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Direct Determination of Cationic Polar Pesticides in Fruits and Vegetables using Ion Chromatography and MS/MS or High Resolution Accurate Mass Spectrometry

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ABSTRACT

Here polar cationic pesticides determinations are demonstrated using cation-exchange chromatography as the chromatography separation coupled with tandem mass spectrometry (IC-MS/MS). The method was applied to 23 cationic pesticides. Those suitable to the method were determined in homogenized fruit and vegetable samples using IC-MS/MS. Sensitivities for most analytes in a deionized water matrix was established at triple digit ng/L to single digit µg/L. Method robustness in food samples was also demonstrated with over 100 injections of a prune sample.

A more focused group of six cationic pesticides (mepiquat, trimethylsulfonium, morpholine, chlormequat, diquat, and paraquat) in similar samples were determined for a fast 10 min analysis time using IC with accurate mass spectrometry (IC-HRAM MS). Chromatographic separation was achieved for first four pesticides, whereas, diquat-paraquat were resolved by HRAM MS. The six pesticides had good accurate mass, meeting the SANTE requirements of <5 ppm. Sensitivities were measured in the single digit µg/L or less range by spiking pesticides to the samples. Good accuracy was found, with recoveries of spiked in reagents in the standards and the samples within 80 to 120%.

INTRODUCTION

Polar cationic pesticides (quaternary amine) determinations can be challenging because their ionic nature are not amenable to common HPLC methods. Recently, anionic pesticides determinations methods by IC-MS/MS have been demonstrated using the Quick Polar Pesticides (QuPPe) multi-residue method.[1-5] However, a similar approach is lacking for cation polar pesticides. Here cationic pesticides determinations are demonstrated using IC-MS/MS (23) and IC-HRAM MS (6).

MATERIALS AND METHODS

Samples and Sample Preparation

Baby food samples were used as homogenized vegetable and fruit samples. Figure 1 shows the sample preparation process according to the Quick Polar Pesticides method (QePPe).[3,5]

Figure 1. EURL© QuPPE Sample Preparation Method

Add 10 mL of DI water to 10 g of homogenized material.
Shake vigorously for 5 min.

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Add 30 mL of cold methanol (<5 °C).
Shake vigorously for 1 min.

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Centrifuge (5 min at 4000 rpm)

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Filter an aliquot (syringe filter, 0.2 µm, PES).
Dilute as needed

↓

IC-MS/MS or IC-HRAM Analysis

Method 1: IC-MS/MS Using the TSQ Altis MS

IC Instrument	Thermo Scientific™ Dionex™ Integrion™ HPIC™ system
Column	Thermo Scientific™ Dionex™ IonPac™ CS17, 2 x 250 mm
Methanesulfonic acid (MSA) Gradient Separation	2.5 to 10 µL injection. Equilibrate for 4 min at 1 mM MSA, 1 to 3.2 mM (0.1-4 min), 3.2 to 15 mM (4-10 min), 15 to 40 mM (10-14 min), 40 mM (14-18 min), 10 mM (18-20 min)
Flow Rate	40 mL/min, 20 min run
Eluent Source	Thermo Scientific™ Dionex™ EGC 500™ MSA eluent generator cartridge
Separation Temperatures	Column: 40 °C; CD Detector: 35 °C, Detector compartment: 20 °C
First Detection	Suppressed conductivity (CD), Thermo Scientific™ Dionex™ CERS™ 500e or Dionex 500es suppressor, 71 mA, external water mode at 0.5 mL/min
MS Instrument	Thermo Scientific™ TSQ Altis™ Triple Quadrupole Mass Spectrometer
MS Detection	+ESI, 3.5V, HESI, SIM and SRM modes
Temperatures	Vaporizer 250 C, Ion Transfer: 310 C
Gas	Sheath: 35, Aux: 15, Sweep: 1 Arb
Q1 SIM	10 V, 4 ms, 0.7 resolution
Q3 SRM	CID: 1.5 mTorr, 1.2 resolution
Desolvation solvent	Acetonitrile, Fisher Scientific™ Optima™ grade, at 0.23 mL/min
Data Analysis	Thermo Scientific™ Chromeleon™ Chromatography Data Systems (CDS) 7.2, version 6.

Method 2: IC-HRAM MS Using the Q Exactive MS

IC Instrument	Dionex Integrion HPIC system
Column	Dionex IonPac CS17, 2 x 250 mm
MSA Gradient Separation	100 µL injection Equilibrate for 4 min at 2 mM MSA, 2 to 6.4 mM (0.1-2 min), 6.4 to 30 mM (2-5 min), 30 to 60 mM (5-7 min), 60 mM (7-9 min), 10 mM (9.0-10 min)
Flow Rate	40 mL/min, 10 min run
Eluent Source	Dionex EGC 500 MSA eluent generator cartridge, Dionex CR-CTC electrolytic trap column
Separation Temperatures	Column: 40 °C; CD Detector: 35 °C, Detector compartment: 20 °C
First Detection	Suppressed conductivity (CD), Dionex CERS 500e suppressor, 77 mA, external water mode at 0.5 mL/min
MS Instrument	Thermo Scientific™ Q Exactive™ Focus Hybrid Quadrupole-Orbitrap™
MS Detection	+ESI, 3.5V, HESI II, full scan, Parallel Reaction Monitoring MS/MS (PRM)
Gas	Sheath: 40, Aux: 5, Sweep: 1 Arb
Temperature	Capillary: 425 °C, Ion Transfer: 260 °C
Full scan	50-300 m/z, AGC 1e6, MIT: 100 mS, resolution: 30,000
PRM	AGC 2e5, MIT: 100 mS, 30,000 resolution, fixed first mass: 50.0 m/z, NCE (Figure 8): 10-140V Inclusions list
Desolvation solvent	Acetonitrile, Optima grade, at 0.23 mL/min
Data Analysis	Thermo Scientific™ Xcalibur™, Thermo Scientific™ TraceFinder™

RESULTS

Table 1 shows the twenty-three cationic pesticides evaluated for cation-exchange separations and compatibility with cation suppressors. The IC-MS and IC-MS/MS SIM and SRM tables are also shown. Figures 1-7 show the MS/MS results of select ions.

Table 1. Cationic Pesticides and SIM and SRM Tables

Analyte	Amenable to IC(cation)-MS	SIM	SRM (CE in V)
Amitrol	No [1]		
Chlormequat	Yes	122/124	58 (30)
Cyanuric Acid	No [1]		
Cyromazine	Yes [2]	167	125 (18)
Daminozide	No [1]		
Diethanolamine	Yes	106	70 (16)
N,N-Dimethylhydrazine	Yes	61	44 (20)
Diquat	Yes	183	157 (20)
Ethylene Thiourea	Yes [2,3]	103	44 (23)
Kasugamycin	No [1]		
Maleic Hydrazide	No [1]		
Melamine	Yes [2]	127	85 (19)
Mepiquat	Yes	114	98 (30)
Morpholine	Yes	88	44 (23)
Nereistoxin	Yes [2]	150	105 (20)
Paraquat	Yes	185	170 (19)
Propamocarb	Yes	189	102 (20)
Streptomycin	Yes	600	263 (33)
1,2,4-Triazole	No [1]		
Triazole-acetic acid	No [1]		
Triazole Alanine	No [1]		
Triethanolamine	Yes	150	132 (15)
Trimethylsulfonium	Yes	77	62 (16)

1: Not detectable by suppressed conductivity
2. Peak tailing with resin based suppressors. Use a suppressor without resin
3. UV detectable

Figure 1. Morpholine, SRM (Method 1)

Figure 2. Trimethylsulfonium, SRM (Method 1)

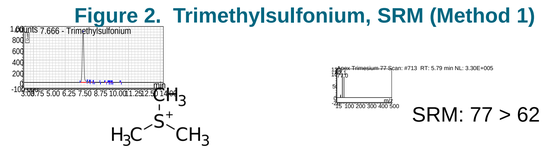

Figure 3. Chlormequat, SRM (Method 1)

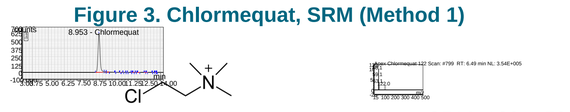

Figure 4. Cyromazine, SRM (Method 1)

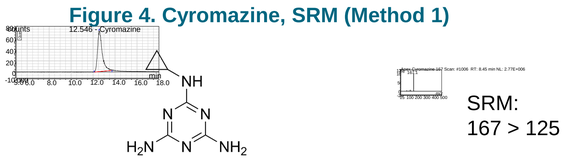

Figure 5. Melamine, SRM (Method 1)

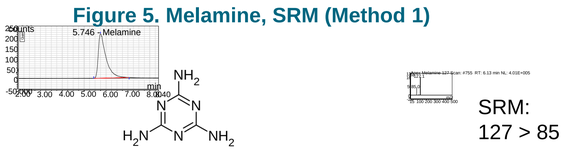

Figure 6. Diquat, SRM (Method 1)

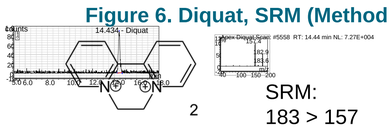

Figure 7. Paraquat, SRM (Method 1)

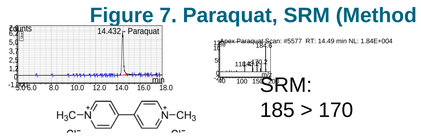

Figure 8 shows the PRM results using HRAM MS for detection (Method 2). Figure 9 shows Method 2 applied a diluted methanol/water extract of a green bean sample spiked with 10 µg/L of standards. The accurate mass and confirming ion results are shown in Table 2.

Figure 8. Six Pesticides using IC-HRAM, PRM mode

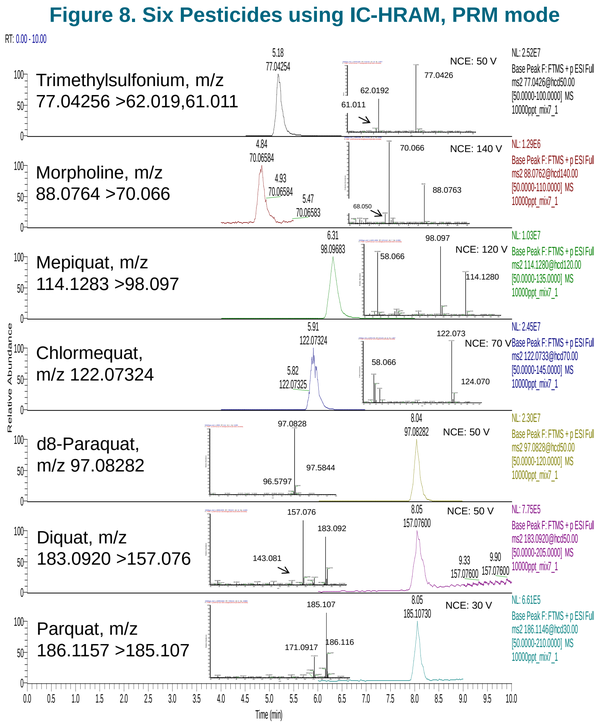

Figure 9. Comparing 50 µg/L Diquat and Paraquat in 10-fold diluted QePPe Extraction of Green Bean Sample (PRM, Method 2)

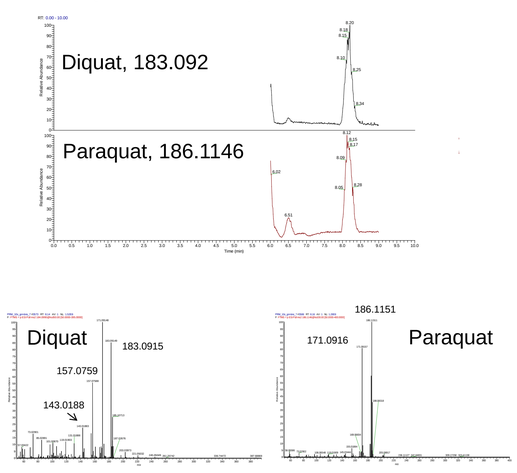

Table 2. Accurate Mass Results

Precursor Ion	Product Ions[6]	Accurate mass	Measured	SANTE[6] (< 5 ppm)
Chlormequat	124.070 58.066	122.0736	122.0736	--
Diquat	157.076 143.081	183.0920	183.0917	-1.6 ppm
Mepiquat	98.097 58.066	114.1283	114.1280	-2.6 ppm
Morpholine	70.066 68.050	88.0764	88.0763	-1.0 ppm
D8-Paraquat	97.5844 96.5797	97.0832	97.0828	-4.2 ppm
Paraquat	185.107 171.092	186.1146	186.1157	+0.5 ppm
Trimethylsulfonium	62.019 61.011	77.0043	77.0043	--

CONCLUSIONS

Although not all of the data are shown here, sensitive and accurate determinations of cationic polar pesticides using IC-MS are demonstrated on two MS platforms: 1) tandem MS on the TSQ Altis, and 2) HRAM MS on the Q Exactive Focus MS. Both methods were applied to homogenized fruit and vegetable samples using the EURL QePPe sample preparation method. This fast and easy sample preparation method provides robust samples for analysis.

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TRADEMARKS/LICENSING

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