

# A New Cation-Exchange Phase with Optimized Hydrophilic Amine Selectivity and Compatible with Either Suppressed or Nonsuppressed Conductivity Detection

M. Rey, A. Bordunov, and C. Pohl, Dionex Corporation, Sunnyvale, CA, USA

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## ABSTRACT

We have developed a more universal cation-exchange phase consisting of a novel proprietary copolymer containing carboxylic acid groups, resulting in optimized selectivity for a much wider range of amines, specifically small to medium-size hydrophilic amines and polyamines. Commonly analyzed monovalent amines such as mono-, di-, and triethanolamine and methyl-, dimethyl-, and trimethylamine can be separated from the common inorganic Group I and Group II cations and ammonium ion, with simple aqueous acidic eluents.

Until now, the most successful cation-exchange columns for nonsuppressed ion chromatography of cations were based on silica beads coated with a copolymer containing maleic anhydride. Due to the pH limitations of the silica substrate, use of these columns is restricted to a narrow eluent pH range. Furthermore, it was found early on that leachates from the column contaminate the suppressor when used with suppressed conductivity detection.

The new cation-exchange phase discussed here can be used with either suppressed or nonsuppressed conductivity detection. This flexibility offers the conveniences of nonsuppressed conductivity, such as not having to use a suppressor if the concentrations of the analytes are high enough. To determine cations present at lower concentrations, the column must be used in the suppressed conductivity mode. Methods that require eluent gradients and/or step changes of eluent concentration can only be used in the suppressed conductivity mode. These are especially suited to this new column because the background conductivity remains relatively constant, offering almost flat baselines.

## SILICA-BASED NONSUPPRESSED CATION-EXCHANGE COLUMN

### Advantages Over Other Cation-Exchange Columns

- Best peak efficiencies
- Optimum ammonium/ethanolamine selectivity

### Disadvantages

- Cannot be used with suppressed conductivity detection therefore:
  - No eluent step changes and gradients
  - Higher MDLs

- Cannot be used with an eluent generator (for ease of operation)
- Overloads easily (low capacity)
- Limited eluent pH range (silica)

## GOAL

To develop a polymer-based cation-exchange phase that:

- Can be used with suppressed conductivity detection
  - Lower MDLs
  - Can be used with eluent step changes and gradients
  - Can be used with the eluent generator in the suppressed conductivity mode
- Can be used with nonsuppressed conductivity
  - Simpler for higher concentration analytes
- Has optimized ammonium/ethanolamine selectivity
- Has peak efficiencies more comparable to silica-based phases
- Can be used at elevated temperature and at very low eluent pH

Figure 1 is a diagram of the new polymer-based IonPac® CS18. In a first step, the raw resin is surface-modified to minimize adsorption and maximize elution efficiency of amines on the macroporous beads. A second synthesis step is used to functionalize the resin with cation exchange groups in an alternating polymer.

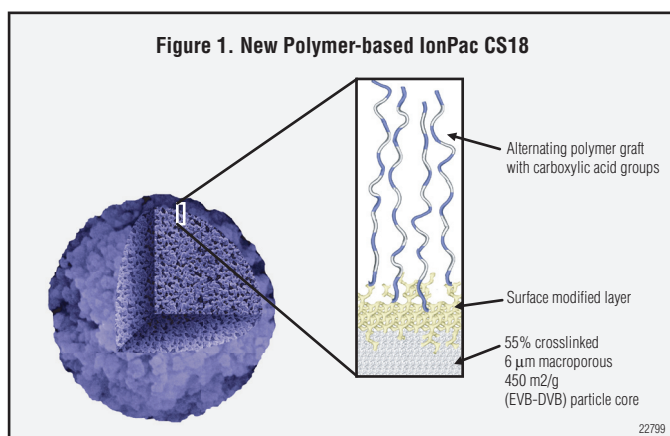


Figure 2 compares chromatograms A and B run under the same conditions achieving similar selectivity and cation-exchange capacity with the polymer-based stationary phase as with the silica-based column. Efficiencies for the monovalent analytes are comparable, while those for the divalent peaks are lower with the polymeric CS18 column.

In nonsuppressed ion chromatography, the operating background (approximately 1450  $\mu\text{S}$  for 4 mM MSA) is much higher than in suppressed IC (approximately 0.2  $\mu\text{S}$  for 5 mM MSA) and, consequently, the noise is much higher for nonsuppressed IC (more than 10 times higher). Differences between signal levels, depending on the cation, are at most 50% higher for nonsuppressed IC. Therefore, MDLs will be lower for suppressed IC, as can be inferred from chromatograms B and C in Figure 2.

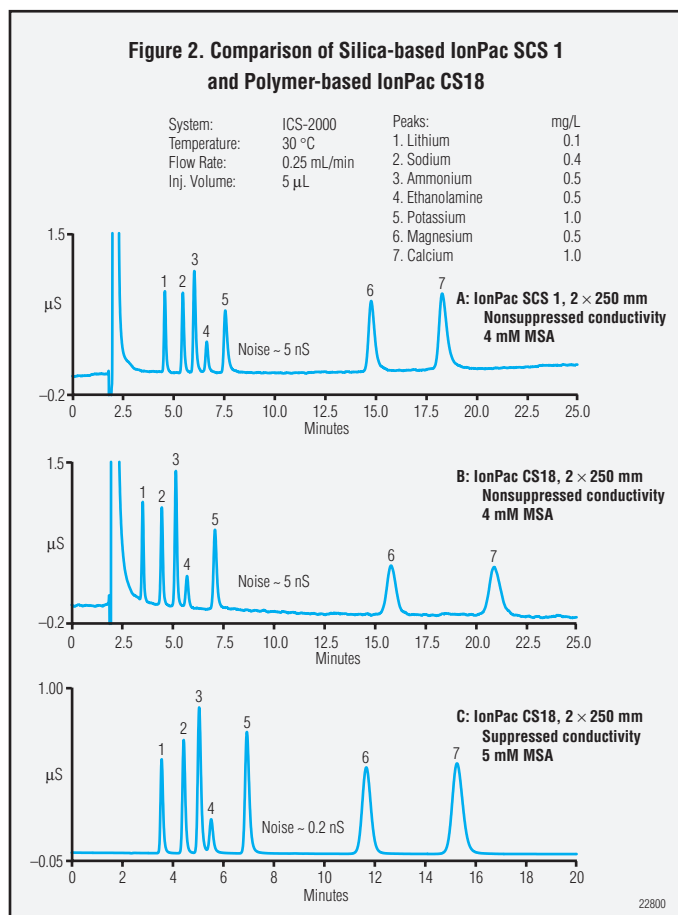
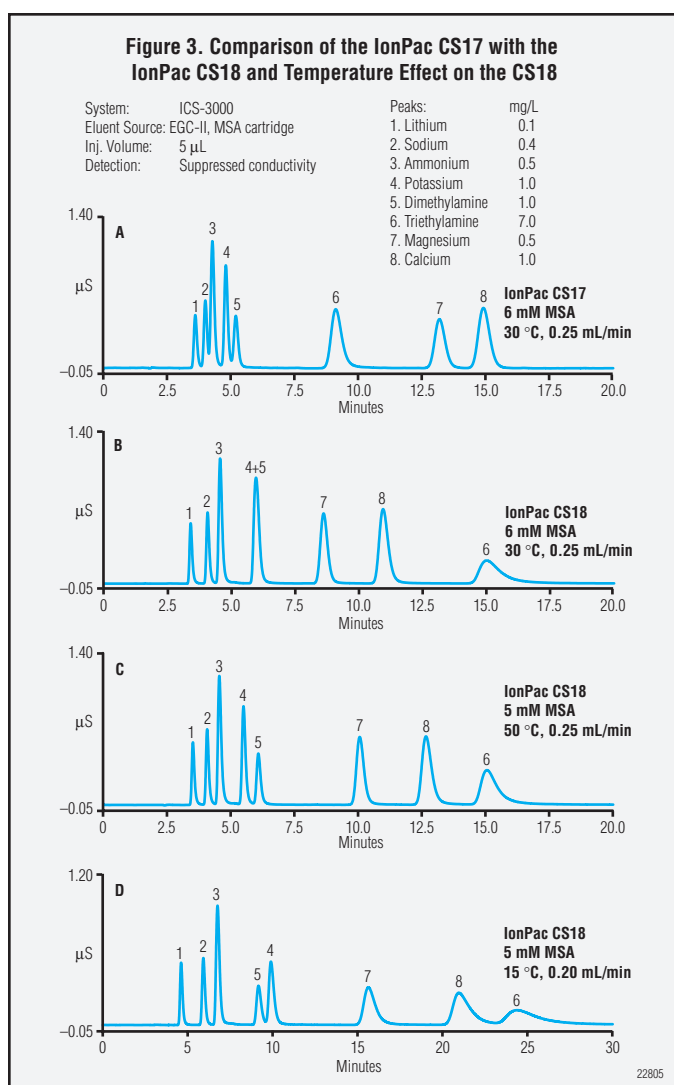
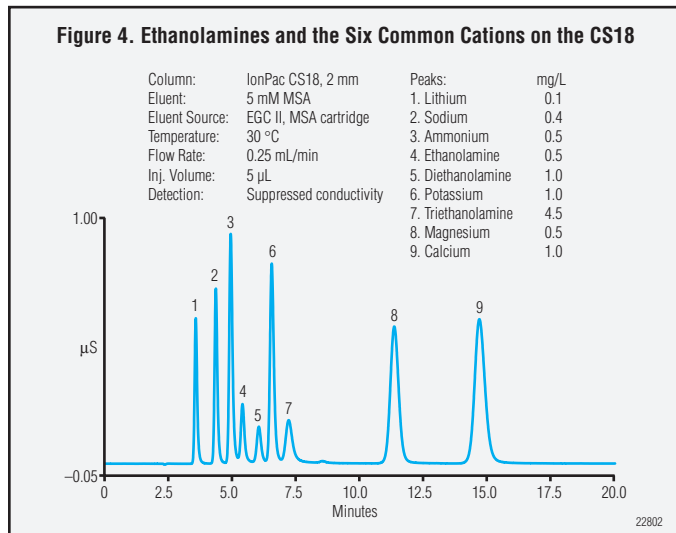


Figure 3 compares the IonPac CS17 with the IonPac CS18 and shows the effect of temperature on the CS18. The IonPac CS17 is the predecessor amine column to the CS18. Chromatograms A and B were run under the same conditions, and the difference in selectivities for the two columns can be seen here. The CS17 is a more hydrophilic column, and therefore peak shape for the most hydrophobic of the analytes shown here, triethylamine, is better on it than on the CS18. Notice also that except for the potassium/dimethylamine pair, there is better monovalent peak selectivity on the CS18. The coeluting pair can be resolved by decreasing the eluent concentration and changing the temperature of the column, as is shown in chromatograms C and D. At the higher temperature, potassium elutes first, and peak efficiencies are higher. At the lower temperature, the elution order switches. The column was run using an ICS 3000 chromatographic system, which, besides heating, can also cool the column below ambient temperatures.

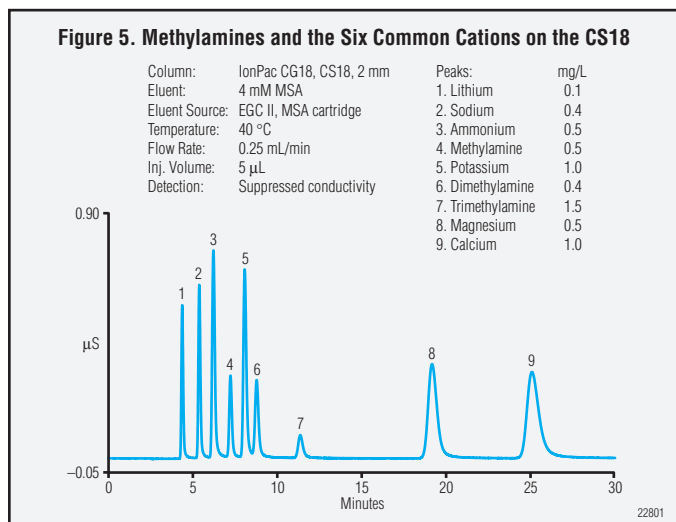


## APPLICATIONS ON IONPAC CS18

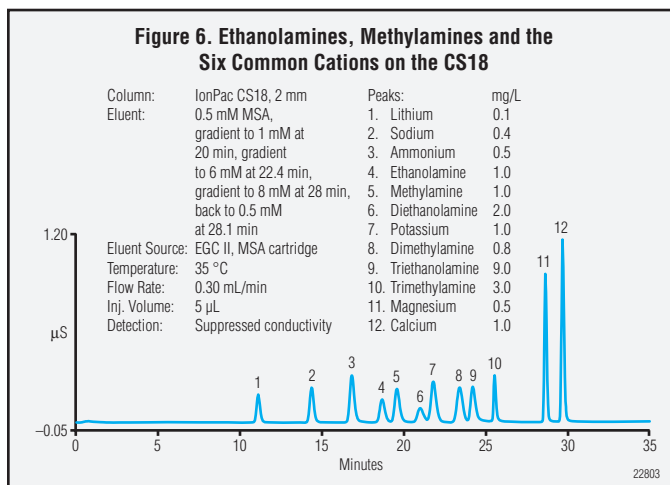
Selectivity of this new phase allows isocratic separation of the three ethanolamines together with the six common cations. Peak efficiencies and selectivities shown for these analytes, with a simple isocratic eluent, were not previously attainable on a polymeric phase (Figure 4).



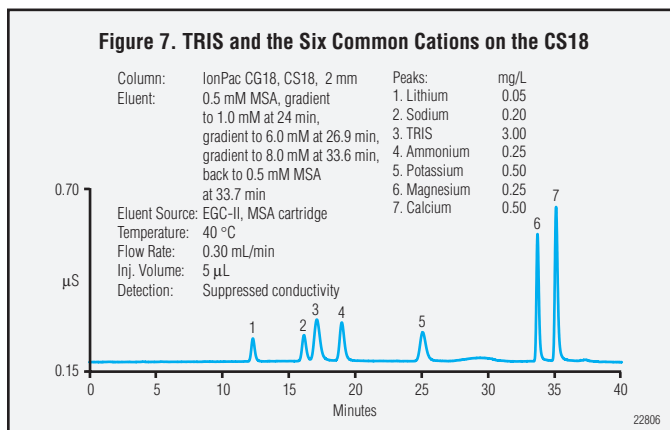
Similarly, methyl-, dimethyl- and trimethylamines can be separated isocratically from the six common cations with this new phase. A lower eluent concentration and elevated temperature is needed to separate potassium from dimethylamine. At the higher temperature, potassium elutes earlier and is resolved from dimethylamine (Figure 5).



By using suppressed conductivity detection, an eluent gradient can be used to further separate the methylamines and ethanolamines together with the six common cations in one run. Notice that there is almost no baseline change when performing the gradient (Figure 6).



TRIS, or tris(hydroxymethyl)aminomethane, is a weak base, very hydrophilic, and only slightly retained on most cation-exchange columns. On most stationary phases it coelutes with sodium. With an eluent gradient at elevated temperature, it is baseline resolved from sodium on the CS18 column (Figure 7).

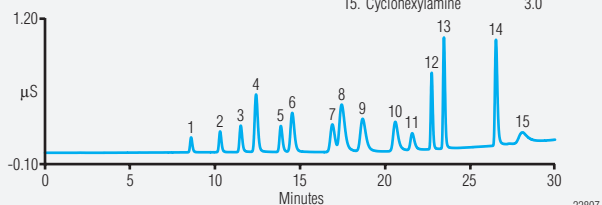


Today, most U.S. power plants use one or more "advanced amines" as additives for secondary system pH control. To be effective in corrosion prevention, the proportions and amounts of these amines have to be carefully monitored. The amines separation shown in this chromatogram represents the most widely used amines in the power industry (Figure 8).

**Figure 8. Power Amines and the Six Common Cations on the CS18**

Column: IonPac CS18, 2 mm  
 Eluent: 0.5 mM MSA, gradient to 3 mM at 16 min, gradient to 25 mM at 30 min, back to 0.5 mM MSA at 30.1 min  
 Eluent Source: EGC II, MSA cartridge  
 Temperature: 40 °C  
 Flow Rate: 0.30 mL/min  
 Inj. Volume: 5 µL  
 Detection: Suppressed conductivity

Peaks:	mg/L
1. Lithium	0.05
2. Sodium	0.20
3. Ammonium	0.25
4. Ethanolamine	2.0
5. Potassium	0.50
6. 2(2-aminoethoxy)ethanol	3.0
7. 5-amino-1-pentanol	3.0
8. Morpholine	3.0
9. 3-methoxypropylamine	3.0
10. 2-diethylaminoethanol	3.0
11. 3-quinuclidinol	2.0
12. Magnesium	0.25
13. Calcium	0.50
14. Ethylene diamine	2.0
15. Cyclohexylamine	3.0



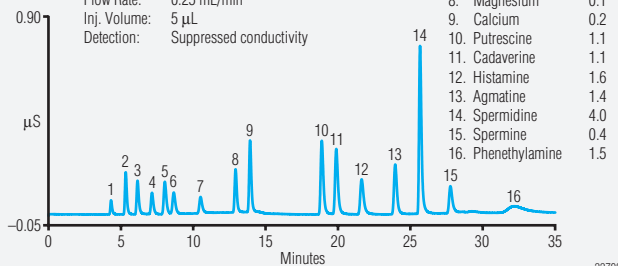
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The amines shown in Figure 9 separated on the CS18 are of interest in the food industry. For example, histamine is formed by bacterial decomposition of histidine, and is important to determine its content in wine. The freshness of seafood and meat products is determined by the amounts of biogenic amines present. An organic solvent-free eluent is used to elute the polyvalents spermidine and spermine from this column, with the help of a higher acidic eluent concentration and elevated temperature. Eluent gradient conditions require the use of a suppressor.

**Figure 9. Biogenic Amines, Methylamines and the Six Common Cations on the CS18**

Column: IonPac CS18, 2 mm  
 Eluent: 3 mM MSA, isocratic to 5 min, gradient to 18 mM at 20 min, gradient to 45 mM at 25 min, isocratic to 35 min, back to 3 mM MSA at 35.1 min  
 Eluent Source: EGC II, MSA cartridge  
 Temperature: 40 °C  
 Flow Rate: 0.25 mL/min  
 Inj. Volume: 5 µL  
 Detection: Suppressed conductivity

Peaks:	mg/L
1. Lithium	0.02
2. Sodium	0.08
3. Ammonium	0.10
4. Methylamine	0.25
5. Potassium	0.20
6. Dimethylamine	0.20
7. Trimethylamine	0.75
8. Magnesium	0.1
9. Calcium	0.2
10. Putrescine	1.1
11. Cadaverine	1.1
12. Histamine	1.6
13. Agmatine	1.4
14. Spermidine	4.0
15. Spermine	0.4
16. Phenethylamine	1.5



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The selectivity of the CS18 has been found to be especially suited for the determination of small water soluble amines in refinery processes (Figure 10). It is excellent for analyzing amine-scrubbing solutions in the sulfur removal units and to determine amine-based additives used for pH, corrosion and foam control. At 40 °C, peaks 7 and 8 (potassium and ethylamine) and peaks 11 and 12 (morpholine and 1-dimethylamino-2-propanol) coelute. At 42 °C, resolution of these two pairs improve, with potassium, the most temperature-sensitive of the analytes, eluting earlier between diethanolamine and ethylamine. At 50 °C, there is baseline resolution of peaks 11 and 12, and potassium coelutes completely with diethanolamine.

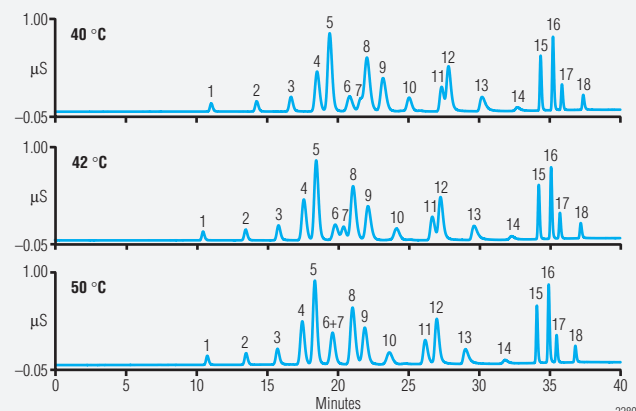
The three chromatograms in Figure 11 were run isocratically. At 5 mM methanesulfonic acid, monovalents elute first followed by divalents. At 7 mM acid, all peaks elute sooner with a reversal of elution order for peaks 6 and 7, cesium and magnesium. At 8 mM MSA, elevated temperature and higher flow rate, the common six cations can elute within 6 minutes to provide a fast run for high sample throughput.

Alkyl diamines are well separated on the CS18 using a methanesulfonic acid gradient at 40 °C. Up to a chain length of ten carbons, no organic solvent is required in the eluent (Figure 12).

**Figure 10. Amines of Interest in the Petrochemical Industry**

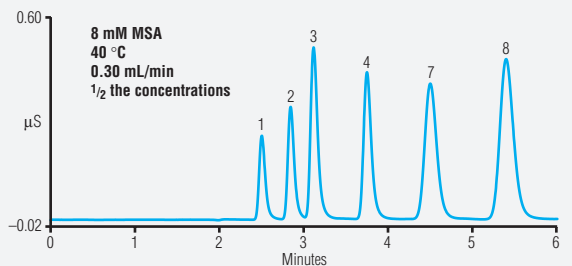
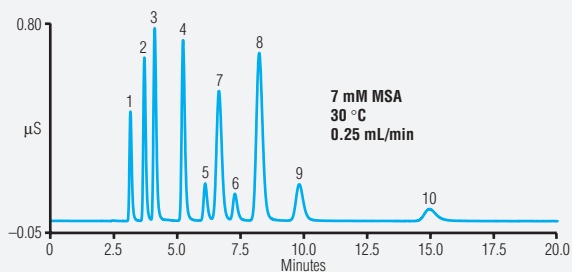
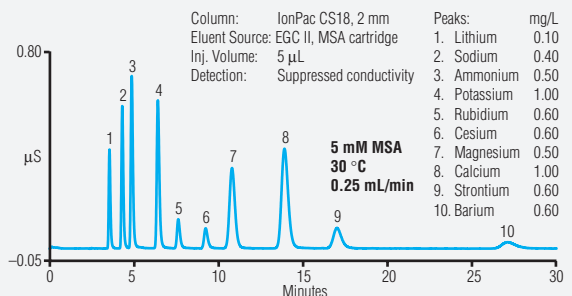
Column: IonPac CS18, 2 mm  
 Eluent: 0.5 mM MSA, gradient to 1 mM at 20 min, gradient to 4 mM at 28 min, gradient to 11 mM at 34 min, isocratic to 40 min, back to 0.5 mM MSA at 40.1 min  
 Eluent Source: EGC II, MSA cartridge  
 Flow Rate: 0.30 mL/min  
 Inj. Volume: 5 µL  
 Detection: Suppressed conductivity

Peaks:	mg/L	10. N-methyldiethanolamine	3.0
1. Lithium	0.05	11. Morpholine	3.2
2. Sodium	0.2	12. 1-dimethylamino-2-propanol	3.7
3. Ammonium	0.25	13. N-methylmorpholine	7.5
4. Ethanolamine	3.0	14. Butylamine	1.5
5. Methylamine	3.6	15. Magnesium	0.25
6. Diethanolamine	3.6	16. Calcium	0.5
7. Potassium	0.5	17. Strontium	0.5
8. Ethylamine	3.0	18. Barium	0.5
9. Dimethylamine	1.4		



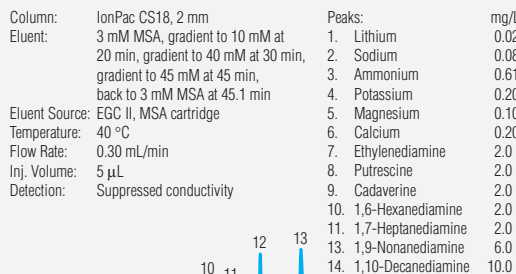
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**Figure 11. Group I and Group II Cations plus Ammonium on the CS18**



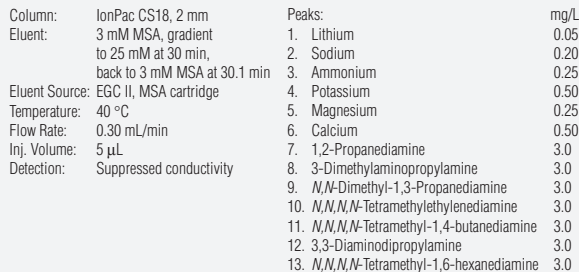
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**Figure 12. Alkyl Diamines and the Six Common Cations on the CS18**



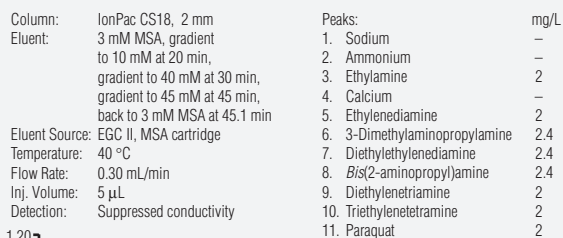
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**Figure 13. Diamines and the Six Common Cations on the CS18**



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**Figure 14. Polyamines and the Six Common Cations on the CS18**



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## CONCLUSION

A new polymeric weak cation-exchange phase has been developed to provide:

- Suppressed and nonsuppressed conductivity detection
- Optimized selectivity for the separation of the common cations and a wide range of polar amines, including ethanolamine and ammonium ions.
- High peak efficiencies for amines and the common cations

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**Dionex Corporation**

1228 Titan Way  
 P.O. Box 3603  
 Sunnyvale, CA  
 94088-3603  
 (408) 737-0700

**North America**

Sunnyvale, CA (408) 737-8522 Westmont, IL (630) 789-3660  
 Houston, TX (281) 847-5652 Atlanta, GA (770) 432-8100  
 Marlton, NJ (856) 596-0600 Canada (905) 844-9650

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