Direct Determination of Paraquat, Diquat, Mepiquat, Morpholine, and Chlormequat Pesticides Using Ion Chromatography and High Resolution Accurate Mass Spectrometry

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ABSTRACT
Purpose: Determine quaternary amine pesticides in homogenized vegetable and fruit samples using ion chromatography coupled with high resolution accurate mass spectrometry (IC-HRAMS).

Methods: Homogenized fruit and vegetable samples were extracted using European Research Laboratories (EURL) Quick Polar Pesticides (QuPPe) multiresidue extraction method. Six cationic pesticide of interest in homogenized vegetable and fruit sample were separated by cation-exchange chromatography (CEX) on a Thermo Scientific™ Dionex™ IonPac™ CS17 cation-exchange column using an electrolytically-generated methanesulfonic acid (MSA) gradient of 0 to 50 µL over 10 min at 0.4 µL/min. The Dionex IonPac CS17 column was selected as the most suitable for separations of quaternary amines because it is optimized for hydrophilic ion separations. Additionally, a Thermo Scientific™ Dionex™ IonPac™ CS17 cation-exchange column was evaluated as a future product to separate diquat and paraquat. The quaternary amine ions were detected serially by suppressed amine separations. Additionally, a Thermo Scientific™ Dionex™ IonPac™ Dionex prototype (JM006) cation exchange column was implemented as a future product to separate diquat and paraquat. Results: Paraquat, diquat, mepiquat, and chlormequat exhibited good peak shape with peak asymmetry from 1.0 to 1.1 (Asep) and eluted from the column within 10 min. Mepiquat and chloromiquat exhibited good chromatographic resolutions with Rs >2. In contrast, diquat-paraquat with the carbon isotopic masses within 2 m/z fully coeluted but were easily resolved in MS/MS by HRAM MS. The four pesticides were evaluated as a future product to separate diquat and paraquat. The quaternary amine ions were detected serially by suppressed amine separations. Additionally, a Thermo Scientific™ Dionex™ Dionex prototype (JM006) cation exchange column was implemented as a future product to separate diquat and paraquat. The quaternary amine ions were detected serially by suppressed amine separations.

INTRODUCTION
Recently, amine pesticides have been determined by IC-MSMS using the Quick Polar Pesticides (QuPPe) method. However, a similar approach is lacking for cationic pesticides.1-3 Robust, sensitive analytical methods are needed for determination of paraquat, diquat, and the related quaternary amine pesticides chloromiquat, and mepiquat due to their acute and chronic toxicity. Paraquat and diquat are used extensively and they have more column development is needed. Treatment of pesticides in food products using CEX with serial detection by suppressed conductivity and high resolution accurate mass spectrometry (HRAM MS) is in full scan and MS/MS modes.

MATERIALS AND METHODS

Sample Preparation
Homogenized green bean, green pea, squash, prune, pear, and mixed apple-blueberry samples were prepared according to the EURL QuPPe method.1 Six cationic polar pesticides of interest in homogenized vegetable and fruit samples were eluted from the column within 10 min. Mepiquat and chlormequat exhibited good chromatographic resolution with Rs >2. In contrast, diquat-paraquat with the carbon isotopic masses within 2 m/z fully coeluted but were easily resolved in MS/MS by HRAM MS. The four pesticides were good peak shape. The ion chromatograms of these compounds often yield poor peak shapes and separation-pairing peaks to achieve adequate peak shape. Quaternary amines are cationic and therefore best suited to CEX. Here we demonstrate direct determinations of quaternary amine pesticides in food products using CEX with serial detection by suppressed conductivity and high resolution accurate mass spectrometry (HRAM MS) in full scan and MS/MS modes.

Results:
Paraquat, diquat, mepiquat, and chlormequat exhibited good peak shape with peak asymmetry from 1.0 to 1.1 (Asep) and eluted from the column within 10 min. Mepiquat and chloromiquat exhibited good chromatographic resolutions with Rs >2. In contrast, diquat-paraquat with the carbon isotopic masses within 2 m/z fully coeluted but were easily resolved in MS/MS by HRAM MS. The four pesticides were evaluated as a future product to separate diquat and paraquat. The quaternary amine ions were detected serially by suppressed amine separations. Additionally, a Thermo Scientific™ Dionex™ Dionex prototype (JM006) cation exchange column was implemented as a future product to separate diquat and paraquat. The quaternary amine ions were detected serially by suppressed amine separations.


Conclusions
• Fast determination of six quaternary amine pesticides (TMS, morpholine, mepiquat, chloromiquat, diquat, and paraquat) in homogenized fruit and vegetable samples were demonstrated by IC-HRAM MS.
• TMS, mepiquat, and chloromiquat pesticides were chromatographically separated, where as diquat and paraquat were resolved by accurate mass spectrometry.
• The JM0006 prototype column improved the chromatographic resolution of diquat and paraquat but more column development is needed.

REFERENCES

TRADEMARKS/LICENSES
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