

The IonPac® CS12A-8µm cation-exchange column provides fast analysis of mono- and divalent cations, ammonium, and aliphatic amines simultaneously using methanesulfonic or sulfuric acid eluents. The column resin is functionalized with a mixture of carboxylic acid and phosphonic acid groups, which permit excellent peak shape and efficiency for amines. Manganese is easily separated from calcium and magnesium with the use of a simple isocratic methanesulfonic acid eluent. The IonPac CS12A-5µm column is a high-efficiency column for very fast separations of common inorganic cations. The IonPac CS12A-MS (2 × 100 mm) column is specifically designed for IC-MS detection.

### High-Performance Chromatography

- Superior isocratic separation of mono- and divalent cations, ammonium, and aliphatic amines simultaneously using methanesulfonic acid (MSA) or sulfuric acid eluents.
- Ideal for analyzing inorganic cations and amines in drinking water, power plant waters, soil extracts, acid digests, chemical additives, chemical process solutions, scrubber solutions, plating baths, and solvents.

- Quick and efficient: Fast analysis time of 4 min for similar cation concentrations using the high-efficiency CS12A-5µm column. For more demanding samples with disparate concentration ratios (up to 1:1000), use the CS12A-8µm column (15 min run time).
- Excellent fourfold and 100-fold increase in mass sensitivity, respectively, with the 2 mm i.d. microbore and 0.4 mm i.d. capillary formats.
- Fourfold (2 mm) and 100-fold (0.4 mm) decrease in eluent consumption compared to 4 mm columns.
- Simplified operation provided by an Eluent Generator, which requires only a deionized water source to produce MSA eluent.

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## Versatile Cation-Exchange Separations

The IonPac CS12A-8 $\mu$ m cation-exchange columns provide fast, isocratic separation of lithium, sodium, ammonium, potassium, magnesium, and calcium in less than 15 min using a dilute MSA or sulfuric acid eluent. Outstanding selectivity and efficiency allow manganese and many aliphatic amines to be resolved from the alkali and alkaline earth metals with simple acid eluents.

Solvent is used as an eluent additive to reduce retention time and improve peak efficiency of hydrophobic amines; it enhances sample solubility and allows easy column clean-up after the analysis of complex matrices. The column can be operated at elevated temperatures to improve peak efficiencies and in some cases to modify column selectivity. Typical applications include the determination of inorganic cations and amines in drinking water, wastewater, power plant waters, soil extracts, acid digests, chemical additives, chemical process solutions, scrubber solutions, plating baths, and solvents.

## Isocratic Analysis of Alkali and Alkaline Earth Metals

Common mono- and divalent cations can be separated isocratically by the IonPac CS12A-8 $\mu$ m standard bore and capillary columns in less than 15 min, as illustrated in Figures 1 and 2. Operation is even easier when MSA is generated using an eluent generator.

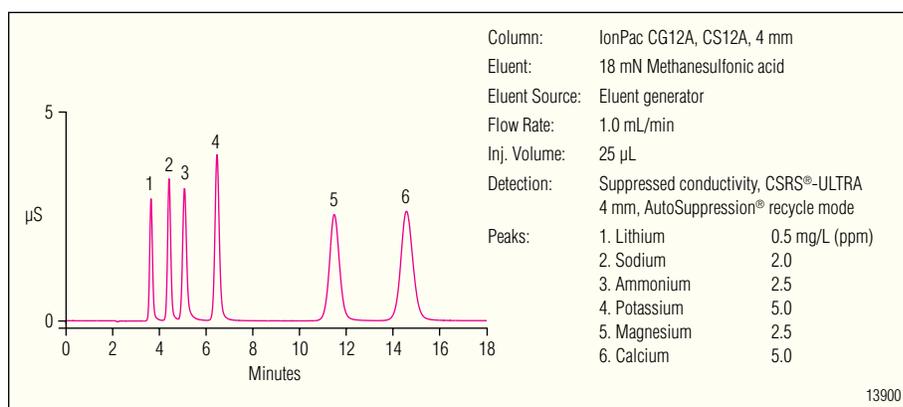


Figure 1. The IonPac CS12A column is used with an eluent generator for the separation of the common cations. Only a deionized water source is required. Eluent and regenerant preparation with corrosive chemicals are completely eliminated.

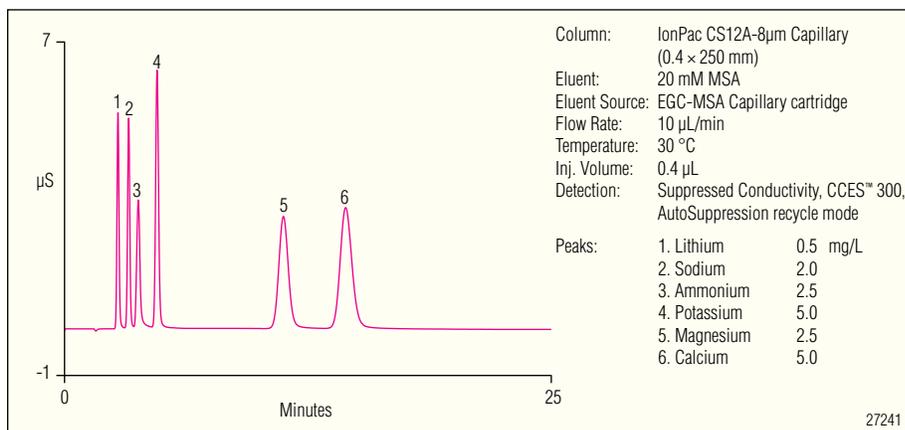


Figure 2. The IonPac CS12A Capillary column is used for the separation of the common cations. The analysis uses 100-fold less water, and produces only one-hundredth of the waste.

## Fast Separation of Alkali and Alkaline Earth Metals

The high-efficiency CS12A-5 $\mu$ m column is designed specifically for the fast analysis of mono- and divalent cations and ammonium present at similar concentrations. The CS12A-5 $\mu$ m column uses the same carboxylate and phosphonate functional groups as the CS12A-8 $\mu$ m columns, but differs in column format and resin particle size. As a result, the CS12A-5 $\mu$ m column provides the advantages of faster analysis time for inorganic cations and ammonium, reduced eluent consumption, and increased sensitivity. Figures 3 and 4 illustrate the fast, isocratic separation of the common inorganic cations and ammonium using the CS12A-5 $\mu$ m standard bore and capillary columns.

The CS12A-5 $\mu$ m column is recommended for trace cation analysis using a large-loop injection. For ultratrace analysis, the TCC-LP1, TCC-ULP1, TCC-XLP1, or the CG12A columns are recommended as the preconcentration column.

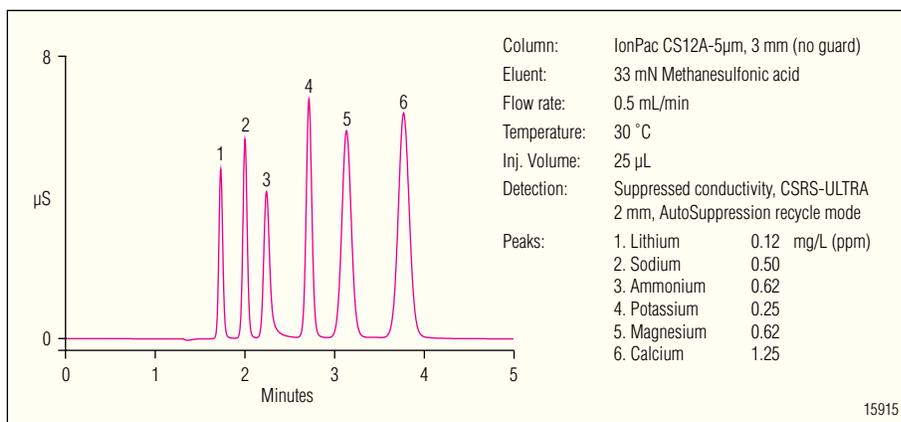


Figure 3. Fast isocratic separation of the common inorganic cations in four minutes using a 33 mN methanesulfonic acid eluent.

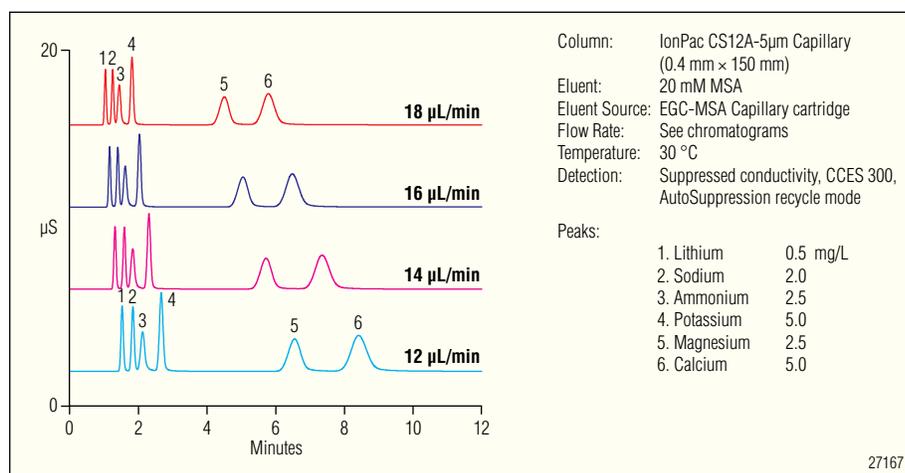


Figure 4. Fast isocratic separation of the common inorganic cations at increasing flow rates on a capillary IonPac CS12A-5 $\mu$ m column.

## Determination of Manganese for Power Plant Corrosion Monitoring

Manganese can be quantified in cooling waters using the IonPac CS12A with an MSA eluent to enhance the resolution of manganese from magnesium and calcium as shown in Figure 5.

## Economical Operation

The IonPac CS12A improves monovalent cation separations and reduces operating costs by eliminating the need for diaminopropionic acid monohydrochloride (DAP•HCl) in the eluent to elute divalent cations. Dilute sulfuric acid can be used as an economical eluent. For added economy, this eluent can be used with the Auto-Suppression recycle mode of the CSRS Cation Self-Regenerating Suppressor, CCES Cation Capillary Electrolytic Suppressor, or CAES Cation Atlas<sup>®</sup> Electrolytic Suppressor. MSA is recommended as the eluent for separations involving divalent cations such as barium, strontium, and manganese as shown in Figures 5 and 6. Also, the CS12A-5 $\mu$ m and CS12A-8 $\mu$ m (2  $\times$  250 mm and 0.4  $\times$  250 mm) are operated at lower flow rates, which provides the added benefit of reduced eluent consumption.

## Unique Carboxylate Cation Exchanger

The IonPac CS12A column is a unique hydrophilic, carboxylate/phosphonate-functionalized cation exchanger that provides excellent peak efficiency and peak shape for alkali and alkaline earth metals and amines. The IonPac CS12A 4 mm, 2 mm, and 0.4 mm  $\times$  250 mm packing is an 8  $\mu$ m diameter macroporous particle and the CS12A-5 $\mu$ m 3 mm and 0.4 mm  $\times$  150 mm column substrate is a 5  $\mu$ m diameter macroporous particle; both consist of ethylvinylbenzene cross-linked with 55% divinylbenzene. The substrate is functionalized with a mixed hydrophilic carboxylic acid/phosphonic acid layer that permits the elution of mono- and divalent cations using a dilute hydronium ion eluent, such as sulfuric acid or MSA. Prior to conductivity detection, the sulfuric acid or

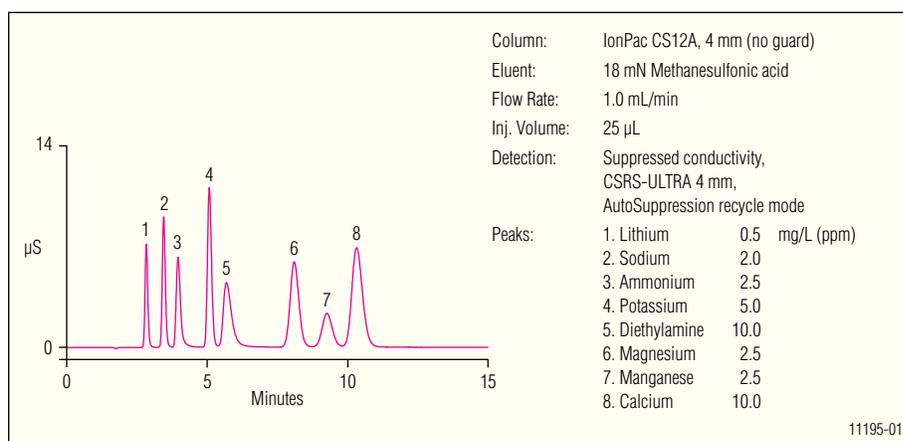


Figure 5. Isocratic determination of manganese in the presence of lithium, sodium, ammonium, potassium, diethylamine, magnesium, and calcium.

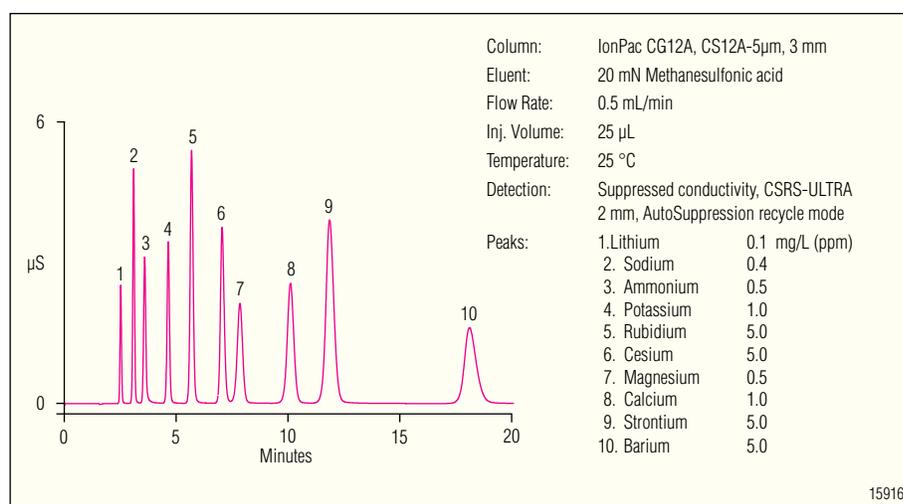


Figure 6. Separation of the extended Group I and Group II inorganic cations.

MSA eluent conductance is suppressed with a CAES, CSRS, or CCES using the AutoSuppression electrolytic mode.

Hydrochloric acid also can be used as an eluent with equivalent chromatography; however, the CSRS must be in the chemical suppression mode with tetrabutylammonium hydroxide as the chemical regenerant.

## High Loading Capacity

The IonPac CS12A column achieves baseline resolution of Group I and II cations, even for samples high in ionic strength. The column is compatible with acidic eluents and samples. Column performance does not deteriorate with the injection of acidic samples up to approximately 50 mM in hydronium ion for the 4 mm and

2 mm columns. Thus acid-digested or acid-preserved samples can be injected without pH adjustment. Peaks from a sample containing 50 mg/L of sodium and 0.05 mg/L of ammonium are easily resolved as illustrated in Figure 7. The CS12A-5 $\mu$ m 3-mm column has approximately one-third the column cation-exchange capacity as the CS12A 4 mm and therefore is not as tolerable with respect to sample pH. The CS12A-5 $\mu$ m 3 mm can withstand up to 20 mM in hydronium ion with a 25  $\mu$ L sample volume. Smaller sample volumes can be used with the CS12A-5 $\mu$ m in this case. Another way is using the OnGuard<sup>®</sup> II A pretreatment cartridge to pretreat the sample, enabling the CS12A-5 $\mu$ m 3 mm to analyze for samples with up to 50 mM in hydronium ion.

## Solvent-Compatible Packing

Since the IonPac CS12A column is 100% HPLC solvent-compatible, acetonitrile can be used to modify column selectivity to facilitate elution of hydrophobic amines, for efficient column clean-up, or to enhance sample solubility. This feature allows complex matrices to be analyzed with minimal sample preparation and extends the utility of the column to new applications requiring solvents as shown in Figures 8 and 9.

## Solvent and Temperature Increase Flexibility for Methods Development

The solvent compatibility of the IonPac CS12A permits the use of acetonitrile in the eluent to modify ion-exchange selectivity. Simultaneous sulfuric acid concentration gradients and organic solvent gradients can be used to achieve optimum resolution of closely eluting analyte pairs. The retention of hydrophobic analytes is decreased significantly by the addition of solvent. Operation at elevated temperatures is useful in improving peak efficiencies and asymmetry and for resolving closely eluting pairs. Figures 8 and 9 illustrate the use of solvent in the eluent together with elevated temperature to optimize the separation of several closely eluting amines.

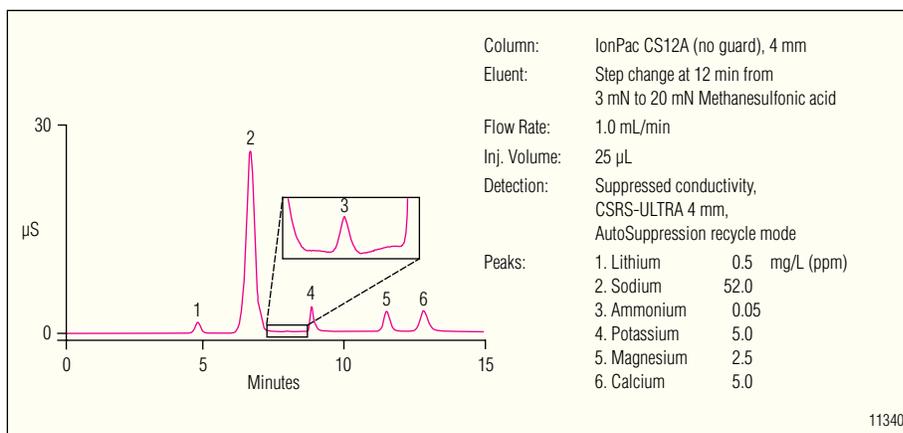


Figure 7. Trace-level quantification of ammonium in brine (1000:1 ratio) is fast and easy using the IonPac CS12A coupled with cation AutoSuppression.

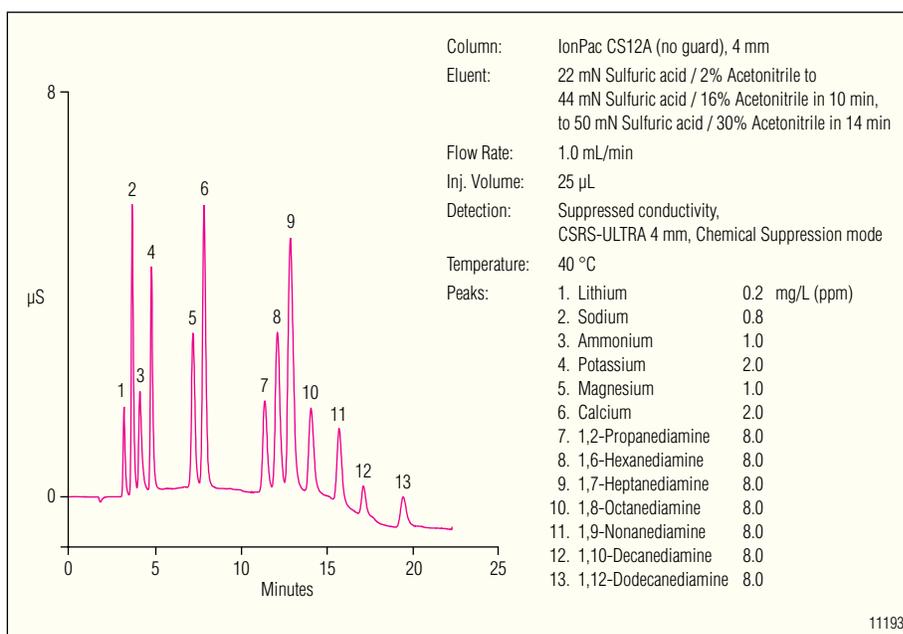


Figure 8. A sulfuric acid gradient coupled with an acetonitrile gradient and elevated temperature are used to optimize the separation of a wide range of amines and the alkali and alkaline earth metals.

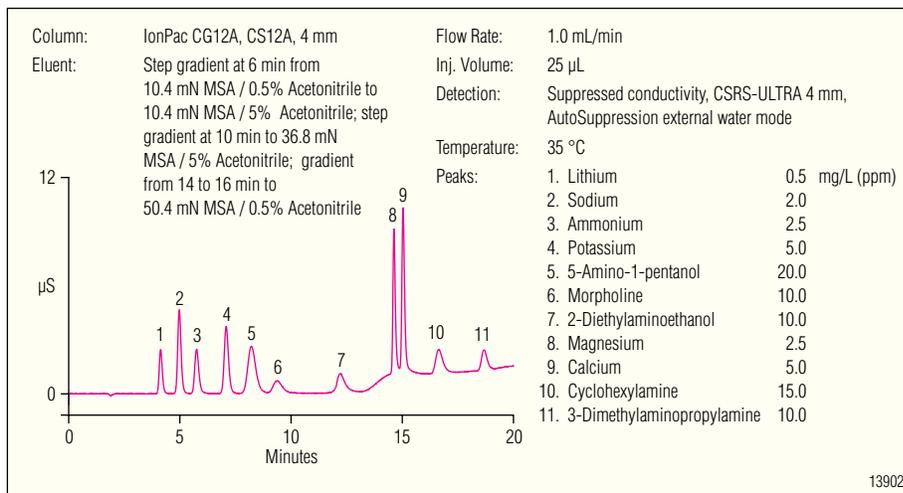


Figure 9. The IonPac CS12A, with an MSA/acetonitrile gradient, separates Group I and II cations, ammonium, and amines in cooling waters.

## Trace Analysis Is Easier with an Eluent Generator and Direct Large Loop Injection on a CS12A-5µm

Combining the IonPac CS12A-5µm 3 mm column with an eluent generator makes trace cation analysis even easier. An eluent generator produces methanesulfonic acid eluents electrolytically, eliminating the need for eluent preparation. Only a source of deionized water is needed. The use of this ultrapure MSA as an eluent results in a low, stable baseline. Routine ppb-level analysis of inorganic cations and ammonium by direct injection is possible with the CS12A-5µm 3 mm column and a 1000 µL injection loop, as illustrated in Figure 10. The large-loop direct-injection technique allows detection of cations to mid-ppt concentrations.

### Trace Cations Using Preconcentration

The preconcentration technique is used when measuring ions in the low ng/L (ppt) levels. With this technique, the injection loop is replaced by either a guard or preconcentration column containing ion-exchange material similar to that used in the analytical column. This column concentrates ions from measured volumes of pure water, lowering detection limits by several orders of magnitude.

Preconcentration is often used with online process IC instruments to obtain the lowest detection limits possible. In Figure 11, a 40 mL sample was concentrated on a 2 mm CG12A guard column, followed by separation of the trace cations on a 2 mm IonPac CS12A.

Sample preconcentration can also be used to determine lithium as an additive tracer in industrial process waters. In Figure 12, 7.5 mL of a hydrazine-treated sample was concentrated on a CG12A guard column, permitting the determination of lithium at sub-ppb concentrations.

### Calcium and Magnesium in Brine

A MetPac™ CC-1 concentrator column, which selectively retains calcium and magnesium but has a

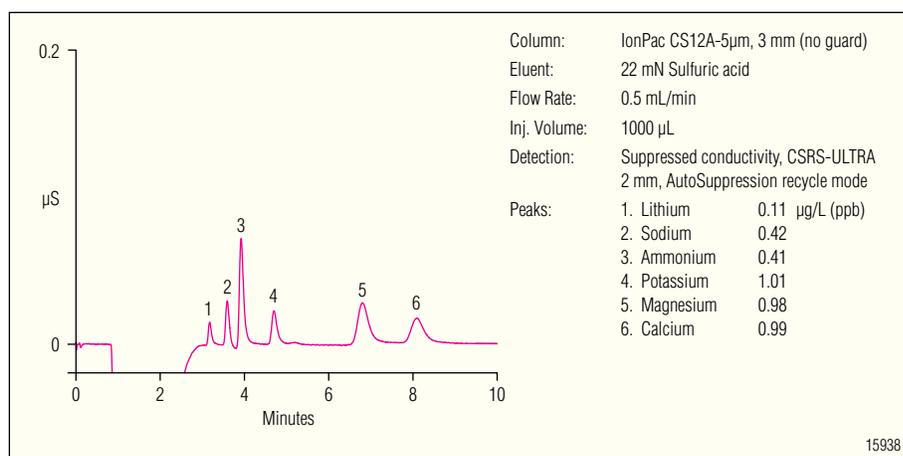


Figure 10. Trace cations determined by large-loop direct injection.

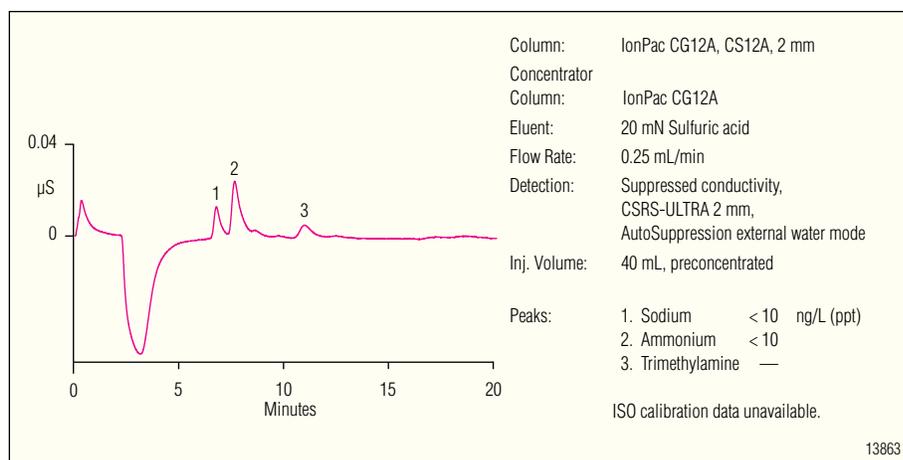


Figure 11. Trace-level cations in ultrapure water using sample preconcentration.

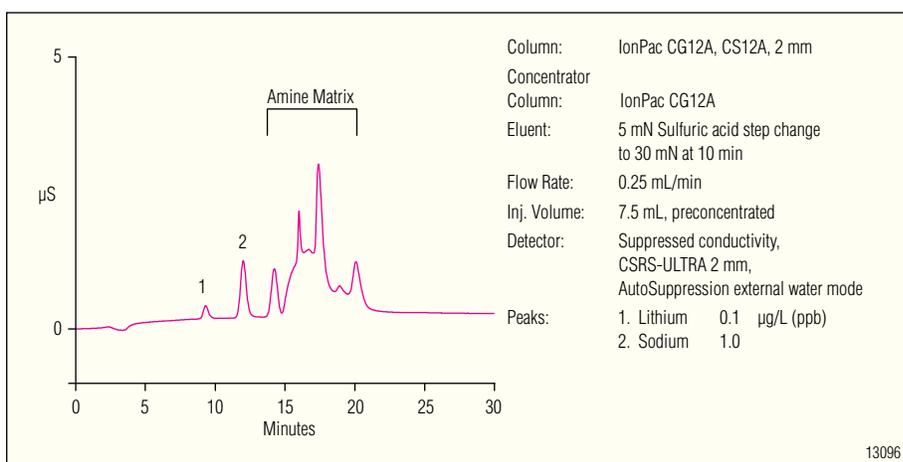


Figure 12. Trace lithium in a hydrazine sample matrix.

low affinity for sodium, is used to concentrate calcium and magnesium from brines. The concentrated calcium

and magnesium are then eluted from the concentrator column and separated on an IonPac CS12A cation-exchange column.

### CS12A-MS (2 × 100 mm) Column for IC-MS

The IonPac CS12A-MS (2 × 100 mm) column is specifically designed to separate inorganic cations, polar hydrophilic amines, and other small organic molecules (such as theophylline, caffeine, and uracil) prior to detection with MS. The CS12A-MS (2 × 100 mm) column format was specifically developed for MS operation.

The CS12A-MS (2 × 100 mm) column is ideally suited for fast elution and low flow rates required for interfacing with IC-MS detectors. Typically, the CS12A-MS column will be operated in an ion chromatography system containing a post column cation eluent suppressor for removal of salt counter anions, followed by a conductivity detector and an ESI-MS detector in series as illustrated in Figure 13. A grounded union is installed between the conductivity cell and the chassis to eliminate voltage buildup between the two detectors.

### Advantages of Using a Cation Suppressor with IC-MS

The use of a suppressor in IC-MS provides several advantages. Methods developed for conductivity detection can be used without modification. The counteranions are removed reducing MS maintenance. The electrospray signal is improved when the ionic load entering the interface is lowered, even in comparison to volatile eluent systems. Detection limits are improved due to better signal stability and the elimination of ionization suppression.

The availability of a high-sensitivity conductivity trace provides information in addition to the MS detector.

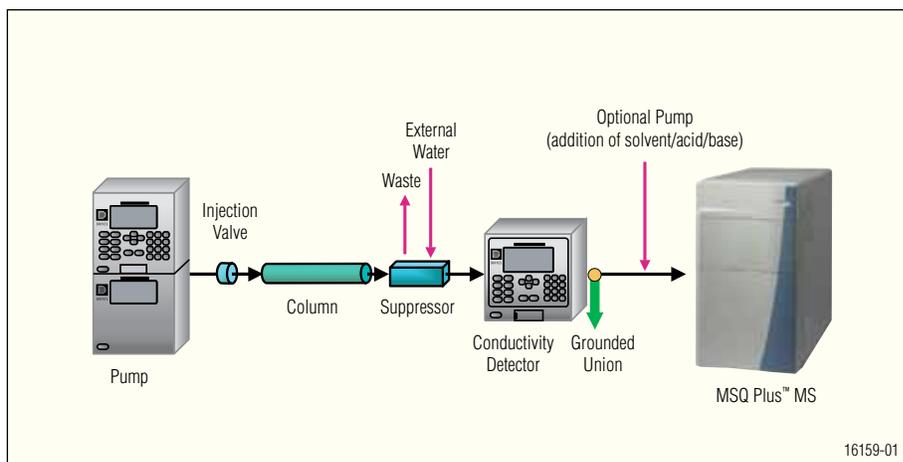


Figure 13. IC-ES-MS System Schematic.

## Extended Application Capabilities with the CS12A-MS Column

Figure 14 shows an overlay of single ion traces of the M+H signals for 6 small amines with a large sensitivity difference among the amines. The triethanolamine forms hydrogen bonds easily inhibiting the electrospray process, thus leading to poor sensitivity. In contrast, trimethylamine is very volatile. The other amines have good sensitivity. This work was done with minimal separation of the amines using the fast CS12A-MS (2 × 100 mm) column.

Inorganic cations can easily be determined in a Biaxin Extract as shown in Figure 15. A methanesulfonic acid/ acetonitrile gradient was used to elute inorganic as well as organic amines for screening purposes. Sodium and potassium are easily detected under these conditions as clusters with acetonitrile and/or water. For example, the highest masses are clusters with 19 water molecules while the lower masses contain acetonitrile.

Figure 16 demonstrates the analysis of a guanidine stock with quantification of a sodium impurity in guanidine. Using optimized conditions with low solvent, sodium and guanidine can quickly be determined with excellent sensitivity.

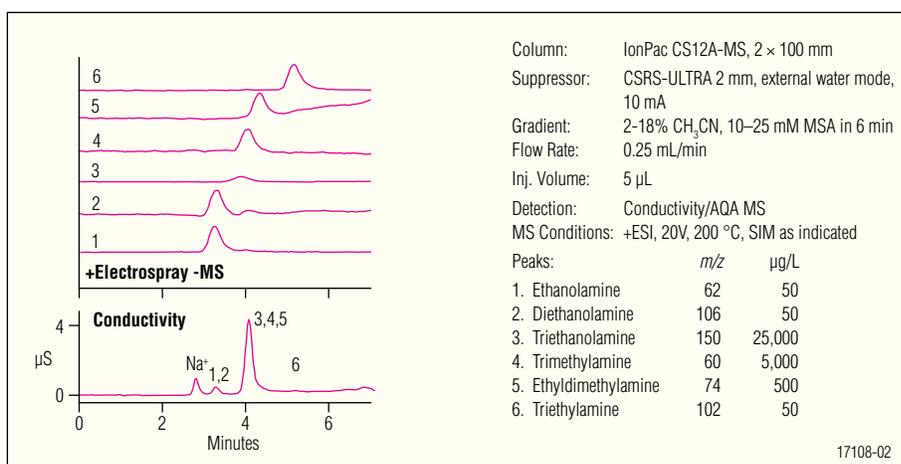


Figure 14. Determination of alkylamines and alkanolamines using IC-MS detection.

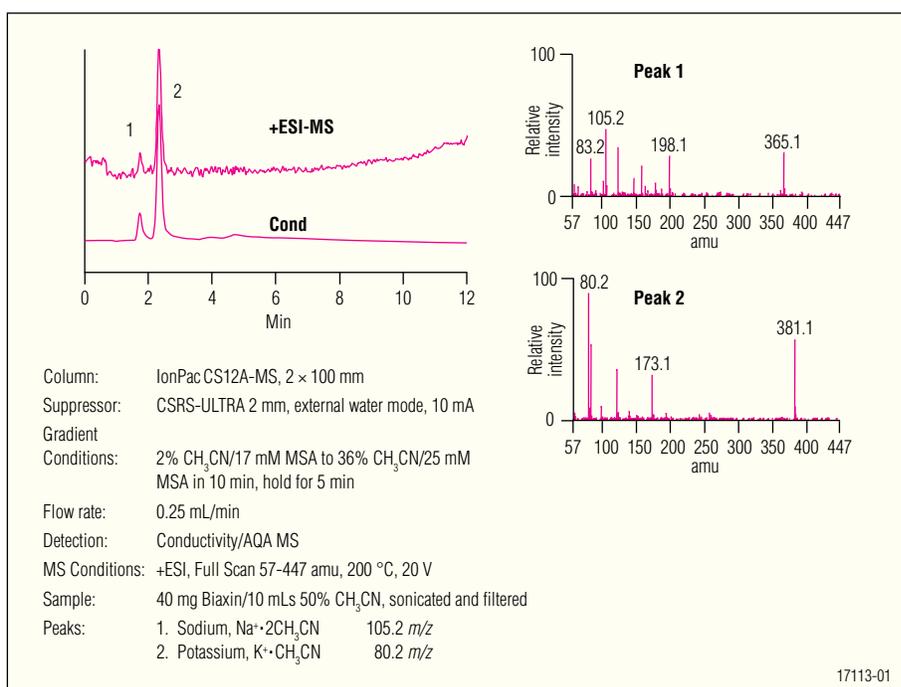


Figure 15. Separation of inorganic cations in a biaxin extract using MS detection.

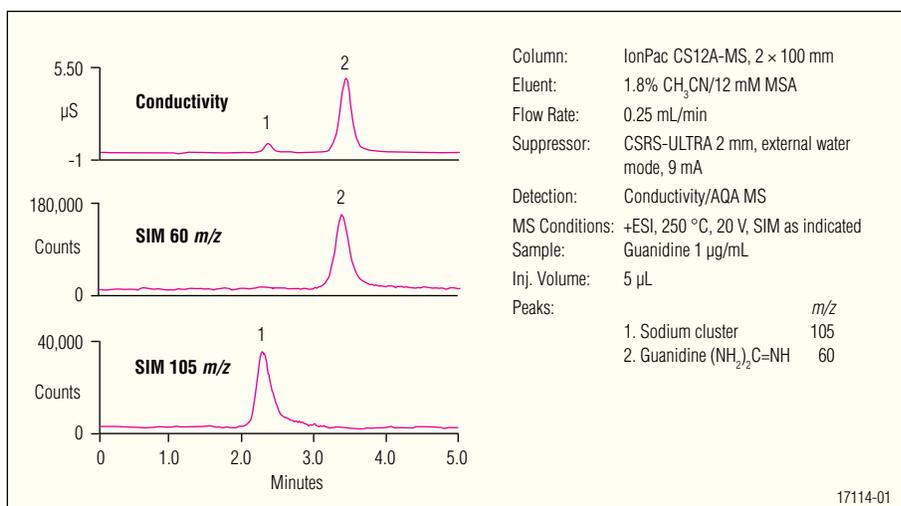


Figure 16. Determination of a sodium impurity in a guanidine stock solution using IC-MS detection.

Figures 17 and 18 demonstrate the use of a dual gradient to resolve cations in complex sample matrices. Figure 17 illustrates a general cation screening method for a generic cold medication. The sample was dissolved in water and filtered prior to injection. The overlays of four chromatograms show the conductivity and the electrospray MS traces along with the blank runs. The MS was operated in full scan mode and the mass shown here were extracted. The mass for the M+H and the M+H+CH<sub>3</sub>CN are shown.

Figure 18 shows the use of a dual gradient applied to an antiseptic swab sample. Masses of the various alkyl chain lengths were extracted from the full scan run, four of which are shown here. The conductivity trace did not indicate multiple peaks.

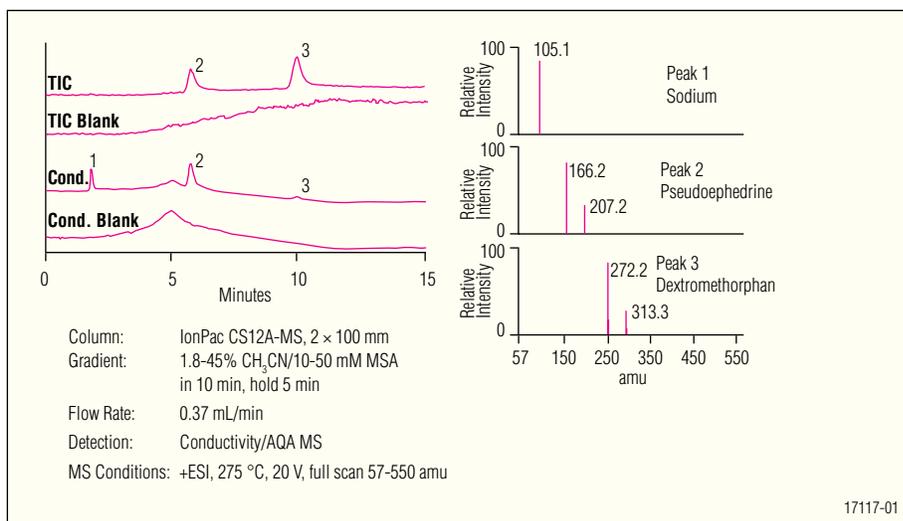


Figure 17. Inorganic cation screening of a generic cold medication using IC-MS detection.

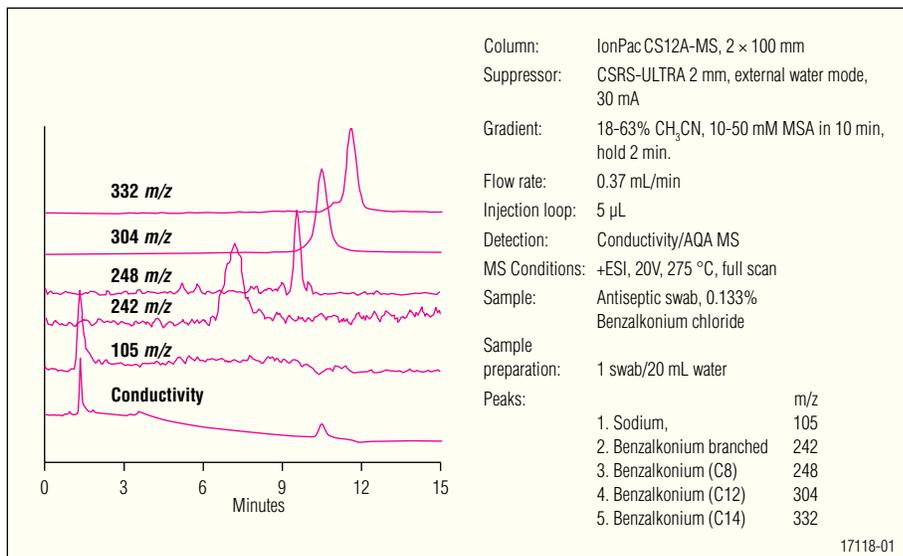


Figure 18. Determination of benzalkonium chlorides in an antiseptic swab sample using IC-MS detection.

### **System Recommendations**

The CS12A column in the suppressed conductivity mode is recommended for use with the ICS-2100 or ICS-5000 IC Systems equipped with an Eluent Generator. The CS12A can be used with older Dionex IC Systems equipped with an Eluent Generator or an RFC-30 Reagent-Free Controller. The eluentgenerator is used to automatically produce methanesulfonic acid gradients from deionized water.

### **Suppressors**

For optimum ease of use and economy, the CS12A column can be used with the CSRS 300 Anion Suppressor or the CCES 300 Cation Capillary Electrolytic Suppressor.

### **Cation Trap Columns**

When using the Eluent Generator for eluent delivery, a CR-CTC II Continuously Regenerated Cation Trap Column should be installed between the Eluent Generator cartridge and the eluent generator degas module. Alternatively, a CTC Cation Trap Column can be installed between the gradient pump and the injection valve to remove cationic contaminants from the eluent.

### **Concentrator Columns**

For trace analysis work, use the IonPac CG12A guard column when a single piston pump such as the AXP pump is used for sample delivery. Use the TCC-LP1, TCC-ULP1, or the TCC-XLP1 Cation Concentrator Column when the sample is delivered with a syringe or with an autosampler.

## SPECIFICATIONS

### *Dimensions:*

IonPac CS12A Analytical Columns:

2 × 100 mm, 2 × 250 mm,  
3 × 150 mm, and 4 × 250 mm

IonPac CS12A Capillary Columns:

0.4 × 150 mm and 0.4 × 250 mm

IonPac CS12A Guard Columns:

2 × 50 mm, 3 × 30 mm  
and 4 × 50 mm

IonPac CS12A Capillary

Guard Columns:

0.4 × 50 mm

### *Maximum Operating Pressure:*

4000 psi (standard and microbore)

5000 psi (capillary)

### *Mobile Phase Compatibility:*

Acidic eluents, 100% acetonitrile.

Alcohols should be avoided.

### *Ion-Exchange Groups:*

Grafted carboxylic acid and  
phosphonic acid

### *Substrate Characteristics:*

Bead Diameter:

8 μm (0.4 × 250 mm, 2 × 100 mm,  
2 × 250 mm, and 4 × 250 mm)

5 μm (0.4 × 150 mm and 3 × 150 mm)

Crosslinking (%DVB): 55%

### *Functional Group Characteristics:*

Medium hydrophilic

### *Capacity (μeq/column):*

9.4 μeq (0.4 × 150 mm)

28 μeq (0.4 × 250 mm)

280 μeq (2 × 100 mm)

700 μeq (2 × 250 mm)

940 μeq (3 × 150 mm)

2800 μeq (4 × 250 mm)

### *Column Construction:*

PEEK™ with 10-32 threaded

ferrule-style end fittings. All

components are nonmetallic.

## ORDERING INFORMATION

To order in the U.S., call 1-800-346-6390 or contact the Dionex regional office nearest you. Outside the U.S., order through your local Dionex office or distributor. Refer to the following part numbers.

Description	Part Number
<b>IonPac CS12A Columns</b>	
IonPac CS12A-8 $\mu$ m Analytical Column, (4 $\times$ 250 mm).....	046073
IonPac CG12A-8 $\mu$ m Guard Column (4 $\times$ 50 mm).....	046074
IonPac CS12A-5 $\mu$ m Analytical Column (3 $\times$ 150 mm).....	057185
IonPac CG12A-5 $\mu$ m Guard Column (3 $\times$ 30 mm).....	057184
IonPac CS12A-8 $\mu$ m Analytical Column (2 $\times$ 250 mm).....	046075
IonPac CG12A-8 $\mu$ m Guard Column (2 $\times$ 50 mm).....	046076
IonPac CS12A-MS Analytical Column (2 $\times$ 100 mm).....	059960
IonPac CS12A-8 $\mu$ m Capillary Column, (0.4 $\times$ 250 mm).....	079914
IonPac CG12A-8 $\mu$ m Capillary Guard Column (0.4 $\times$ 50 mm).....	072067
IonPac CS12A-5 $\mu$ m Capillary Column, (0.4 $\times$ 150 mm).....	072068
IonPac CG12A-5 $\mu$ m Capillary Guard Column (0.4 $\times$ 35 mm).....	072069
<b>Concentrator Column</b>	
TCC-LP1 Trace Cation Concentrator-Low Pressure (4 $\times$ 35 mm).....	046027
TCC-ULP1 Trace Cation Concentrator-Ultralow Pressure (5 $\times$ 23 mm).....	063783
TCC-XLP1 Trace Cation Concentrator-Extremely Low Pressure (6 $\times$ 16 mm).....	063889
<b>Trap Columns</b>	
CR-CTC II Continuously Regenerated Cation Trap Column.....	066262
CR-CTC Continuously Regenerated Cation Trap Column (Capillary) (For use with Capillary Cation Columns).....	072079
CTC-1 Cation Trap Column (9 $\times$ 24 mm) (For gradient operation of 4 mm columns).....	040192
CTC-1 Cation Trap Column (4 $\times$ 35 mm) (For gradient operation of 2 mm columns).....	043132

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