INTRODUCTION

Pesticide residues in fruit juices have always been inspected to monitor pesticide contamination and accordingly taking into account the high consumption of juice by children. Reports of the fungicide carbendazim in orange juice has drawn widespread public attention. Since carbendazim is not licensed for use on citrus fruits in the U.S., the FDA began testing shipments of orange juice from foreign sources.

Due to the low detection levels required by regulatory bodies (many pesticides have a maximum residue limit (MRL) of 10 ng/mL in the US, Japan and Europe), and the complexity of matrices in which the targeted analytes are present, identification and quantification of pesticides at low levels is a must.

Many published methods are capable of analyzing pesticides in fruit juice for regulatory purposes. However, sample preparation is required for these methods to minimize matrix interferences often found in LC-MS/MS technologies, namely UPLC separation and ultra-sensitive MS detection, a fast screening method using a simple ‘dilute-and-shoot’ approach was evaluated for multi-residue analysis of pesticides in orange juice.

METHODS

Three orange juice samples were purchased to assess the detection and quantification of pesticide residues at trace levels using the simple dilute and shoot protocol. A multi-residue MS method for the analysis of 80 pesticides was developed and each of the 375 pesticides was created using the Quanpedia database. All the compounds were analyzed under ESI positive mode.

EXPERIMENTAL

UPLC Conditions

Column: ACQUITY BEH C18 2.1 x 100 mm, 1.7 µm
Column temp: 45 °C
Injection volume: 1 µL
Flow rate: 0.45 mL/min
Mobile phase A: 10 mM ammonium acetate (pH 5) in water
Mobile phase B: 10 mM ammonium acetate (pH 5) in methanol

LC Conditions

MS system: Xevo® TQ-S
Ionization mode: ESI Positive
Capillary voltage: 3 kV
Desolvation temp: 500 °C
Desolvation gas flow: 1 L/min
Source temp: 150 °C

Table 1. UPLC method for pesticide analysis.

Orange juice samples

The orange juice samples were diluted 100 times with water and filtered with 0.45 µm PTFE membrane syringe filters prior to analysis. Atrazine d5 and carbendazim d5 were used as internal standards and were spiked at 10 ng/mL in each sample. A description of the samples is given in Table 2.

Table 2. Description of the orange juice samples.

For spiked samples, a standard mix of 80 pesticides was prepared and spiked into the orange juice at various concentrations ranging from 5 to 200 ng/mL, followed by 100 times dilution with water. Samples were filtered and injected for LC-MS/MS analysis.

RESULTS AND DISCUSSION

Figure 1 shows an overlay of the MRM chromatograms of the 80 pesticides in OJ1 at 10 ng/mL.

The majority of the pesticides were detected at 5 ppb in orange juice without any further sample preparation. Figure 2 shows the total number of pesticides detected at different concentrations using the simple dilute and shoot approach.

Figure 3. Recovery of various pesticides in orange juice samples.

For those compounds detected at the MRL, the linearity of both solvent curves and curves in the matrix ranged from 0.991 to 0.999 (data not shown). Figure 3. shows the average recoveries of the pesticides detected at 10 ng/mL, in the three orange juice samples with error bars indicating standard deviations.

Table 3. Recovery of various pesticides in orange juice samples.

Figure 4 shows that OJ1 and OJ2 have limited matrix effects and the dilute and shoot method was applied for these samples.

Matrix effects

The pesticide screening method with 2 MRM transitions allows for confirmatory analysis in fruit juice using a simple dilute and shoot protocol. Figure 5 shows the MRM chromatograms of carbendazim spiked at 10 ng/mL, prepared with QuEChERS method and (C) spiked at 10 ng/mL in OJ and prepared with dilute and shoot method.

CONCLUSION

The pesticide screening method with 2 MRM transitions allows for confirmatory analysis in fruit juice using a simple dilute and shoot protocol. An incurred carbendazim residue was quickly and accurately detected and quantified well below the regulatory limit. The combination of ultra performance LC with ultra sensitive tandem mass spectrometer facilitates trace level detection of pesticides well below the legislative limit. The use of a multi-residue method with rapid and simple sample preparation reduces time to result and improves laboratory efficiency.

REFERENCES


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