used to identify detected compounds based on mass spectral library searching.

PeakView™ software with the XIC Manager add-in was used for targeted and non-targeted data processing. The XIC Manager consists of a table for defining a list of masses or formulae to generate extracted ion chromatograms (XIC), and the ability to review results for the identification of detected compounds. High confidence in results is based upon retention times, accurate mass, isotopic pattern and MS/MS library searching.

Introduction

Liquid Chromatography coupled to Tandem Mass Spectrometry (LC-MS/MS) is a widely used analytical tool for the screening of food residues and contaminants. Triple quadrupole based mass analyzers operated in Multiple Reaction Monitoring (MRM) mode deliver highly selective and sensitive quantitative results, but are limited to targeted screening only.

With an increasing demand for retrospective and non-targeted analyses full scan mass analyzers gain popularity. The AB SCIEX TripleTOF™ 5600 system allows the acquisition of highly sensitive full scan MS spectra with high resolution and mass accuracy. In addition, Information Dependent Acquisition (IDA) can be used to collect MS/MS spectra with unmatched speed for compound identification based on MS/MS library searching.

Here we present examples of using the AB SCIEX TripleTOF™ 5600 system for the screening and identification of pesticides in extracts of fruit and vegetable samples. Features of the XIC Manager for targeted and non-targeted screening are highlighted.

Method Details

- A standard of 289 pesticides was used to determine retention times on a Shimadzu UFLCXR system with a Restek Ultra Aqueous C18 3 μm (100x2.1 mm) column and a 15 min gradient of water and methanol with ammonium formate buffer at a flow rate of 0.5 mL/min.
- Different fruit and vegetable samples were extracted using a modified QuEChERS procedure and diluted 5 times with the aqueous mobile phase to optimize chromatographic peak shape and minimize possible ion suppression effects.
- The injection volume was set to 10 μL.
- The AB SCIEX TripleTOF™ 5600 system was operated with Turbo V™ source and Electrospray Ionization (ESI) probe.
- An IDA method was used containing a TOF-MS survey of 100 ms and up to 10 dependent TOF-MS/MS scans with Collision Energy (CE) of 35 V and Collision Energy Spread (CES) of 15 V.
Results

Defining an XIC List and Processing Options in the XIC Manager

After opening a data file in PeakView™ software the XIC Manager can be launched from the ‘Show’ menu.

The table contains a number of columns with values that can be edited, including name, formula, adduct/modification, retention time, width, and more. To define an XIC, a mass must be entered. This can be done by: directly editing the cell, having the software calculate the value based on formula, isotope, and adduct provided, or by pasting values from a spreadsheet. The generated XIC list can be saved for future processing (Figure 1).

A number of processing and display settings can be adjusted in the ‘Options’ dialog. This includes intensity, signal-to-noise threshold, and confidence settings for mass error, retention time, isotope matching, and library searching (Figure 2).

To start data processing, simply click the button in the lower right of the table.

The XIC Manager will automatically calculate XICs, perform compound identification, and display results.
Result Display in the XIC Manager

After processing, the results are displayed in the chromatogram pane and the XIC table. This includes found at mass, mass error (ppm or mDa), found at retention time, and library search results.

XICs above a defined intensity threshold are highlighted in green and confidence data for compound identification is visualized using ‘traffic lights’ (Figure 3).

Figure 2. Confidence settings for compound identification

Figure 3. The result display of the XIC Manager, XICs of all target pesticides (injection of a standard mix containing 289 pesticides at 5 ng/mL) are displayed (top) and information for compound identification, including retention time, mass error and library search results, is displayed and visualized using ‘traffic lights’ (bottom)
Application of Targeted Screening and Identification

Different fruit and vegetable samples obtained from a supermarket were processed using the XIC Manager and an XIC table containing 289 targeted pesticides. An established MS/MS library was used for identification (Figures 4-6).

![Figure 4. Chinese Broccoli sample, Imidacloprid, Metalaxyl, Spirotetramat, and Cyprodinil were identified using accurate mass and MS/MS library searching](image)

![Figure 5. Tomato sample, Piperonyl butoxide was identified using accurate mass and MS/MS library searching](image)

Application of Non-Targeted Screening with Identification using MS/MS Library Searching

In addition, samples were processed using the non-targeted peak finding algorithm built into the XIC Manager. Automatically acquired TOF-MS/MS spectra were searched against the MS/MS library to assist compound identification (Figures 7 and 8).

![Figure 6. Mustard greens sample, Flonicamid was identified using accurate mass and MS/MS library searching](image)

![Figure 7. Kohlrabi sample processed using the non-targeted peak finding algorithm, Methoxyfenozide and Imidacloprid (at a very low concentration) were identified based on MS/MS library searching](image)
Figure 8. Tomato sample processed using the non-targeted peak finding algorithm, Carbendazim was identified based on MS/MS library searching.

Conclusion

High resolution and accurate mass LC-MS/MS was used to screen extracts of fruit and vegetable samples for pesticide residues. The XIC Manager add-in of PeakView™ software was used for targeted and non-targeted data processing.

The AB SCIEX TripleTOF™ 5600 system was operated in IDA with TOF-MS as a survey scan and up to 10 dependent MS/MS scans. Extracted ion chromatograms of targeted pesticides were generated using the XIC Manager based on molecular formulae and retention time information.

Acknowledgements

The authors would like to thank Jon Wong and Kai Zhang of the FDA Center for Food Safety and Applied Nutrition (CFSAN) in College Park, MD for providing standards and samples for analysis.

References

2. XIC Manager User Manual: AB SCIEX (2011)