Routine Targeted Quantitation and Identification of Pesticide Residues using Triple Quadrupole LC-MS/MS and Advanced Scheduling of MRM Transitions

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OVERVIEW

Pesticides are widely used in agriculture to protect crops and to improve efficiency of production. Pesticide residues may pose a potential threat to human health. Modern analytical techniques, such as LC-MS/MS, in combination with generic extraction methods, such as QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe), allow the screening for pesticide residues in a food samples. Here we present a new method using QuEChERS extraction with Phenomenex roQ™ kits, separation using a Kinetex™ Biphenyl 2.6u (50 x 2.1mm) column, and the new AB SCIEX Triple Quad™ 3500 system. The mass spectrometer was operated in highly selective and sensitive Multiple Reaction Monitoring (MRM) mode. A new algorithm was designed to obtain the best data quality. Compound identification and quantitation was achieved by monitoring two MRM transitions for each pesticide. The MRM ratio was automatically evaluated in MultiQuant™ software.

INTRODUCTION

LC-MS/MS is a powerful analytical tool capable of screening samples for numerous compounds. MRM is typically used because of its excellent sensitivity, selectivity, and speed. Generic extraction procedures, like QuEChERS, ultra high performance LC systems combined with core-shell particles columns, providing good resolution and excellent peak shape, made it possible to detect pesticides of a wide variety of compound classes and chemical properties in each sample. State-of-the-art LC-MS/MS systems make it possible to detect hundreds of pesticides and other food residues in a single run.

The new AB SCIEX Triple Quad™ 3500 system takes the best features of the API 3200™ system and enhances them with modern engineering and electronics. The proven design of Turbo V™ source and Curtain Gas™ interface provide exceptional robustness and ruggedness. The advanced aQ™ electronics and the curved LINAC™ collision cell were designed for unparalleled speed of MRM detection and fast polarity switching for comprehensive multi-component analysis.

Advanced software tools like the Scheduled MRM™ Pro algorithm intelligently uses information of retention times to automatically optimize MRM dwell time of each transition and total cycle time of the experiment resulting in best data quality. Two MRM transitions were monitored for each pesticide to use the ratio of quantifier and qualifier for ion compound identification.

EXPERIMENTAL

• The SCIEX ID/Quant™ standards kit for pesticide analysis was used for method setup and preparation of calibration standards.
• Store-bought fruit and vegetable samples were extracted using Phenomenex roQ™ QuEChERS kit buffer-salt mix and dSPE kits following the European standard method 15662.
• Extracts were diluted 5 times with water in Thomson filter vials, filtered using the 0.45 µm PVDF membrane and directly placed into the autosampler for LC-MS/MS analysis. The injection volume was set to 2 µL.
• LC separation was achieved using a Phenomenex Kinetex™ Biphenyl 2.6u (50 x 2.1mm) column and a fast gradient of water and methanol with 5 mM ammonium formate buffer at a flow rate of 0.5 mL/min (see Table 1).
• The new AB SCIEX Triple Quad™ 3500 system was operated with Turbo V™ source and Electrospray Ionization (ESI) probe set to 400 ºC.
• Approximately 400 MRM transitions were monitored in positive polarity. Optimized transitions for all compounds were obtained through the MRM™ Pro algorithm application for Pesticide Screening version 2.1.
• The Scheduled MRM™ Pro method was used with a target cycle time of 0.5 sec and compound-dependent acquisition windows and thresholds (Figure 1).
• MultiQuant™ software version 3.0 was used for quantitative and qualitative data processing.

RESULTS

Sensitivity, Reproducibility, Linearity and Accuracy

Chromatograms of a solvent standard at 10 ng/mL analyzed using the API 3200™ and Triple Quad™ 3500 are shown in Figure 2. An average gain in sensitivity of 3x was observed. Most pesticides were detectable at a concentration below 1 ng/mL, and all pesticides had a limit of detection of 2 ng/mL or lower. Example chromatograms at a concentration of 5 ng/mL are shown in Figure 3. The achieved sensitivity allows sample extract dilution by 5x to minimize possible matrix effects.

Findings in Fruit and Vegetable Samples

The developed method was applied to the quantitation and identification of pesticides in real food extracts. Different dispersive SPE kits of Phenomenex roQ™ K5013, K914, K915, K916) were used for sample cleanup depending on the type of matrix following the European standard method 15662. Extracts were diluted 5 times with water to minimize possible matrix effects. The diluted extracts were filtered using the Thompson 0.45 µm PVDF membrane and directly placed into the autosampler for LC-MS/MS analysis.

Example chromatograms of different type of food samples with detected compounds are presented in Figure 5. Quantitative results are presented in the Table below. All quantitative and qualitative results were automatically calculated in MultiQuant™ software (Figure 7).

SUMMARY

The AB SCIEX Triple Quad™ 3500 system was used for multi-pesticide quantitation and identification in food samples. The developed method combined QuEChERS extraction, LC using a Phenomenex Kinetex™ Biphenyl column and selective and sensitive detection using the Scheduled MRM Pro algorithm. Compound identification was achieved using automatic calculation of MRM ratios.

REFERENCES

4. CN EN 15662: 2008

TRADEMARKS/LICENSING

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