

Fast determination of cationic polar pesticides in high ionic strength samples

Keywords: Cation exchange chromatography, inorganic cations, quaternary amines, chlormequat, mepiquat, diquat, paraquat, IC-MS/MS

Benefits

- Optimized for use with IC-MS, IC-MS/MS, and IC-HRAM-MS
- Resolves diquat and paraquat
- Elutes quaternary amines away from sample cations
- Solvent compatible

The Thermo Scientific™ Dionex™ IonPac™ CS21-Fast-4μm cation-exchange column is recommended for the analysis of quaternary amine cationic polar pesticides including chlormequat, mepiquat, paraquat, and diquat using suppressed conductivity coupled with triple-quadrupole mass spectrometric detection. The Dionex IonPac CS21-Fast-4μm column is ideally used with a Thermo Scientific™ Dionex™ Reagent-Free™ Ion Chromatography (RFIC™) system for automatic methanesulfonic acid (MSA) eluent generation, and electrolytic eluent suppression. Available in a 2 x 150 mm column format, the Dionex IonPac CS21-Fast-4μm column has been optimized for use with mass spectrometers, allowing flow rates from 0.3 mL/min to 0.375 mL/min without the need for make-up solvents or flow splitting.



- Compatible with temperatures ranging from 20°C to 60°C to improve some critical pair separations.
- Compatible with 100% organic solvents such as acetonitrile and acetone (excluding alcohols) to enhance analyte solubility, modify column selectivity, and allow effective column cleanup.
- Microbore format is compatible with mass spectrometry flow rates and offers reduced eluent consumption and lower operating costs.
- Fast analysis of cationic polar pesticides in diverse sample matrices including environmental waters, foods, and beverages.

High-efficiency particle structure

The Dionex IonPac CS21-Fast-4 μ m column is a high capacity, hydrophilic cation exchange column that provides excellent peak shape and selectivity for cationic polar pesticides. The macroporous resin bead structure of the Dionex IonPac CS21-Fast-4 μ m column is composed of a highly cross-linked polymeric 4 μ m substrate. The raw resin bead is then grafted with carboxylic acid groups as shown in Figure 1.

Specifically designed to separate quaternary amine cationic polar pesticides

The Dionex IonPac CS21-Fast-4 μ m column features a large separation window between monovalent and divalent cations, making it ideal for eluting most quaternary amine cationic polar pesticides between the alkali and alkaline earth metals. This large separation window is advantageous for samples that typically pose quantitation challenges, where amines are present at much lower concentrations than matrix cations.

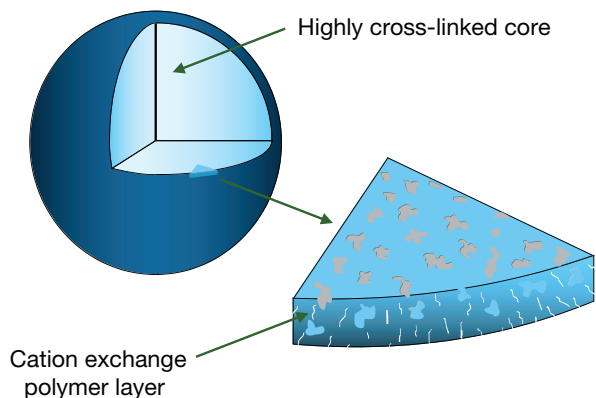


Figure 1. Structure of a Dionex IonPac CS21-Fast-4 μ m resin particle

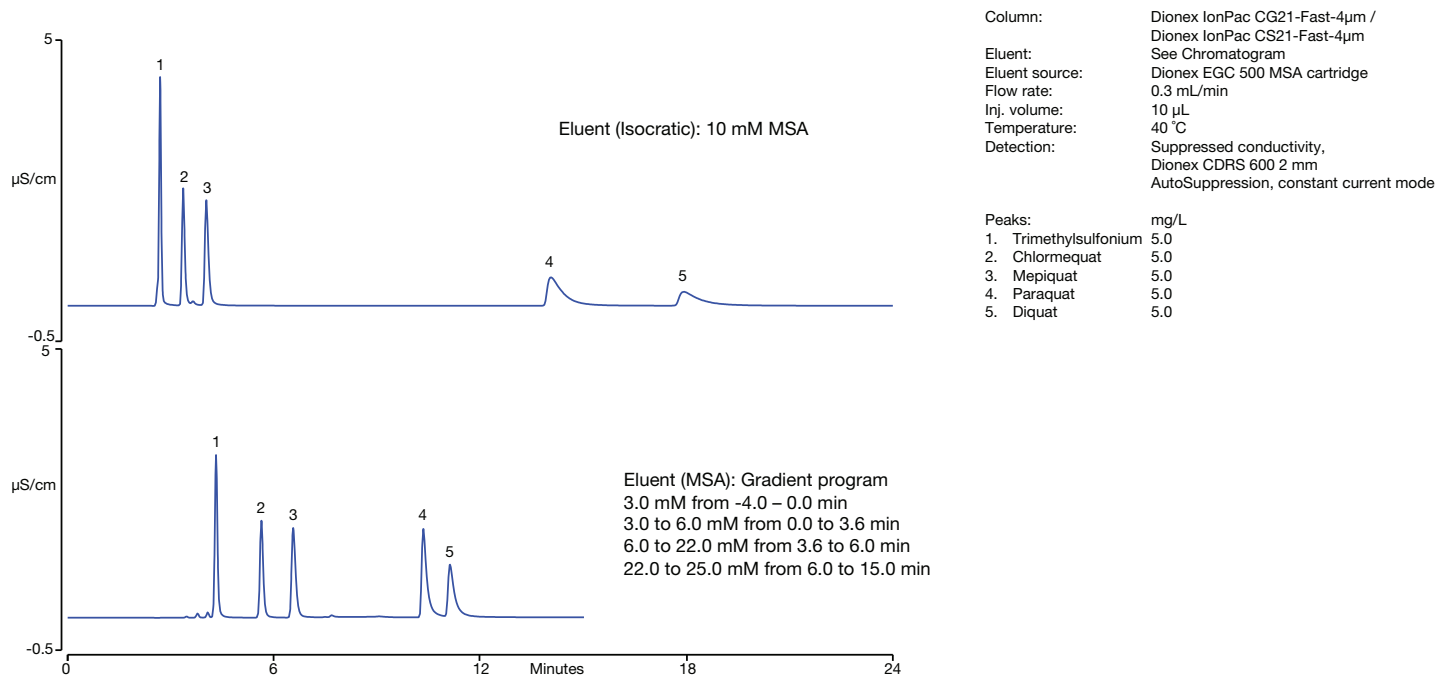


Figure 2. Comparison of isocratic and gradient separation of four quaternary amine cationic polar pesticides and trimethylsulfonium using a Dionex IonPac CS21-Fast-4 μ m column

Optimized selectivity for analyses in high ionic strength matrices

The Quick Polar Pesticides (QuPPE) method, developed by the European Union Reference Laboratories for Single Residue methods (EURL-SRM), is the recommended approach for extracting polar analytes from food samples. Samples prepared by QuPPE method often contain high concentrations of matrix ions that make accurate quantification difficult. Figure 3 illustrates the separation of four quaternary amine cationic polar pesticides in a high ionic strength matrix using the Dionex IonPac

CS21-Fast-4µm column. These analytes can be separated in approximately 15 min using an electrolytically generated MSA gradient and suppressed conductivity detection. Figure 4 shows that more sensitive determination of these analytes at 1 µg/L can be achieved using IC-MS/MS detection. The selectivity of the Dionex IonPac CS21-Fast-4µm column allows good separation of chlormequat, mepiquat, paraquat, and diquat from common inorganic cations in the sample matrix. Matrix ions can be diverted to waste, leaving only the analytes of interest going to the mass spectrometer.

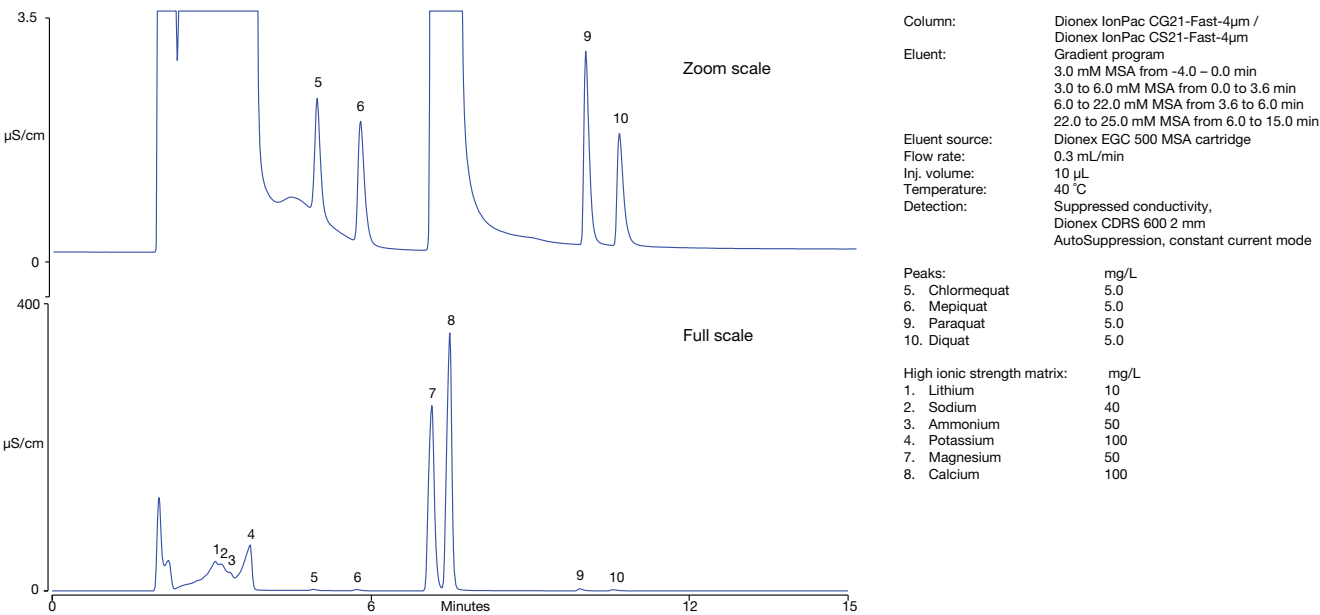


Figure 3. Gradient elution of four quaternary amine cationic polar pesticides in a high ionic strength matrix using a Dionex IonPac CS21-Fast-4µm column

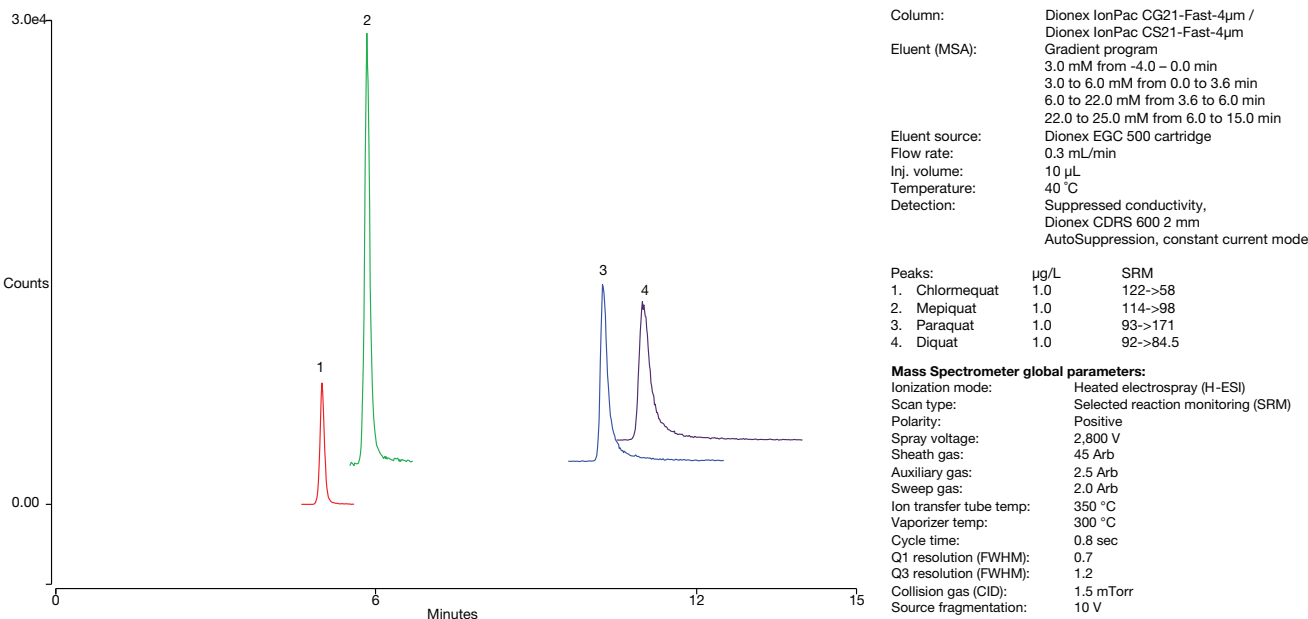
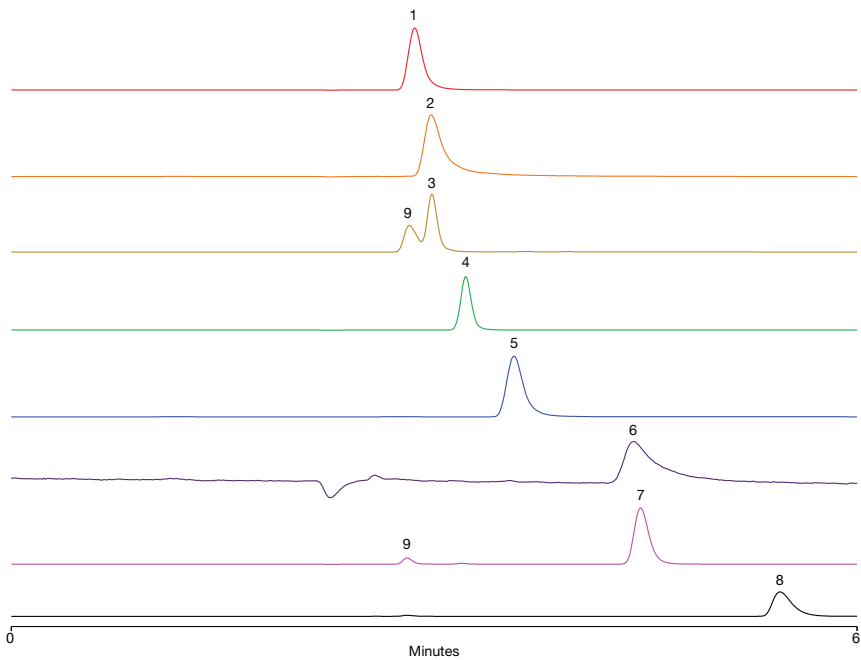


Figure 4. Sensitive determination of chlormequat, mepiquat, paraquat, and diquat at 1.0 µg/L using a Dionex IonPac CS21-Fast-4µm column and MS/MS detection

Extended application capabilities

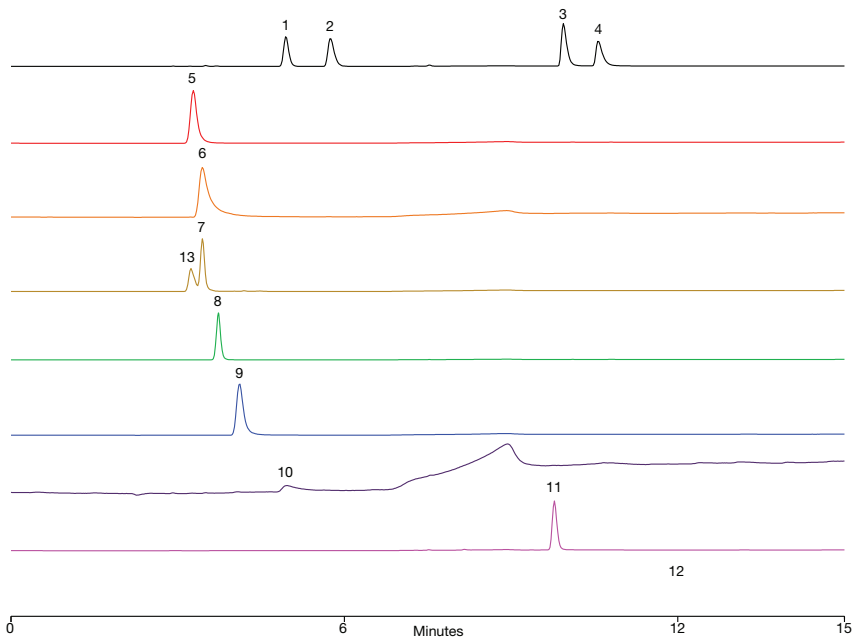
A variety of cationic polar pesticides can be resolved with the Dionex IonPac CS21-Fast-4µm column. Figure 5 shows fast, isocratic screening of eight cationic polar pesticides and compounds of interest in approximately 6 min. The gradient allows more analytes of interest to be eluted from the column in a reasonable amount of time as shown in Figure 6.



Column: Dionex IonPac CG21-Fast-4µm /
Dionex IonPac CS21-Fast-4µm
Eluent: 4 mM MSA
Eluent source: Dionex EGC 500 MSA cartridge
Flow rate: 0.3 mL/min
Inj. volume: 10 µL
Temperature: 40 °C
Detection: Suppressed conductivity,
Dionex CDRS 600 2 mm
AutoSuppression, constant current mode

Peaks:	mg/L
1. Diethanolamine	5.0
2. Triethanolamine	5.0
3. N,N-Dimethylhydrazine	5.0
4. Trimethylsulfonium	5.0
5. Morpholine	5.0
6. Melamine	15.0
7. Chlormequat	5.0
8. Mepiquat	5.0
9. Ammonium	NQ

Figure 5. Isocratic elution of eight cationic polar pesticides and compounds of interest using a Dionex IonPac CS21-Fast-4µm column



Column: Dionex IonPac CG21-Fast-4µm /
Dionex IonPac CS21-Fast-4µm
Eluent (MSA): Gradient program
3.0 mM from -4.0 – 0.0 min
3.0 to 6.0 mM from 0.0 to 3.6 min
6.0 to 22.0 mM from 3.6 to 6.0 min
22.0 to 25.0 mM from 6.0 to 15.0 min
Eluent source: Dionex EGC 500 MSA cartridge
Flow rate: 0.3 mL/min
Inj. volume: 10 µL
Temperature: 40 °C
Detection: Suppressed conductivity,
Dionex CDRS 600 2 mm
AutoSuppression, constant current mode

Peaks:	mg/L
1. Chlormequat	5.0
2. Mepiquat	5.0
3. Paraquat	5.0
4. Diquat	5.0
5. Diethanolamine	5.0
6. Triethanolamine	5.0
7. N,N-Dimethylhydrazine	5.0
8. Trimethylsulfonium	5.0
9. Morpholine	5.0
10. Melamine	15.0
11. Streptomycin	10.0
12. Nereistoxin	10.0
13. Ammonium	NQ

Figure 6. Gradient elution of twelve cationic polar pesticides and compounds of interest using a Dionex IonPac CS21-Fast-4µm column

times due to hydrophobic interactions, and improve the peak shapes of hydrophobic amines. Time and expense can be saved by eliminating time-consuming sample preparation steps. This feature allows complex sample matrices to be analyzed with minimal sample preparation.

Cation trap column

When using the eluent generator for eluent delivery and to achieve an almost flat baseline when using gradient elution, we recommend installing a Thermo Scientific™ Dionex™ CR-CTC III Continuously Regenerated Cation Trap Column to remove cationic contaminants from the eluent. The Dionex CR-CTC III trap column should be installed between the Thermo Scientific™ Dionex™ EGC 500 Eluent Generator Cartridge and the eluent generator degas module.



Figure 7. For best chromatographic performance, Dionex IC PEEK Viper fittings are recommended with Dionex IonPac CS21-Fast-4µm columns.

System requirements

Dionex IonPac CS21-Fast-4µm columns are recommended for use with the Thermo Scientific™ Dionex™ ICS-6000 HPIC™ system or Thermo Scientific™ Dionex™ Integriion™ HPIC™ system equipped with an eluent generator. These systems can operate continuously up to 5000 psi to support the back pressure generated by the Dionex IonPac CS21-Fast-4µm column under standard operating conditions. The eluent generator automatically produces methanesulfonic acid gradients from deionized water. To achieve the lower detection limits for quaternary amine cationic polar pesticides, the Dionex HPIC systems can be paired with a Thermo Scientific™ TSQ Altis™ Triple Quadrupole mass spectrometer and Thermo Scientific™ Dionex™ AXP-MS Auxiliary Pump.

For all systems, Thermo Scientific™ Dionex™ IC PEEK Viper™ fittings are recommended to achieve consistent low dead volume connections and ensure optimum chromatographic performance.

Suppressor recommendations

For optimum ease-of-use and performance, the Dionex IonPac CS21-Fast-4µm analytical columns should be used with a Dionex™ Thermo Scientific™ CDRS 600 Cation Dynamically Regenerated Suppressor.

Specifications	
Dimensions	Dionex IonPac CS21-Fast-4µm Analytical Column: 2 x 150 mm Thermo Scientific™ Dionex™ IonPac CG21-Fast-4µm Guard Column: 2 x 30 mm
Maximum operating pressure	5000 psi (100 psi = 0.6894 MPa)
Mobile phase compatibility	Acidic eluents (pH 0–7), HPLC solvents (100% acetonitrile and up to 20% isopropyl alcohol); primary and secondary alcohols should be avoided.
Substrate characteristics	
Separator and guard columns	Macroporous resin Particle diameter: 4 µm Surface area: 500 m ² /g Crosslinking (%DVB): 80%
Functional group	Carboxylic acid Hydrophobicity: low
Capacity (µeq/column)	110 µeq/column (2 x 150 mm) 22 µeq/column (2 x 30 mm)
Column construction	PEEK™ with 10-32 threaded ferrule-style end fittings. All components are nonmetallic.

Ordering information

To order in the US, visit thermofisher.com, call (800) 532-4752, or contact the nearest Thermo Fisher Scientific office. Outside the US, order through your local Thermo Fisher Scientific office or distributor. Refer to the following part numbers:

Description	Part number
Analytical and guard columns	
Dionex IonPac CS21-Fast-4µm Analytical Column (2 x 150 mm)	303348
Dionex IonPac CG21-Fast-4µm Guard Column (2 x 30 mm)	303349
Eluent generator accessories	
Dionex EGC 500 MSA Eluent Generator Cartridge	075779
Dionex CR-CTC III Continuously Regenerated Cation Trap Column (for Dionex Integrion and ICS-6000 HPIC systems)	104-60001
Suppressor	
Dionex CDRS 600 (2 mm) Cation Dynamically Regenerated Suppressor with Consumables Monitoring Disabled	088667CMD
Dionex IC PEEK Viper fittings kits	
Dionex IC PEEK Viper Fittings Kit for Dionex Integrion systems with conductivity detectors	088798
Dionex IC PEEK Viper Fittings Kit for Dionex ICS-6000 systems with conductivity detectors	302965
Dionex IC-MS Installation Kit (includes Dionex IC PEEK Viper Fittings for the IC-MS interface)	22153-62049

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