

Determination of cationic polar pesticides in cereals using improved cation-exchange separation technology combined with suppressed conductivity and tandem mass spectrometry

Richard J. Fussell¹, Terri T. Christison², John E. Madden², and Jeff Rohrer², ¹Thermo Fisher Scientific, Hemel Hempstead, ²Thermo Fisher Scientific, 1214 Oakmead Parkway, Sunnyvale, CA, USA

Abstract

Purpose: To develop a method based on acidified extraction followed by cation-exchange chromatography and triple quadrupole mass spectrometry for the simultaneous determination of quaternary amine polar pesticides (mepiquat, chlormequat, paraquat, and diquat) in oat cereal samples.

Methods: Four quaternary amine polar pesticide residues were extracted from oat cereals using version 12 of the European Union Reference Laboratory (EURL) Quick Polar Pesticide Extraction (QuPPE) method. The pesticides were separated using a Thermo Scientific™ Dionex™ IonPac™ CS21-Fast-4µm ion-exchange column, designed to resolve quaternary amine pesticides and the matrix ions in a chromatographic run of 15 minutes. The quaternary amine polar pesticides of interest were determined and quantitated by tandem MS detection using selective reaction monitoring (SRM).

Results: The oat cereal samples were found to contain 0.4 to 1.7 µg/kg of quaternary amines polar pesticides, well below the respective MRLs (0.02 to 15 mg/kg). Samples extracted with HCl required an additional 15 min 1 mM MSA wash to remove the sample matrix from the column. Excellent recoveries (85-117%) and sensitivity with Limits of determination < 0.5 µg/kg were achieved.

Introduction

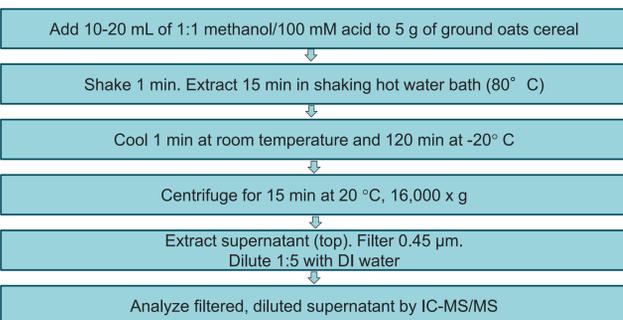
Diquat and paraquat have been applied as desiccants prior to harvest while chlormequat and mepiquat are used as a growth regulators, all on various crops including cereals. These applications result in a high risk of residues of quaternary amine pesticide residues in the food supply. Due to their ionic and charged nature, ion chromatography separations are more suitable than traditional separation methods. Anionic polar pesticides have been previously demonstrated by IC-MS¹, but cationic polar pesticides are more challenging due to their chemical structures and strong interaction with cation-exchange columns. Extraction, chromatographic separation, and sensitive detection methods are needed to quantify polar pesticide residues in food, such as oat cereals.

Materials and methods

Sample preparation

Ground oatmeal and ground toasted oat cereal were extracted according to the EURL-FV version 12 extraction method² (Figure 1). For quantitative determinations the recommended acid for chlormequat and mepiquat is 100 mM formic acid and for paraquat and diquat it is 100 mM HCl.

Figure 1. EURL-FV QuPPE version 12 extraction method recommended for quantitation of quaternary amine pesticides in cereals



Equipment

Thermo Scientific™ Dionex™ ICS-6000 HPIC IC system. Thermo Scientific™ Dionex™ AS-AP autosampler. Thermo Scientific™ TSQ Altis™ Plus triple quadrupole mass spectrometer.

Software

Thermo Scientific™ Chromeleon™ Data System (CDS) 7 version 3

IC-MS Conditions

Figure 2. IC-MS/MS flow diagram

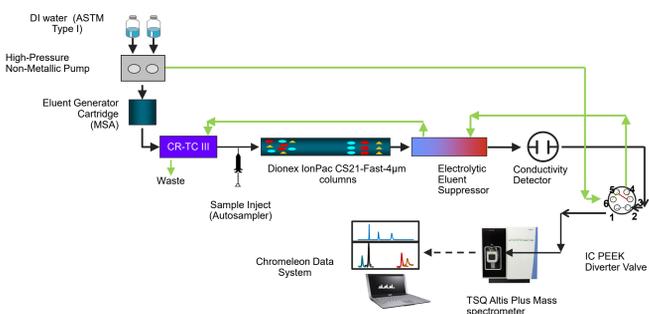


Table 1. IC-MS/MS conditions.

IC-MS/MS Conditions	
Columns:	Thermo Scientific™ Dionex™ IonPac™ CG21-Fast-4µm guard, and Thermo Scientific™ Dionex™ IonPac™ CS21-Fast-4µm analytical column, 2 mm i.d.
MSA Gradient:	3 mM MSA (-4 to 0 min), 3-6 mM (0.1 to 3.6 min), 6-22 mM (3.6 to 6 min), 22-25 mM (6 to 15 min), 1 mM (15-30 min), 3 mM (30 min)
Eluent Source:	Thermo Scientific™ Dionex™ EGC 600 MSA eluent cartridge, Thermo Scientific™ Dionex™ CR-CTC™ III Electrolytic trap column and high pressure degas module
Flow Rate	0.30 mL/min
Inj. Vol.:	10 µL
IC Temp.:	Column: 40 °C; Detector-suppressor compartment: 20 °C
1 st Detection:	Suppressed conductivity, Thermo Scientific™ Dionex™ CDRS™ 600 suppressor, 2 mm, 22 mA, constant current and external water modes at 0.3 mL/min.
Run time:	34 min
2 nd Detection:	Thermo Scientific™ TSQ Altis™ plus triple quadrupole mass spectrometer, HESI-II, SRM mode
Flow (N ₂):	Sheath: 45 (arb), Aux: 3 (arb), Sweep: 2 (arb)
MS temp.:	Vaporizer: 300 °C, Ion transfer tube: 350 °C
Make-up solv.:	None
SRM Cond.:	Polarity: Positive; Cycle time (s): 0.8 s; Resolution (FWHM): Q1: 0.7; Q3: 1.2; CID gas (mTorr): 1.5; Source fragmentation: 10; Chromatography: Peak width: 6 s

Table 2. SRM table.

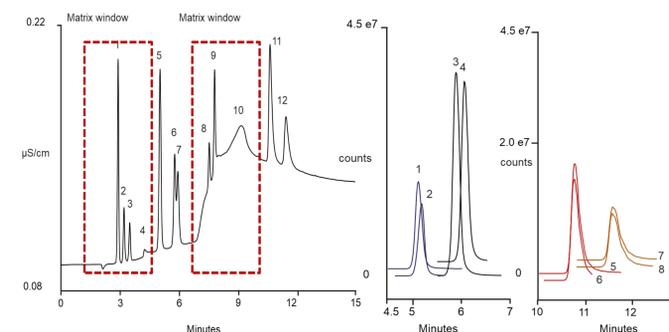
	Precursor (m/z)	Product	
		(m/z)	CE (V)
Chlormequat-d ₄	126	57.9	30
Chlormequat	122.1	62.9	30
Mepiquat-d ₁₆	130	110	30
Mepiquat	114.1	98.1	30
Paraquat-d ₈	97	179	19
Paraquat	93	171	19
Diquat-d ₈	96	88.5	19
Diquat	92	157.1	19

Results

The IC and SRM chromatograms of a standard are shown in Figure 3, while the IC and SRM chromatograms of a diluted, formic acid-methanol extracted oatmeal sample are shown in Figure 4. The pesticide peaks are well resolved by IC-MS/MS. Calibration curves (not shown) were generated by the MS responses to five standards from 1-100 µg/L and found to be second order, quadratic. The estimated LODs, using 3x S/N *t*-test were 0.07-0.09 µg/L.

Tables 3 and 4 summarize the recovery data and results for incurred residues which were well below the respective EU MRLs.

Figure 3. IC (left) and SRM (right) chromatograms show separation of mixed cations and resolution of quaternary amine pesticide standards.



IC Chromatogram. Analyte peaks are well resolved from matrix peaks. Peaks 1. Sodium; (30 µg/L); 2. Ammonium (10); 3. Potassium (10); 4. Unknown; 5. Chlormequat; (50); 6. Mepiquat-d₁₆; (50); 7. Mepiquat; (50); 8. Magnesium; (10); 9. Calcium; (20); 10. System peak; 11. Paraquat; (50); 12. Diquat; (50).

SRM Chromatograms. Peaks 1. Chlormequat-d₄; 2. Chlormequat; 3. Mepiquat-d₁₆; 4. Mepiquat; 5. Paraquat-d₈; 6. Paraquat; Diquat-d₈; 8. Diquat

Figure 4. SRM chromatograms of formic acid-methanol extracted oatmeal showing: A) quaternary amine pesticides and B) added quaternary amine pesticide standards.

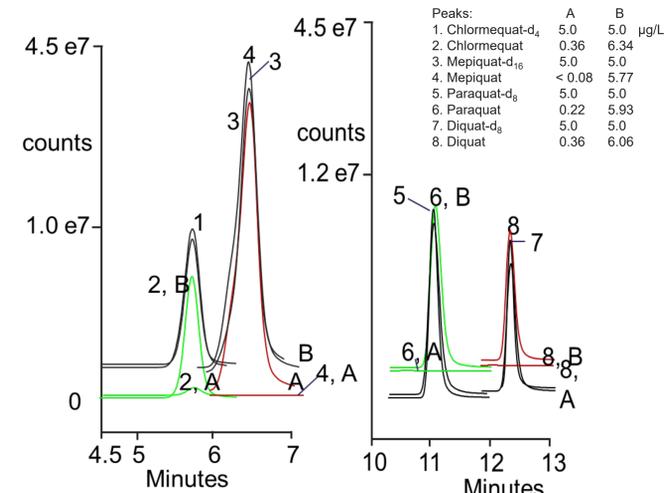


Table 3. Recovery results of 5 µg/L of added standard.

	Chlormequat		Mepiquat		Paraquat		Diquat	
	Found (µg/L)	Rec. (%)						
Ground Oatmeal								
A	0.36	117	<0.08	116	0.22	113	0.36	113
B	0.51	98.9	<0.08	118	0.24	95.4	0.37	96.3
Ground Toasted Oats								
A	<0.09	85.8	<0.08	85.6	0.29	88.2	0.42	94.3
B	<0.09	96.5	<0.08	113	0.24	95.4	0.37	90.8

A: formic acid-methanol extraction.
B: HCl-methanol extraction.

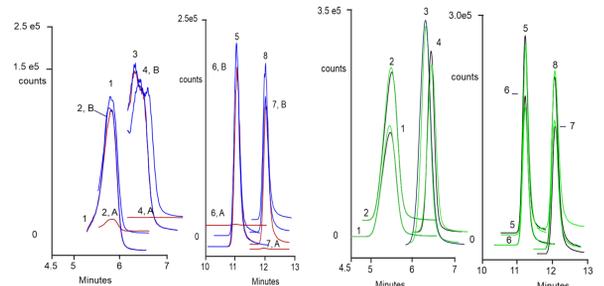
Table 4. Incurred residue results.

	Chlormequat	Mepiquat	Paraquat	Diquat
	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)
EU MRLs	15	3.0	0.02	2.0
Ground Oatmeal				
A	0.00072	< 0.00021	0.00044	0.00071
B	0.00102	< 0.00021	0.00047	0.00074
Ground Toasted Oats				
A	< 0.00046	< 0.00042	0.00116	0.00168
B	< 0.00046	< 0.00042	0.00094	0.00147

A: formic acid-methanol extraction.
B: HCl-methanol extraction.

Matrix interferences observed with HCl-methanol extracted toasted oat cereal (Figure 5) were removed by introducing a 15 min wash (1 mM MSA) as shown in Figure 6.

Figure 5. Matrix impacting responses: HCl extraction of toasted oats cereal **Figure 6. Added 1 mM MSA wash for 15 min**



HCl-methanol extracted toasted oat cereal with 5 µg/L ISTD and unlabeled standard. Peaks 1. Chlormequat-d₄; 2. Chlormequat; 3. Mepiquat-d₁₆; 4. Mepiquat; 5. Paraquat-d₈; 6. Paraquat; 7. Diquat-d₈; 8. Diquat.

Conclusions

This application note demonstrated an IC-MS/MS method for accurate (86 to 118% recoveries), and sensitive limits of determinations of < 0.1 µg/L or < 0.5 µg/kg for, chlormequat, diquat, mepiquat, and in oat cereals.

These determinations were facilitated by a Dionex IonPac CS21-Fast-4µm column which was specifically designed to resolve cations and quaternary amines, including the paraquat and diquat ions. More information can be found in Technical Note TN73990 and Application Note AN000607 in AppsLab.com^{3,4}

References

- Kolberg, D.I.S, Mack, D., Anastasiades, M., Hetmanski, M.T., Fussell, R.J., Meijer, T., Mol, H.G. DOI 10.1007/s00216-012-6340-9
- European Commission, Quick Polar Pesticide method, QuPPE-PO_v.12
- Madden, J.E., Saini, C., Thermo Scientific TN73990
- Christison, T., Madden, J.E., Rohrer, J. Thermo Scientific AN000607

Further information

<https://www.thermofisher.com/uk/en/home/about-us/events/industrial/polar-pesticides.html>
<https://www.thermofisher.com/anionicpesticides>

Trademarks/licensing

© 2022 Thermo Fisher Scientific Inc. All rights reserved. All trademarks are the property of Thermo Fisher Scientific. EURL is a trademark of European Commission and European Research Laboratories. This information is presented as an example of the capabilities of Thermo Fisher Scientific products. It is not intended to encourage use of these products in any manner that might infringe the intellectual property rights of others.