TECHNICAL NOTE 73990

Determination of four quaternary ammonium polar pesticides in food and beverage samples by tandem IC-MS/MS

Authors: John Madden, Charanjit Saini, Chris Pohl, and Yan Liu
Thermo Fisher Scientific, Sunnyvale, CA

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Goal

To demonstrate the new Thermo Scientific™ Dionex™ IonPac™ CS21-Fast-4µm cation exchange column for baseline chromatographic resolution of quaternary amine cationic polar pesticides in complex matrices, and detection, identification, and quantitation at low concentrations, when used with a Thermo Scientific™ Dionex™ ICS-6000 or Thermo Scientific™ Dionex™ Integrion™ Ion Chromatography System coupled to a triple quadrupole electrospray mass spectrometer system

Introduction

Ionic polar pesticides include some of the most frequently used pesticides worldwide.[1] Recent developments in the analysis of anionic polar pesticides[2] have led to an increase in testing and regulation in surface and drinking water as well as food and beverages. However, developments in the analysis of cationic polar pesticides have lagged their anionic counterparts, primarily because of the analytical challenges and high costs associated with the analysis. The current IC-MS method requires the use of an HRAM instrument due to poor chromatographic resolution of the paraquat—diquat pair.[3,4]

The most popular extraction method for ionic polar pesticides is the Quick Polar Pesticides (QuPPe) extraction method developed by the European Reference Laboratory for Single Residue Methods (EURL-SRM).[5] The method is based on extraction with methanol/water, followed by centrifugation and filtering. Because no liquid/liquid partitioning or sold phase extraction is used, the extracts can contain high levels of co-extractives that can contaminate the MS detection system and suppress the MS response if adequate resolution of the analytes from the matrix is not achieved. Thus, ion chromatography (IC) has become the preferred separation technique for polar ionic analytes in the presence of high levels of anions, cations, and sugars.

Mass spectrometry, specifically triple quadrupole MS/MS systems, offers very low detection limits and high detection selectivity when operated in selected reaction monitoring (SRM) mode. The system robustness allows the analysis of food and environmental samples. The aim of this work is to develop and validate an IC-MS/MS method for the direct analysis of polar cationic pesticides (Figure 1) in various simulated and real samples and to assess its applicability under routine conditions.

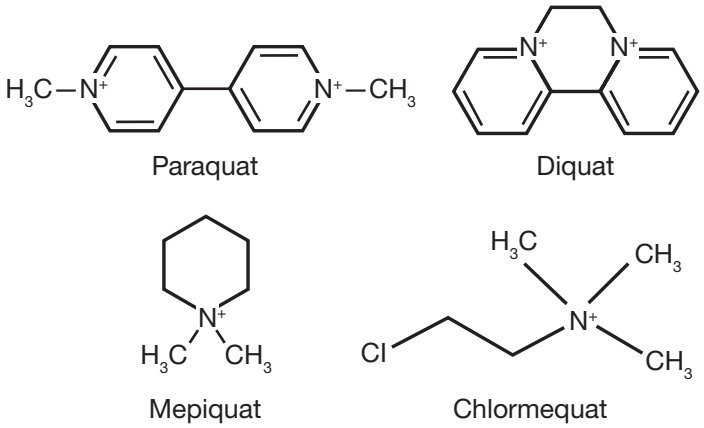

Figure 1. Four target compounds

Experimental

Sample preparation

Simulated samples were prepared by diluting the appropriate amount of Six-Cation Std II in deionized water to obtain the total ionic strength (TIS) desired.

Tea infusions were prepared by boiling 10.0 g of tea leaves in 100 mL of water for 30 s, then allowing the mixture to cool before filtering.

For the carrot baby food and wheat flour samples, the same technique developed for the extraction of anionic polar pesticides[6] in food was used. This technique is a simplified version of the QuPPe method developed by the EU Reference Laboratory for Residues of Pesticides in Stuttgart, Germany.[7] By using the same sample preparation method, samples prepared for anionic polar pesticide analysis can be analyzed for cationic polar pesticides without modification.

Instrumentation

- Thermo Scientific™ Dionex™ ICS-6000™ HPIC™ System
  - Thermo Scientific™ Dionex™ AS-AP Autosampler
  - Thermo Scientific™ Dionex™ ICS-6000 DP Dual Pump
  - Thermo Scientific™ Dionex™ ICS-6000 EG Eluent Generator
  - Thermo Scientific™ Dionex™ ICS-6000 DC Detector/ Chromatography Compartment
- Thermo Scientific™ TSQ Altis™ Triple Quadrupole MS
- Thermo Scientific™ Dionex™ AXP-MS Auxiliary Pump
- System control and data evaluation by Thermo Scientific™ Chromeleon™ 7.2.10 software

Consumables

- Thermo Scientific™ Dionex™ EGC 500 MSA Eluent Generator Cartridge, P/N 075779
- Thermo Scientific™ Dionex™ CDRS 600 (2 mm) Cation Dynamically Regenerated Suppressor, P/N 088670
- Thermo Scientific™ Dionex™ CR-CTC II Continuously Regenerated Cation Trap Column, P/N 066262
- Thermo Scientific™ Dionex™ IonPac™ CS21-Fast-4µm Analytical Column (2 × 150 mm), P/N 303348
- Thermo Scientific™ Dionex™ IonPac™ CG21-Fast-4µm Guard Column (2 × 30 mm), P/N 303349

Reagents and standards

- Deionized (DI) water, 18 MΩ·cm resistivity (ASTM Type I water), 0.2 µm
- Thermo Scientific™ Dionex™ Six Cation-II Standard, P/N 046070
- Chem Service, Inc. Diquat dibromide monohydrate, P/N N-11816-500MG

- Honeywell Fluka™ PESTANAL™ Mepiquat chloride, P/N 36151-100MG
- Honeywell Fluka™ PESTANAL™ Paraquat dichloride hydrate, P/N 36541-100MG
- Honeywell Fluka™ PESTANAL™ Chlormequat chloride, P/N 45387-250MG
- Absolute Standards, Inc. Paraquat-d8, P/N 95305
- Absolute Standards, Inc. Chlormequat-1,1,2,2-d4 chloride, P/N 96081
- Absolute Standards, Inc. Mepiquat-d16 chloride, P/N 96082
- C/D/N Isotopes, Inc. Diquat-d8 Dibromide (dipyridine-d8), P/N D-7990

Instrument and method setup

The instrument system comprised a metal-free Dionex ICS-6000 HPIC ion chromatograph and Dionex AS-AP autosampler coupled to a TSQ Altis mass spectrometer via a six port divert valve, as shown in Figure 2. By switching the divert valve it is possible to divert flow from the IC away from the mass spectrometer while maintaining a constant flow to the suppressor / Thermo Scientific™ Dionex™ CR-TC Continuously Regenerated Trap Column Regen path and the mass spectrometer, as shown in Figure 3. If the IC pump and auxiliary pump are set to the same flow rate, flow to both the suppressor / Dionex CR-TC Regen path and the mass spectrometer remains constant as the system is switched between Analyze and Divert modes. This way the matrix ions can be diverted away from the mass spectrometer without interrupting system equilibrium.

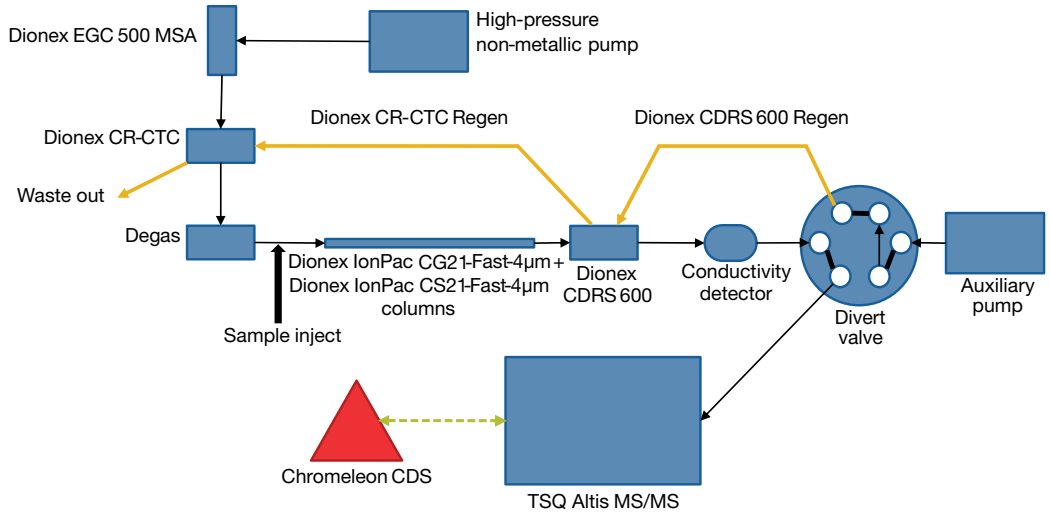

Figure 2. IC-MS/MS system in Analyze Mode (Flow from IC enters MS; flow from auxiliary pump enters suppressor and Dionex CR-CTC 600 Regen path)

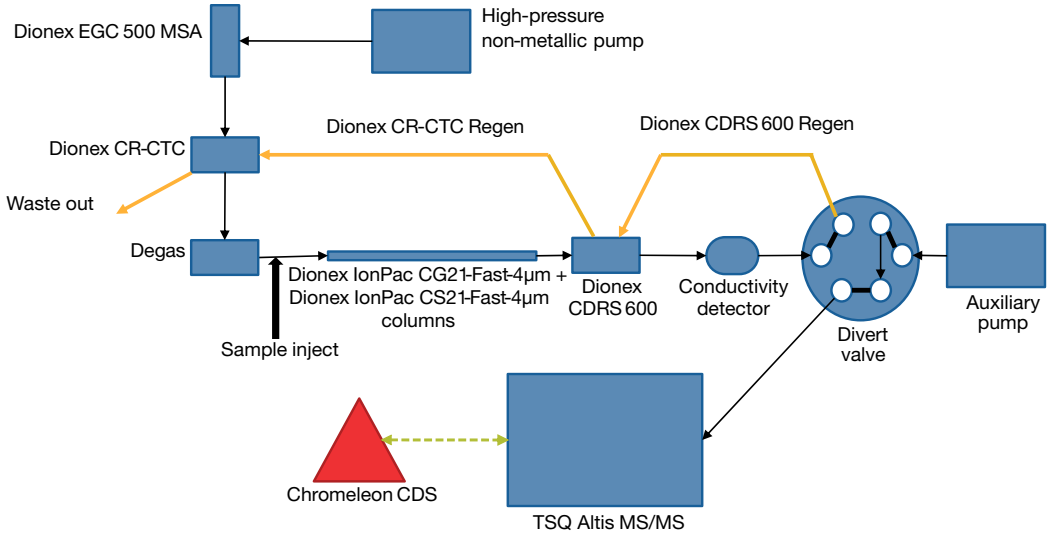

Figure 3. IC-MS/MS system in Divert Mode (Flow from IC is diverted away from MS to suppressor and Dionex CR-TC 600 Regen path; flow from auxiliary pump enters MS)

The chromatographic separation was carried out using a Dionex IonPac CS21-Fast-4µm column with guard in the 2 mm format. This column was developed specifically to address the diquat—paraquat co-elution issue identified on the Dionex IonPac CS17 column, as well as to speed up the analysis. On the Dionex IonPac CS21-Fast-4µm column, the separation of the four quaternary amines with an electrolytically generated methanesulfonic acid (MSA) gradient is achieved in 15 min. Under these conditions, the main cationic matrix components lithium, sodium, ammonium, potassium, magnesium, and calcium elute from the Dionex IonPac CS21-Fast-4µm column in two zones without impairing the resolution of the four quaternary amine cationic polar pesticides, see Figures 4 and 5. Instrument parameter details are listed in Tables 1 and 2.

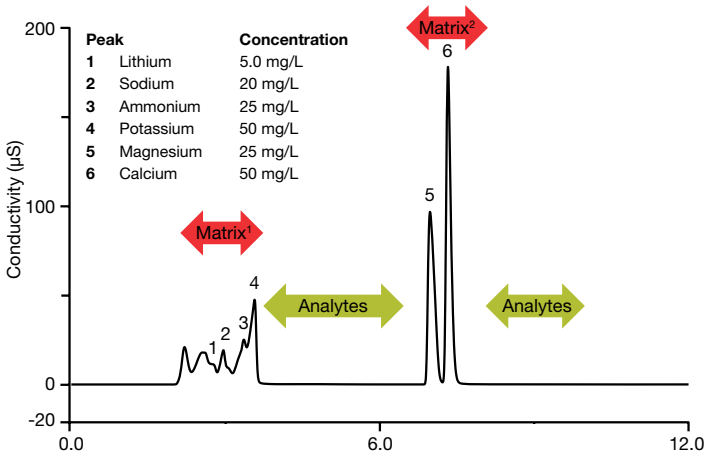

Figure 4. Chromatographic separation of the matrix components in the simulated matrix; Li, Na, NH_4, and K (Matrix Zone 1), and Mg and Ca (Matrix Zone 2) using the Dionex IonPac CS21-Fast-4µm column and the conditions outlined in Tables 1 and 2 with suppressed conductivity detection

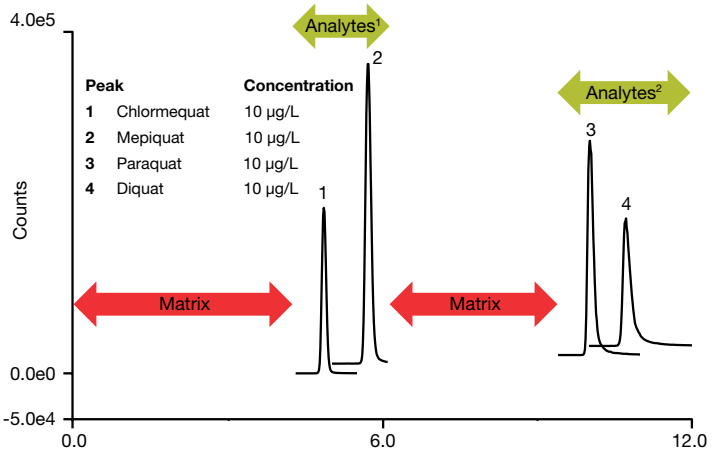

Figure 5. Chromatographic separation of the four quaternary ammonium polar pesticides—CQ and MQ (Analyte Zone 1), and PQ and DQ (Analyte Zone 2) using the Dionex IonPac CS21-Fast-4µm column and the conditions outlined in Tables 1 to 4 with suppressed Mass Selective detection

Table 1. IC conditions

Mobile phase	MSA (Gradient conditions in Table 2)
Eluent source	Dionex EGC 500 MSA Dionex CR-CTC 600
Column	Dionex IonPac CS21-Fast-4µm with Guard
Suppressor	Dionex CDRS 600 (2 mm), 22 mA
External flow pump	0.3 mL/min
Eluent flow rate	0.3 mL/min
Injection volume	10 µL
Column temperature	40 °C

Table 2. Gradient conditions

Time (min)	MSA concentration (mM)
-4.0	3.0
0.0	3.0
3.6	6.0
6.0	22.0
15.0	25.0

After separation, the eluent is passed through the electrolytically regenerated Dionex CDRS 600 suppressor where the anions from the eluent and sample are replaced with hydroxide ions, effectively neutralizing the acidic eluent and rendering it compatible with the mass spectrometer. Water flow to maintain the electrolytic processes of the suppressor and Dionex CR-TC is supplied by the Auxiliary Pump (Analyze Mode, Figure 2) or by recycling the waste from the conductivity detector (Divert Mode, Figure 3). No make-up solvent was employed.

To prevent contamination of the mass spectrometer ESI ion source, the divert valve must always be in the divert position when the conductivity detector reads above 3 µS/cm or when not actively collecting data. During data collection, Chromeleon software can be programmed to automatically move the divert valve to the divert position when an error is detected, or when the conductivity reading rises above 3 µS/cm. Application Note 73339[8] contains a detailed section titled “Creating IC-MS methods with emergency shutdown subprograms” that explains how to set up Chromeleon software to do this. The High conductivity emergency trigger should be set to a high level of 3 µS/cm and set time of 10 s.

Mass spectrometer conditions

Data acquisition was performed in Selected Reaction Monitoring mode (SRM). All SRM traces (parent, quantifier, and qualifier ions) were individually tuned for each target analyte by injecting the corresponding standard solution (100 µg/L). The global mass spectrometer parameters are shown in Table 3, and SRM parameters for analyzing targeted analytes are shown in Table 4.

Calculations

Identification of the pesticides was indicated by the presence of two transition ions measured in SRM mode corresponding to the retention times of standards (±0.1 min). The quantifier and qualifier ions were selected among the product ions produced by the fragmentation of the selected precursor ion based on their intensity and selectivity. The highest intensity fragmentation ion was used as the quantifier ion, the second highest as the qualifier ion.

Table 3. Mass spectrometer global parameters

Ionization mode	Heated Electrospray (H-ESI)
Scan type	Selected Reaction Monitoring (SRM)
Polarity	Positive
Spray voltage	2,800 V
Sheath gas	45 Arb
Auxiliary gas	2.5 Arb
Sweep gas	2.0 Arb
Ion transfer tube temp	350 °C
Vaporizer temp	300 °C
Cycle time	0.8 s
Q1 resolution (FWHM)	0.7
Q3 resolution (FWHM)	1.2
Collision gas (CID)	1.5 mTorr
Source fragmentation	10 V

For quantification, a single point calibration was applied. To account for potential detector non-linearity, the calibration concentration was selected to be in the same order of magnitude as the target analyte. It is recommended that if the target analyte is found to be more than one order of magnitude away from the calibration, a fresh sample should be spiked with a matching calibration concentration.

Due to expected matrix-induced signal suppression (matrix effects), the quantification for all matrices (teas, vegetables, and grains) was performed by isotopically labeled internal standard addition. A normalization run with all four target analytes along with their isotopically labeled versions at 10 µg/L was used to normalize the ratio of the response between the naturally occurring and isotopically labeled analyte isotopologues (Table 5). These ratios were applied to all measured isotopically labeled internal standards.

Table 4. IC-MS/MS parameters for selected reaction monitoring transitions

Compound	Acquisition window (min)	Transition type	Precursor (*m/z*)	Product (*m/z*)	Collision energy (V)
Chlormequat	4.3–5.5	Quantifier	122.1	57.9	30
		Qualifier	122.1	62.9	30
Chlormequat-d4	4.3–5.5	Quantifier	126.0	57.9	30
Mepiquat	5.0–6.1	Quantifier	114.1	98.1	30
		Qualifier	114.1	58.0	30
Mepiquat-d16	5.0–6.1	Quantifier	130.0	110.0	30
Paraquat	9.4–11.0	Quantifier	93.0	171.0	19
		Qualifier	93.0	85.0	19
Paraquat-d8	9.4–11.0	Quantifier	97.0	179.0	19
Diquat	10.0–12.0	Quantifier	92.0	84.5	19
		Qualifier	92.0	157.1	19
Diquat-d8	10.0–12.0	Quantifier	96.0	88.5	19

Table 5. Response ratios of the naturally occurring and isotopically labeled analytes at 10 µg/L

Compound	Response (count·min @ 10 µg/L)	Ratio
Chlormequat	25,207	0.8166
Chlormequat-d4	30,867	
Mepiquat	56,071	0.8484
Mepiquat-d16	66,089	
Paraquat	64,132	0.9445
Paraquat-d8	67,902	
Diquat	55,661	1.0561
Diquat-d8	52,705	

Measurement precision was evaluated by spiking standard solutions into DI water, simulated matrix, tea samples, and QuPPe extracted food samples at three concentrations levels for each quaternary amine polar pesticide in replicates of five. The isotopically labeled isotopes were spiked in at the same level as the standard analytes prior to injection.

Results and discussion

The objective of this study was to evaluate the possibility of an IC-MS/MS application for the fast routine analysis of cationic polar pesticides in food and beverage extracts. Various analytical parameters were assessed, and the results of these experiments are described.

Samples

For recovery experiments, blank matrices of DI water, simulated matrix (TIS = 25 and 250 mg/L), green tea, white tea, carrot baby food and wheat flour were used. Sample preparation was performed as described above. For the remaining experiments, DI water and simulated matrix (TIS = 250 mg/L) were used.

Matrix effects

When considering the calibration of the system, the possibility of matrix-induced signal suppression in the HESI ion source must be considered. The most severe signal suppression was observed during the analysis of high ionic strength matrices, such as the simulated matrix upon the divalent species (paraquat and diquat).

To examine the influence of high ion matrix concentrations on the measurements, a simulated matrix was prepared with a TIS of 250 mg/L. This sample was based on IC analysis of a QuPPe baby carrot food extraction and consisted of 5 mg/L Li^+, 20 mg/L Na^+, 25 mg/L NH_4^+, 50 mg/L K^+, 25 mg/L Mg^{2+}, and 50 mg/L Ca^{2+}. The multi-standard solution with a concentration of 1 mg/L of the four quaternary polar pesticides was diluted using this simulated matrix. Multi-level responses for four target analytes were prepared in both the simulated matrix as well as in DI water.

Figures 6 and 7 present the differences in response curves obtained for chlormequat and mepiquat (monovalent species) and paraquat and diquat (divalent species) in the two different matrices and their effect on the MS signals.

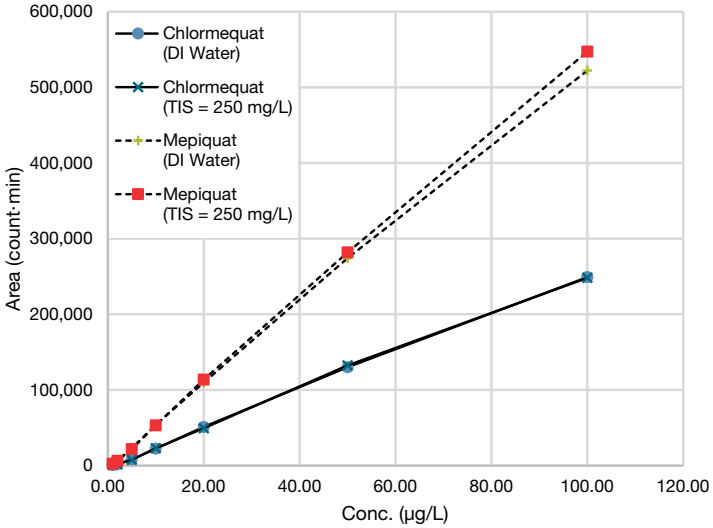

Figure 6. Response curves of CQ (solid lines) and MQ (dashed lines) obtained in two different matrices (deionized water and simulated matrix with TIS = 250 mg/L)

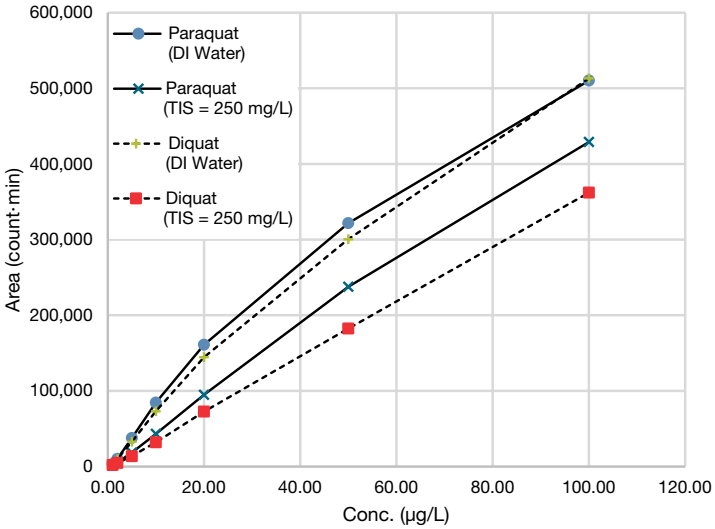

Figure 7. Response curves of PQ (solid lines) and DQ (dashed lines) obtained in two different matrices (deionized water and simulated matrix with TIS = 250 mg/L)

For chlormequat and mepiquat, almost no matrix dependency was observed. However, paraquat and diquat sensitivity and response were strongly affected by the high ionic strength of the simulated matrix. It should be noted that the simulated matrix was selected to imitate the maximum concentration levels seen in real-life food extracts; thus, the concentrations of the major cationic components can be expected to be lower in real-life food extracts.

Two of the most common techniques to compensate for the effects of matrix-induced MS ion source signal suppression are matrix-matched calibration and isotopically labeled internal standard addition. Isotopically labeled internal standard addition has the benefit of being more robust and less laborious but requires isotopically labeled compounds to be readily available. For this study isotopically labeled internal standard addition was used as isotopically labeled chlormequat, mepiquat, diquat, and paraquat are all readily available.

Figures 8 and 9 present the normalized response curves obtained for chlormequat and mepiquat, and paraquat and diquat in the two different matrices. Signals for the analytes were normalized against the responses of isotopically labeled compounds spiked into the sample at the same concentration. The effect of normalizing the response compensates for the effect of signal suppression, improving both the linearity (Table 6) and the reproducibility of the responses.

Identification

Identification was based on the presence of the transition ions (quantifier and qualifier) at the retention times corresponding to those of the respective target compounds. The measured peak area ratios of qualifier/quantifier were within a range of ±40% (relative), and the retention time difference of qualifier and quantifier within 0.1 min. Identification was assessed by analyzing DI water and simulated matrix (TIS = 250 mg/L) spiked at 1.0, 10.0, and 100 µg/L for all analytes (Table 7).

Limits of quantitation and detection

Raw detector performance was assessed by analyzing DI water and a simulated matrix (TIS = 250 mg/L) spiked at different concentration levels down to 1 µg/L for all analytes. The LOQ was determined as the lowest calibration level meeting the 20% RSD criterion. Table 8 shows the detector precision at 1.0 µg/L for the four pesticides, the lowest level assessed; based on this criterion the LOQs for all four compounds were determined to be at or below 1 µg/L.

By measuring the ratio of naturally occurring analyte to a separately spiked isotopically labeled analyte, the overall precision is improved by mitigating matrix-induced signal suppression in the detector. Thus, normalized precision (Table 9) outperforms raw detector precision (Table 8) considerably.

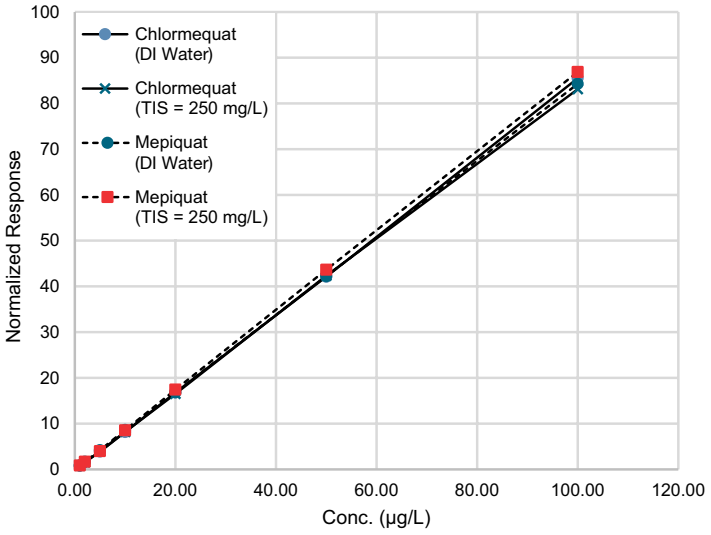

Figure 8. Normalized response curves of CQ (solid lines) and MQ (dashed lines) obtained in two different matrices (DI water and simulated matrix with TIS = 250 mg/L)

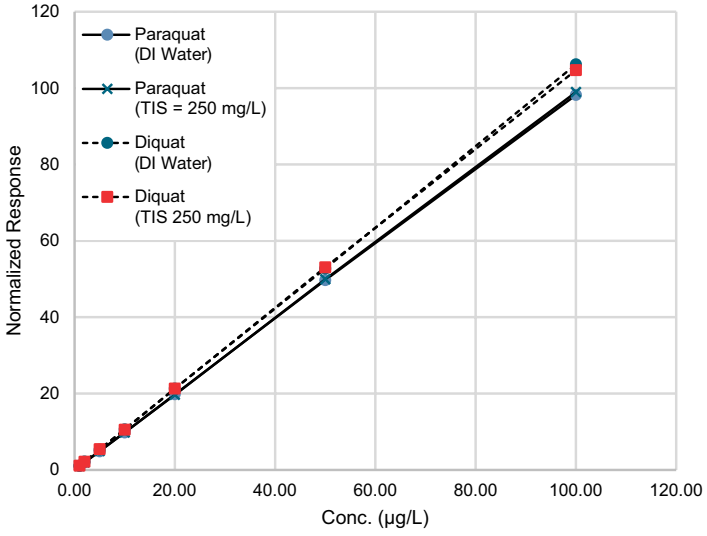

Figure 9. Normalized response curves of PQ (solid lines) and DQ (dashed lines) obtained in two different matrices (DI water and simulated matrix with TIS = 250 mg/L)

LOQ and LOD can be more accurately calculated by the t-test method, based on standard deviation and slope of the calibration curve, where LOQ = 10σ/Slope and LOD = 3.3σ/Slope for n=7. The slope of the calibration curve was measured across the range 1–10 µg/L by injecting three samples at 1.0, 3.0, and 10.0 µg/L. The results of the t-test calculations are shown in Table 10.

Table 6. Normalized response linearity data of four quaternary polar pesticides in two different matrices

Compound	Matrix	Range (µg/L)	r^2
Chlormequat	DI water	1.0–100	0.9999
Mepiquat	DI water	1.0–100	1.0000
Paraquat	DI water	1.0–100	1.0000
Diquat	DI water	1.0–100	1.0000
Chlormequat	Simulated matrix	1.0–100	0.9999
Mepiquat	Simulated matrix	1.0–100	1.0000
Paraquat	Simulated matrix	1.0–100	1.0000
Diquat	Simulated matrix	1.0–100	1.0000

Table 7. Ion ratios (Quan/Qual) in DI water and simulated matrix (TIS = 250 mg/L) at three spike levels (n = 3)

Compound	Ions	Ion ratio					
		DI water			Simulated matrix (TIS = 250 mg/L)		
		1.0 µg/L	10 µg/L	100 µg/L	1.0 µg/L	10 µg/L	100 µg/L
Chlormequat	122.1→57.9 / 122.1→62.9	0.12	0.13	0.21	0.13	0.12	0.20
Mepiquat	114.1→98.1 / 114.1→58.0	0.19	0.30	0.35	0.19	0.28	0.35
Paraquat	93.0→171.0 / 93.0→85.0	0.17	0.16	0.17	0.19	0.15	0.17
Diquat	92.0→84.5 / 92.0→157.1	0.21	0.31	0.34	0.19	0.23	0.32

Table 8. Results of non-corrected precision data (expressed as relative standard deviation—% RSD) at spike level 1.0 µg/L, (n=7)

Compound	RSD	
	DI water	Simulated matrix (TIS = 250 mg/L)
Chlormequat	17.5%	19.7%
Mepiquat	5.7%	18.6%
Paraquat	14.3%	11.9%
Diquat	11.5%	8.2%

Table 9. Results of normalized precision (expressed as RSD) at spike level 1.0 µg/L, (n = 7). Response ratio to the isotopically labeled internal standard was used to compensate for matrix induced signal suppression.

Compound	RSD	
	DI water	Simulated matrix (TIS = 250 mg/L)
Chlormequat	1.6%	1.8%
Mepiquat	2.8%	12.1%
Paraquat	2.1%	2.9%
Diquat	1.8%	1.5%

Table 10. Results of t-test detection limits (expressed as µg/L) at spike level 1.0 µg/L, (n=7)

Compound	Detection limits (µg/L)			
	DI water		Simulated matrix (TIS = 250 mg/L)	
	LOD	LOQ	LOD	LOQ
Chlormequat	0.02	0.05	0.02	0.05
Mepiquat	0.05	0.14	0.21	0.65
Paraquat	0.05	0.14	0.06	0.18
Diquat	0.04	0.13	0.04	0.11

Instrument precision and accuracy

The method's precision and accuracy were determined by analyzing five replicates of DI water samples fortified with the working solution at 1, 10, and 100 µg/L. Isotopically labeled calibrant was spiked into each sample at the same concentration as the target analytes. The relative standard deviation (RSD) for the amount ranged from 0.8 to 2.9% for the 1 µg/L spike, 0.2 to 0.8% for the 10 µg/L spike, and 0.3 to 0.6% for the 100 µg/L spike. The accuracy of the method was evaluated by determining the apparent recoveries of the quaternary amine polar pesticides. Excellent results were achieved with all apparent recoveries in the 80–120% range, as shown in Table 11.

Effect of matrix

Additional data on the accuracy of the method was obtained by analyzing simulated matrix, green tea, white tea, non-acidified QuPPe extracted carrot baby food, and non-acidified QuPPe extracted wheat flour samples fortified with the working solution. The tea and QuPPe extracts were diluted one in ten with DI water prior to fortification and analysis. The absence of the target analytes in the tea and QuPPe extracts was also checked prior to fortification. Isotopically labeled calibrant was spiked into the samples at the same concentration as the target analytes immediately before injection. Five replicates at three different concentration levels were analyzed for each of these samples. Excellent results were achieved with all apparent recoveries in the 80–120% range (Table 12).

Table 11. Instrument apparent recoveries for four quaternary amine polar pesticides in a DI water matrix

Compound	Corrected apparent recoveries in DI water (%)		
	1.0 µg/L	10 µg/L	100 µg/L
Chlormequat	100	105	103
Mepiquat	102	102	99
Paraquat	100	98	95
Diquat	102	105	101

Table 12. Instrument apparent recoveries for four quaternary amine polar pesticides in a series of simulated, beverage and food matrices over a period of 7 days

Compound	Corrected apparent recoveries in simulated matrix (25 mg/L) (%)		
	1.0 µg/L	10 µg/L	100 µg/L
Chlormequat	91	96	97
Mepiquat	108	96	95
Paraquat	101	96	96
Diquat	98	96	94

	Corrected apparent recoveries in simulated matrix (250 mg/L) (%)		
	1.0 µg/L	10 µg/L	100 µg/L
Chlormequat	100	101	102
Mepiquat	94	101	102
Paraquat	106	102	101
Diquat	102	102	102

	Corrected apparent recoveries in green tea (1/10) (%)		
	1.0 µg/L	10 µg/L	100 µg/L
Chlormequat	96	100	103
Mepiquat	101	100	103
Paraquat	103	99	99
Diquat	104	102	100

	Corrected apparent recoveries in white tea (1/10) (%)		
	1.0 µg/L	10 µg/L	100 µg/L
Chlormequat	92	99	101
Mepiquat	92	99	101
Paraquat	106	102	102
Diquat	105	103	102

	Corrected apparent recoveries in QuPPe extracted carrot baby food (1/10) (%)		
	1.0 µg/L	10 µg/L	100 µg/L
Chlormequat	89	98	102
Mepiquat	91	100	100
Paraquat	104	99	98
Diquat	100	100	97

	Corrected apparent recoveries in QuPPe extracted wheat flour (1/10) (%)		
	1.0 µg/L	10 µg/L	100 µg/L
Chlormequat	95	102	106
Mepiquat	100	100	104
Paraquat	106	105	105
Diquat	111	111	109

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Conclusion

Determinations of four quaternary amine cationic polar pesticides using IC-MS/MS were demonstrated in target analytes in simulated matrices, diluted teas, and diluted extracted homogenized food samples.

- In these experiments, the SRM Selected Reaction Monitoring mode used to extract ions of interest from the matrix was effective for qualitative and quantitative determinations in selected food and beverage samples.
- The Dionex IonPac CS21-Fast-4µm column was effective at separating the four quaternary amine cationic polar pesticides from the matrix and each other, making it possible to identify and quantitate all four target compounds using nominal mass selectivity.
- The IC method demonstrated high accuracy (80–120% instrument precision values for all samples.
- In contrast to methods described in the literature, sample preparation was simplified. For the food samples, the sample preparation is consistent with the already established simplified QuPPe method making it possible to screen for both anionic and cationic polar pesticides with a single sample extraction.
- This method can be recommended as a reliable and cost-effective addition to any routine lab dealing with the determination of the target cationic pesticides in a wide range of samples.

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