Thermo Scientific

# Dionex IonPac CS14 Columns

## Product Manual

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Thermo SCIENTIFIC

# PRODUCT MANUAL

## for the

## IONPAC CG14 GUARD COLUMN

**(2 x 50 mm, P/N 044122)**

**(4 x 50 mm, P/N 044124)**

## IONPAC CS14 ANALYTICAL COLUMN

**(2 x 250 mm, P/N 044121)**

**(4 x 250 mm, P/N 044123)**



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# SECTION 1 - INTRODUCTION

The IonPac® CS14 4-mm (P/N 044123) and 2-mm (P/N 044121) Analytical Columns are designed specifically for the separation of alkyl and alkanolamines from the Group I and Group II cations. The CS14 stationary phase consists of a 8.0 µm poly (ethylvinylbenzene/divinylbenzene) macroporous substrate resin that is functionalized with a relatively weak carboxylic acid. It has both cation exchange and reverse phase properties. It differs from other Dionex cation exchange columns such as the IonPac CS3, CS10 and CS11, which have a sulfonic acid functionality making them strong cation exchangers. The CS14 is similar to the CS12 in that both of these stationary phases have carboxylate functionality making them relatively weak cation exchangers with a high selectivity for hydronium ion. These weak cation exchangers use low ionic strength eluents to isocratically elute both monovalent and divalent cations in a relatively short period of time without the use of the divalent eluent modifiers which are necessary for divalent cation elution with the strong cation exchangers. The hydrophilic characteristic of the surface permit alkyl and alkanolamines to be eluted with good peak symmetry and efficiency. However, short-chain alkanolamines, such as monoethanolamines, may exhibit improved separations on the IonPac CS12. The IonPac CS14 Column is compatible with eluents having pH from 0 to 14 and is solvent-compatible. The column can be used with 0-100% acetonitrile, 0-100% methanol, 0-100% isopropanol, 0-20% tetrahydrofuran or 0-100% aqueous eluents without loss of performance.

**Table 1**
**IonPac CS14/CG14 Packing Specifications**

| Column | Particle Diameter µm | Substrate[a] X-linking % | Column Capacity meq/column | Functional Group | Hydrophobicity |
|---|---|---|---|---|---|
| CS14 4 x 250 mm | 8.0 | 55 | 1.3 | Carboxylic acid | Low |
| CG14 4 x 50 mm | 8.0 | 55 | 0.26 | Carboxylic acid | Low |
| CS14 2 x 250 mm | 8.0 | 55 | 0.325 | Carboxylic acid | Low |
| CG14 2 x 50 mm | 8.0 | 55 | 0.065 | Carboxylic acid | Low |

[a] macroporous (100 Å) divinylbenzene/ethylvinylbenzene polymer

**Table 2**
**CS14/CG14 Operating Parameters**

| Column | Typical Back Pressure psi (MPa) | Standard Flow Rate mL/min | Maximum Flow Rate mL/min |
|---|---|---|---|
| CS14 4-mm Analytical | ≤ 1,200 (8.27) | 1.0 | 3.0 |
| CG14 4-mm Guard | ≤ 450 (3.10) | 1.0 | 3.0 |
| **CS14 + CG14 4-mm columns** | **≤ 1,650 (11.37)** | **1.0** | **3.0** |
| CS14 2-mm Analytical | ≤ 1,200 (8.27) | 0.25 | 1.0 |
| CG14 2-mm Guard | ≤ 450 (3.10) | 0.25 | 1.0 |
| **CS14 + CG14 2-mm columns** | **≤ 1,650 (11.37)** | **0.25** | **1.0** |

**Read the system manuals.** This manual assumes that you are familiar with the installation and operation of the Dionex Ion Chromatograph (IC). If you do not understand the operation of the system, take the time to familiarize yourself with the various system components before beginning an analysis.

**You may need to make a liquid line fitting.** The IonPac CS14 Analytical Column and the IonPac CG14 Guard Column have 10-32 PEEK end fittings for use with ferrule/bolt liquid line fittings. If you have an Ion Chromatograph with Tefzel® liquid lines having 1/4-28 ThermoFlare™ fittings, it will be necessary to obtain one or more Tefzel liquid lines with a PEEK bolt and ferrule fitting on one end and a 1/4-28 ThermoFlare fitting on the other end. See, "Dionex Liquid Line Fittings," for detailed instructions on purchasing or making these lines.

**Always remember that assistance is available for any problem that may be encountered during the shipment or operation of Dionex instrumentation and columns through the Dionex North America Technical Call Center at 1-800-DIONEX-0 (1-800-346-6390) or through any of the Dionex Offices listed in, "Dionex Worldwide Offices."**

## SECTION 2 - COMPARISON OF ION CHROMATOGRAPHY SYSTEMS

**The proper configuration of 2-mm system injection volume, mass loading, system void volume and flow rate is based on the ratio of the 2-mm to 4-mm column cross-sectional area which is a factor of 1/4.**

| CONFIGURATION | 2-mm | 4-mm |
|---|---|---|
| **Eluent Flow Rate** | 0.25 mL/min | 1.0 mL/min |
| **SRS** | CSRS® ULTRA (2-mm)<br>(P/N 053949) | CSRS® ULTRA (4-mm)<br>(P/N 053948) |
| **MMS** | CMMS III (2-mm)<br>(P/N 056753) | CMMS III (4-mm)<br>(P/N 056752) |
| **AES** | CAES®<br>(P/N 056118) | CAES®<br>(P/N 056118) |
| **NOTE**<br>Do not run suppressors over 40°C. If application requires a higher temperature, place suppressor outside of chromatographic oven. | | |
| **Regenerant Flow Rate** | See suppressor manual. | See suppressor manual. |
| **Injection Loop** | 2 - 15 µL<br>Use the Rheodyne Microinjection Valve, Model No. 9126 DIONEX P/N 044697) for full loop injections <15 µL. | 10 - 50 µL |
| **System Void Volume** | Eliminate switching valves, couplers and the GM-3 Gradient Mixer. Use only the Microbore GM-4 (2-mm) Mixer (P/N 049135). | Minimize dead volumes. Switching valves, couplers can be used. Use the GM-2 , GM-3 or recommended gradient mixers. |
| **Pumps** | Use the GS50/GP50/GP40/IP20/IP25 in Microbore Configuration with a Microbore GM-4 (2-mm) Gradient Mixer.<br>No External Gradient Mixer is required for GS50/GP50/GP40 Pump when performing gradient analysis<br>The GPM-2 can be used for 2-mm isocratic chromatography at flow rates of 0.5 mL/min or greater but cannot be used for 2-mm gradient chromatography | Use the GP40/GS50/GP50/IP20/IP25 in Standard-Bore Configuration.<br>The GM-3 Gradient Mixer should be used for gradient analysis on systems other than the GP40/GP50/IP20/IP25 and the DX-300 HPLC Pump. |

| CONFIGURATION | 2-mm | 4-mm |
|---|---|---|
| **Detectors** | AD20/AD25 Cell<br>(6-mm, 7.5 µL, P/N 046423)<br>VDM-2 Cell<br>(3-mm, 2.0 µL, P/N 043120)<br>CD20, CD25, CD25A, ED40, ED50, or ED50A<br>Conductivity Cell with DS3<br>P/N 044130 or<br>Conductivity Cell with shield<br>P/N 044132<br>CDM-2/CDM-3 Cell<br>P/N 042770<br>Replace the TS-1 with the TS-2 (P/N 043117) on the CDM-2 or the CDM-3. The TS-2 has been optimized for 2-mm operation. Do not use the TS-2 or the TS-1 with the ED40/ED50/ED50A or the CD20/CD25/CD25A.<br>Ensure 30-40 psi back pressure after the cell (see Table 3). | AD20/AD25 Cell<br>(10-mm, 9 µL, P/N 049393)<br>VDM-2 Cell (6-mm, 10 µL)<br>P/N 043113<br>CD20, CD25, CD25A, ED40, ED50, or ED50A<br>Conductivity Cell with DS3<br>P/N 044130 or with shield<br>P/N 044132<br>CDM-2/CDM-3 Cell<br>P/N 042770<br>Either the TS-1 with the TS-2 can be used with the CDM-2 or the CDM-3. Do not use the TS-2 or the TS-1 with the ED40/ED50/ED50A or the CD20/CD25/CD25A.<br>Ensure 30-40 psi back pressure after the cell (see Table 3). |

**Table 3**
**Tubing Back Pressures**

| Color | Dionex P/N | ID inches | ID cm | Volume mL/ft | Back pressure Psi/ft at 1 mL/min | Back pressure Psi/ft at 0.25 mL/min | Back pressure Psi/cm at 1 mL/min |
|---|---|---|---|---|---|---|---|
| Green | 044777 | 0.030 | 0.076 | 0.137 | 0.086 | 0.021 | 0.003 |
| Orange | 042855 | 0.020 | 0.051 | 0.061 | 0.435 | 0.109 | 0.015 |
| Blue | 049714 | 0.013 | 0.033 | 0.026 | 2.437 | 0.609 | 0.081 |
| Black | 042690 | 0.010 | 0.025 | 0.015 | 6.960 | 1.740 | 0.232 |
| Red | 044221 | 0.005 | 0.013 | 0.004 | 111.360 | 27.840 | 3.712 |
| Yellow | 049715 | 0.003 | 0.008 | 0.001 | 859.259 | 214.815 | 28.642 |

# SECTION 3 - INSTALLATION

## 3.1 System Requirements

### 3.1.1 System Requirements for 2-mm Operation

The IonPac CS14 2-mm Guard and Analytical Columns are designed to be run on the following Dionex Ion Chromatographs equipped with suppressed conductivity detection. Isocratic analyses at flow rates of 0.5 mL/min or greater can be performed on a pump with standard (1/8" pistons) pump heads. For isocratic analyses at flow rates below 0.5 mL/min and gradient analyses, a microbore pump (1/16" pistons) must be employed.

### 3.1.2 System Requirements for 4-mm Operation

The IonPac CS14 4-mm Guard and Analytical Columns are designed to be run on any Dionex Ion Chromatograph equipped with suppressed conductivity detection. Gradient methods and methods requiring solvent containing eluents should be performed on a system having a pump with standard 1/8" pump heads. Isocratic analysis can also be performed on a standard bore pump.

### 3.1.3 System Void Volume

When using 2-mm columns, it is particularly important to minimize system void volume. The system void volume should be scaled down to at least 1/4 of the system volume in a standard 4-mm system. For best performance, all of the tubing installed between the injection valve and detector should be 0.005" (P/N 044221) ID PEEK tubing. 0.010" ID PEEK tubing (P/N 042260) or 0.012" Tefzel tubing (see “Dionex Product Selection Guide”) may be used but peak efficiency will be compromised which may also result in decreased peak resolution. Minimize the lengths of all connecting tubing and remove all unnecessary switching valves and couplers. If you need assistance in properly configuring your system contact the Dionex Office nearest you (see, “Dionex Worldwide Offices”).

## 3.2 Installing the Cation Trap Column for Eluent Step change or Gradient Operation

An IonPac Cation Trap Column (CTC (2-mm), P/N 043132 or CTC-1 (4-mm), P/N 040192) should be installed between the Gradient Pump and the injection valve. Remove the high pressure Gradient Mixer if present. The CTC is filled with high capacity cation exchange resin which helps to minimize the baseline shift caused by increasing cationic contaminant levels in the eluent as the ionic concentration of the eluent is increased over the course of the gradient analysis.

To install the CTC (2-mm) or CTC-1 (4-mm), complete the following steps:

**A.** **Remove the Gradient Mixer.** It is installed between the gradient pump pressure transducer and the injection valve.

**B.** **Connect the gradient pump directly to the CTC.** Connect a waste line to the CTC outlet and direct the line to a waste container.

**C.** **Flush the CTC.** Use 200 mL of a 10X eluent concentrate of the strongest eluent required by the application at a flow rate of 2.0 mL/min. Note that with the guard and analytical columns out of line, there is no need for 2-mm flow rate restrictions.

D. Rinse the CTC with the strongest eluent that will be used during the gradient analysis.

**E. Reconnect the CTC.** Connect the CTC to the eluent line that is connected to the injection valve.

The background conductivity of your system should be less than 3 µS when 10 mM methanesulfonic acid (MSA) is being pumped through the chromatographic system with the CSRS in-line and properly functioning. The baseline shift should be no greater than 1 µS during a gradient concentration ramp from 10 to 40 mM methanesulfonic acid (MSA). If the baseline shifts are greater than 5 µS, the CTC should be cleaned using steps A - E above.

**Flush the CTC at the end of each operating day**. This removes any impurities that may have accumulated on it. This will minimize periodic maintenance and lost data.

**A. Disconnect the CTC.** It should be installed between the injection valve

**B. Direct the outlet of the CTC to a separate waste container.**

**C. Flush the CTC.** Use 30 mL of a 10X eluent concentrate of the strongest eluent required by the application at a flow rate of 2.0 mL/min.

**D. Flush the CTC prior to start-up.** Prior to the use of the chromatographic system on the next day, flush the CTC with 30 mL of the strongest eluent used in the gradient program.

## 3.3 The Injection Loop

**Table 4**
**Smallest Injectable Volumes (µL)**

| Valve Type | Using 0.012" ID Tefzel Tubing | Using 0.007" ID Tefzel Tubing | Using 0.010" ID PEEK Tubing | Using 0.005" ID PEEK Tubing |
|---|---|---|---|---|
| Dionex BF2 Valve (8 µL Internal Volume) (10 cm Loop) | 15.2 | 10.5 | 13.1 | 9.2 |
| Dionex MicroInject Valve (10.5 µL Internal Volume) (14 cm Loop) | 20.5 | 14.0 | 17.6 | 12.2 |
| Rheodyne Microinjection Valve Model 9126 (0.8 µL Internal Volume) (10 cm Loop) | 8.0 | 3.3 | 5.9 | 2.0 |

### 3.3.1 The 2-mm System Injection Loop, 2 - 15 µL

For most applications on a 2-mm analytical system, a 2–15 µL injection loop is sufficient. Dionex recommends that a 2.5 µL injection loop be used to avoid overloading the CS14 2-mm Analytical Column. Generally, you should not inject more than 2.5 nanomoles (100–200 ppm) of any one analyte onto a 2-mm analytical column. Injecting larger volumes of samples can result in overloading the column which can affect the detection linearity. The CS14 2-mm requires a microbore HPLC system configuration. Install an injection loop one-fourth or less (< 15 µL) of the loop volume used with a 4-mm analytical system (Section 2, "Comparison of 2-mm and 4-mm Ion Chromatography Systems").

### 3.3.2 The 4-mm System Injection Loop, 10 - 50 µL

For most applications on a 4-mm analytical system, a 10–50 µL injection loop will be sufficient. Dionex recommends that a 10 µL injection loop be used to avoid overloading the CS14 4-mm Analytical Column. Generally, do not inject more than 10 nanomoles (100–200 ppm) of any one analyte onto the 4-mm analytical column. Injecting larger volumes of samples can result in overloading the column which can affect the detection linearity. This phenomenon will be more prevalent at higher concentrations of the analytes of interest.

## 3.4 Sample Concentration

The Trace Cation Concentrator (TCC-LP1, P/N 046027) or the IonPac CG14 4-mm Guard Column should be used for trace cation concentration work on 4-mm systems. The TCC-LP1 or the IonPac CG14 2-mm Guard Column must be used for trace cation concentrator work on 2-mm systems. See Section 4.5, "Sample Concentration," for details on sample concentration.

## 3.5 IonPac CG14 Guard Columns

An IonPac CG14 Guard Column is normally used with the IonPac CS14 Analytical Column. Retention times will increase by approximately 20% when a guard column is placed in-line prior to the analytical column. A guard is placed prior to the analytical column to prevent sample contaminants from eluting onto the analytical column. It is easier to clean or replace a guard column than it is an analytical column. For maximum life of the analytical column, the guard column should be changed or replaced as part of a regular maintenance schedule or at the first sign of performance deterioration. Use the test chromatogram that is shipped with the analytical column or the initial application run for a performance benchmark.

## 3.6 Eluent Storage

IonPac CS14 columns are designed to be used with sulfuric acid or methanesulfonic acid (MSA) eluents. Storage under a helium atmosphere ensures contamination free operation and proper pump performance (nitrogen can be used on 4-mm systems if eluents do not contain solvents).

## 3.7 Cation Self-Regenerating Suppressor Requirements

A Cation Self-Regenerating Suppressor should be used for applications that require suppressed conductivity detection. It is compatible with solvent containing eluents and aqueous ionic eluents of all concentrations with which the systems and columns are compatible. Aqueous ionic eluents can be used in all CSRS ULTRA modes of operation.

**CAUTION**

**Solvent containing eluents should be used in the AutoSuppression™ External Water Mode.**

If you are installing an IonPac CS14 4-mm Analytical Column, use a CSRS ULTRA (4-mm, P/N 043190).

If you are installing an IonPac CS14 2-mm Analytical Column, use a CSRS ULTRA (2-mm, P/N 043188).

For detailed information on the operation of the Cation Self-Regenerating Suppressor ULTRA, see Document No. 031370, the "Product Manual for the Cation Self-Regenerating Suppressor ULTRA, the CSRS ULTRA."

## 3.8 Cation Atlas Electrolytic Suppressor Requirements

An Cation Atlas® Electrolytic Suppressor (CAES) may be used instead of an CSRS ULTRA for applications that require suppressed conductivity detection. The CAES (P/N 056118) can be used for 2-mm and 4-mm IonPac CS14 applications using eluents up to 25 µeq/min.

For detailed information on the operation of the Cation Atlas Electrolytic Suppressor, see Document No. 031770, the "Product Manual for the Cation Atlas Electrolytic Suppressor."

## 3.9 Cation MicroMembrane Suppressor Requirements

A Cation MicroMembrane Suppressor, CMMS, may be substituted for the CSRS ULTRA. For detailed information on the operation of the Cation MicroMembrane Suppressor, see Document No. 031728, the "Product Manual for the Cation MicroMembrane Suppressor III."

## 3.10 Using AutoRegen

**Dionex recommends using an AutoRegen® Accessory (P/N 039594) with eluents that do not contain acetonitrile.** It should be used with the CSRS ULTRA in the Chemical Suppression mode or with the CMMS III. The AutoRegen Accessory saves regenerant preparation time and reduces regenerant consumption and waste.

**CAUTION**

**Acetonitrile is not compatible with the AutoRegen Cation Regenerant Cartridge. The acetonitrile diffuses into the TBAOH regenerant, concentrates during recirculation and eventually hydrolyzes to acetate and ammonia, depleting the capacity of the AutoRegen Cation Regenerant Cartridge. If acetonitrile is used with suppressed conductivity, a pressurized vessel rather than the AutoRegen must be used.**

When using an AutoRegen System, the regenerant passes over the hydroxide form anion exchange resin in the AutoRegen Cation Regenerant Cartridge where specific anionic contaminants (such as chloride ions) are continuously removed from the regenerant (TBAOH) to restore the salt form of the regenerant to the base form. If solvents are used in the eluent, ionic contaminants from the solvent component of the eluent which are not removed by the AutoRegen Regenerant Cartridge slowly accumulate in the regenerant. This results in slowly increasing background conductivity. The rate at which the background conductivity increases versus the required analysis sensitivity will determine how often the regenerant must be changed. It is not necessary to change the AutoRegen Regenerant Cartridge until it is completely expended.

**Use Dionex Cation Regenerant Solution (TBAOH, 0.1 M tetrabutylammonium hydroxide, P/N 039602).** This ensures maximum system performance. If you are using the AutoRegen Accessory (P/N 039594) equipped with an AutoRegen Cation Regenerant Cartridge (P/N 039563), prepare 0.5 to 1.0 liter of the regenerant. If you plan to use a pressurized vessel, prepare several liters.

**Equilibrate the AutoRegen Cation Regenerant Cartridge to new regenerant.** When replacing the recycled regenerant, the first 200 mL of the regenerant should be pumped to waste before recycling of the regenerant is started. Utilizing AutoRegen in this manner will allow the use of high regenerant flow rates with the minimum of consumption and waste.

**Increase the regenerant flow rate for gradient analysis.** To minimize the baseline shift when performing an analysis that requires a methanesulfonic acid step or linear gradient, a high regenerant flow rate (10–15 mL/min) is required.

## 3.11 Detector Requirements

See Section 2, "Comparison of Ion Chromatography Systems," for 2-mm and 4-mm system detector, cell and thermal stabilizer requirements.

# SECTION 4 - OPERATION

## 4.1 General Operating Conditions

| | |
|---|---|
| Sample Volume: | 2-mm: 2.5 µL Loop + 0.8 µL Injection valve dead volume<br>4-mm: 25 µL Loop + 0.8 µL Injection valve dead volume |
| Column: | 2-mm: CS14 2-mm Analytical Column (+ CG14 2-mm Guard Column)<br>4-mm: CS14 4-mm Analytical Column (+ CG14 4-mm Guard Column) |
| Eluent: | 10 mN MSA |
| Eluent Flow Rate: | 2-mm: 0.25 mL/min<br>4-mm: 1.0 mL/min |
| SRS Suppressor: | Cation Self-Regenerating Suppressor, CSRS ULTRA (2-mm or 4-mm)<br>AutoSuppression Recycle Mode |
| or MMS Suppressor: | Cation MicroMembrane Suppressor, CMMS III (2-mm or 4-mm) |
| MMS Regenerant: | 100 mN tetrabutylammonium hydroxide (TBAOH)<br>Use Dionex Cation Regenerant Solution (P/N 039602). |
| or AES Suppressor: | Cation Atlas Electrolytic Suppressor, CAES<br>(up to 25 µeq/min) |
| Expected Background Conductivity: | ≤ 3 µS |
| Storage Solution: | Eluent |

## 4.2 Operating Precautions

**CAUTION**

**IonPac CS14 Operation Precautions**

**Operate below 4,000 psi (27.57 MPa)**
**Filter and Degas Eluents**
**Filter Samples**

## 4.3 Chemical Purity Requirements

Obtaining reliable, consistent and accurate results requires eluents that are free of ionic impurities. Chemicals, solvents and deionized water used to prepare eluents must be of the highest purity available. Low trace impurities and low particle levels in eluents also help to protect your ion exchange columns and system components. Dionex cannot guarantee proper column performance when the quality of the chemicals, solvents and water used to prepare eluents has been compromised.

### 4.3.1 Deionized Water

The deionized water used to prepare eluents should be Type I Reagent Grade Water with a specific resistance of 18.2 megohm-cm. The deionized water should be free of ionized impurities, organics, microorganisms and particulate matter larger than 0.2 µm Bottled HPLC-Grade Water (with the exception of Burdick & Jackson) should not be used since most bottled water contains an unacceptable level of ionic impurities.

### 4.3.2 Inorganic Chemicals

It is very important for the eluent to be as free of impurities as possible. The chemicals and water required to prepare the eluent should be of the highest purity available. Use deionized water with a specific resistance of 18.2 megohm-cm.

A. Use degassed Type I deionized water with a specific resistance of 18.2 megohm-cm to make all standards, eluents and regenerants.

B. Use Fluka or Aldrich Methanesulfonic Acid (MSA) (>99% pure).

C. In the Chemical Suppression Mode of operation, use Dionex Cation Regenerant Solution (tetrabutylammonium hydroxide (TBAOH), P/N 039602) to ensure maximum system performance when operating with a CSRS ULTRA (4-mm) or (2-mm).

D. Use BAKER INSTRA-ANALYZED® or Aldrich Trifluoroacetic Acid

E. Use Aldrich 18-Crown-6 (99% pure).

F. Use Aldrich Pyrophosphoric Acid (97% pure).

### 4.3.3 Eluents with Solvents

Solvents can be added to the ionic eluents used with IonPac CS14 columns to modify the ion exchange process or improve sample solubility. The solvents used must be free of ionic impurities. However, since most manufacturers of solvents do not test for ionic impurities, it is important that the highest grade of solvents available be used. Currently, several manufacturers are making ultrahigh purity solvents that are compatible for HPLC and spectrophotometric applications. These ultrahigh purity solvents will usually ensure that your chromatography is not affected by ionic impurities in the solvent. Currently at Dionex, we have obtained consistent results using High Purity Solvents manufactured by Burdick and Jackson and Optima® Solvents by Fisher Scientific.

When using a solvent in an ionic eluent, column generated back pressures will depend on the solvent used, concentration of the solvent, the ionic strength of the eluent and the flow rate used. The column back pressure will vary as the composition of water-acetonitrile mixture varies. The practical back pressure limit for the IonPac CS14 columns is 4,000 psi (27.57 MPa).

**The IonPac CS14 is compatible with the HPLC solvents listed in Table 5, "HPLC Solvents for Use with the CS14 Columns."** Solvents and water should be premixed in concentrations which allow proper mixing by the gradient pump and to minimize outgassing. Ensure that all of the inorganic chemicals are soluble in the highest solvent concentration to be used during the analysis.

**Table 5**
**HPLC Solvents for Use with IonPac CS14 Columns**

| Solvent | Maximum Operating Concentration |
|---|---|
| Acetonitrile | 100% |
| Methanol | 100% |
| 2-Propanol | 100% |
| Tetrahydrofuran | 20% |

## 4.4 Making and Using Eluents that Contain Solvents

**When mixing solvents with water remember to mix solvent with water on a volume to volume basis.** If a procedure requires an eluent of 90% acetonitrile, prepare the eluent by adding 900 mL of acetonitrile to an eluent reservoir. Then add 100 mL of deionized water or eluent concentrate to the acetonitrile in the reservoir. Using this procedure to mix solvents with water will ensure that a consistent true volume/volume eluent is obtained. Premixing water with solvent will minimize the possibility of outgassing.

**CAUTION**

**When purging or degassing eluents containing solvents, do not purge or degas the eluent excessively since it is possible that a volatile solvent can be "boiled" off from the solution.**

**Always degas and store all eluents in glass or plastic eluent bottles pressurized with helium. Only helium can be used to purge and degas ionic eluents containing solvents, since nitrogen is soluble in solvent containing eluents.**

**Avoid creating high viscosity pressure fronts that may disrupt the column packing when the eluent solvent component is changed.** To do this, equilibrate the column for approximately 10 minutes with an eluent containing only 5% of the current solvent type. Exchange this eluent for an eluent with 5% of the new solvent type and then equilibrate the column and allow the system to stabilize (approximately 10 minutes). Next run a 15-minute gradient from 5% of the new solvent type to the highest percentage that will be used during the new analysis protocol.

**Properly equilibrate the column when changing to a solvent-free eluent system after using eluents containing solvent.** First equilibrate the column with 1 to 5 percent of the current solvent for approximately 5 minutes. Next run a 10-minute gradient from the eluent with 1 to 5 percent of the current solvent to the new solvent free aqueous eluent.

**CAUTION**

**The Cation Self-Regenerating Cation Suppressor (CSRS ULTRA) must be operated in the AutoSuppression External Water Mode when using eluents containing solvents.**

**Acetonitrile is not compatible with the Cation Regenerant Cartridge when using an AutoRegen Accessory Unit. The acetonitrile diffuses into the TBAOH regenerant, concentrates during recirculation and eventually hydrolyzes to acetate and ammonia, depleting the capacity of the AutoRegen Cation Regenerant Cartridge. If acetonitrile is used with suppressed conductivity, a pressurized vessel rather than the AutoRegen must be used.**

## 4.5 Sample Concentration

**The IonPac CG14 Guard Column or the Low-Pressure Trace Cation Concentrator, TCC-LP1, should be used for trace cation concentrator.** Trace cation concentrators are used primarily in high purity water analysis. The function of trace cation concentrator in these applications is to strip ions from a measured volume of a relatively clean aqueous sample matrix. This can be accomplished by concentrating large volumes of the sample onto a concentrator column and then using this column in place of the sample loop. The sample should be pumped into the concentrator column in the **OPPOSITE** direction of the eluent flow, otherwise the chromatography will be compromised. This process "concentrates" all cationic analyte species onto the trace cation concentrator (the TCC-LP1 or the CG14) leading to a lowering of detection limits by 2-5 orders of magnitude. The unique advantage of the trace cation concentrator (TCC-LP1 or the CG14) for the analytical chemist in these applications is the capability of performing routine trace analyses of sample matrix ions at µg/L levels without extensive and laborious sample pretreatment.

The IonPac CG14 2-mm Guard Column (P/N 046076) or the Low-Pressure Trace Cation Concentrator (TCC-LP1, P/N 0496027) must be used for sample concentration with the IonPac CS14 2-mm Analytical Column.

The IonPac CG14 4-mm Guard Column (P/N 046074) or the Low-Pressure Trace Cation Concentrator (TCC-LP1, P/N 0496027) should be used for sample concentration with the IonPac CS14 4-mm Analytical Column.

**CAUTION**

**The Trace Cation Concentrator (TCC-2, P/N 043103) should not be used for sample concentration. The**
**TCC-2 column packing is functionalized with a strong cation exchange resin and the recommended IonPac CS14 eluents will not properly elute ions concentrated on this column.**

# SECTION 5 - EXAMPLE APPLICATIONS

**The chromatograms in this section were obtained using columns that reproduced the Production test Chromatogram (see Section 5.3, "Production Test Chromatogram") on optimized Ion Chromatographs (see Section 3, "Installation"). Different systems will differ slightly in performance due to slight differences in column sets, system void volumes, liquid sweep-out times of different components and laboratory temperatures.**

Before attempting any of the following example applications, take the time to ensure that your system is properly configured. Ensure that all of the eluents have been made from high purity reagents and deionized water. All water used in the preparation of eluents should be degassed, deionized water. For chemical purity requirements, see Section 4.3, "Chemical Purity Requirements." After running synthetic standards to calibrate your system, you may find that real sample matrices foul your columns. For this reason it is always advisable to use a guard column to protect the analytical column. If column performance deteriorates and it is determined that the guard or the analytical column has been fouled, refer to the column cleanup protocols in, "Column Care." If your sample matrices are relatively low in ionic concentration, you may be able to increase the sensitivity of your system by using sample concentration techniques (see Section 4.5, "Sample Concentration").

## 5.1 Preparation of Eluent Stock Solution Concentrates

**WARNING**

**Methanesulfonic acid (MSA), trifluoroacetic acid and pyrophosphoric acid are corrosives and strong irritants.**

**Avoid breathing the vapors**

**Always prepare these reagents in a fume hood. Wear gloves and goggles.**

### 5.1.1 1.0 M Methanesulfonic Acid (MSA) Stock Solution

A 1.0 M methanesulfonic acid stock solution can be prepared as follows:
Weigh out 96.10 g of methanesulfonic acid (MSA, MW = 96.1). Carefully add this amount to a 1 liter volumetric flask containing about 500 mL of deionized water. Dilute to the mark and mix thoroughly.

### 5.1.2 1.0 M Trifluoroacetic Acid (TFA) Stock Solution

A 1.0 M trifluoroacetic acid stock solution can be prepared as follows:
Weigh out 114.03 g of trifluoroacetic acid (TFA, MW = 114.03). Carefully add this amount to a 1 liter volumetric flask containing about 500 mL of deionized water. Dilute to the mark and mix thoroughly.

### 5.1.3 0.1 M 18-Crown-6 Ether Stock Solution

A 0.1 M 18-Crown-6 stock solution can be prepared as follows:
Weigh out 26.432 g of 18-Crown-6 (Obtain from Aldrich, 99% pure, MW = 264.32). Carefully add this amount to a 1 liter volumetric flask containing about 500 mL of deionized water. Dilute to the mark and mix thoroughly.

**CAUTION**

**18-Crown-6 is an expensive reagent. Calculate your analysis requirements before making a large volume of stock solution.**

### 5.1.4 Pyrophosphoric Acid

A **5.45 mM Pyrophosphoric acid** solution can be prepared as follows:
Add 0.97 g pyrophosphoric acid (MW = 177.98). Dilute to a final volume of 1 L using deionized water. Degas the eluent.

## 5.2 Eluent Preparation

Eluent: X mM Methanesulfonic acid (MSA), Trifluoroacetic acid (TFA) or 18-Crown-6 Ether

Using the table below, pipet X.0 mL of the 1.0 N MSA or TFA eluent concentrate (see Section 5.1, "Preparation of Eluent Stock Solution Concentrates") into a 1-L volumetric flask. Dilute to 1-L using deionized water with a specific resistance of 18.2 megohm-cm. Degas the eluent.

**Table 6**
**mM Eluents from 1.0 M Stock Solutions**

| mM MSA or TFA | # mL of 1.0 M MSA or TFA |
|---|---|
| 4 | 4.0 |
| 8 | 8.0 |
| 9 | 9.0 |
| 10 | 10.0 |
| 100 | 100.0 |

**Table 7**
**mM Eluents from 0.1 M Stock Solutions**

| mM 18-Crown-6 Ether | # mL of 1.0 M 18-Crown-6 Ether |
|---|---|
| 2.5 | 25 |

## 5.3 Production Test Chromatogram

Isocratic elution of amines and inorganic cations on the IonPac CS14 Analytical Column has been optimized utilizing methanesulfonic acid because of its suitability for use with the Cation Self-Regenerating Suppressor CSRS ULTRA (4-mm and 2-mm). By using this eluent, amines and common mono- and divalent inorganic cations can be isocratically separated and quantitated in a single injection. To guarantee that all IonPac CS14 2-mm and 4-mm Analytical Columns meet high quality and reproducible performance specification standards, all columns undergo the following production control test.

| | |
|---|---|
| Sample Loop Volume: | 6.25 µL (2-mm), 25 µL (4-mm) |
| Analytical Column: | IonPac CS14 Analytical Column |
| Eluent: | 10 mM MSA |
| Eluent Flow Rate: | 0.25 mL/min (2-mm), 1.0 mL/min (4-mm) |
| SRS Suppressor: | Cation Self-Regenerating Suppressor, CSRS ULTRA (2-mm or 4-mm) Recycle Mode |
| or MMS Suppressor: | Cation MicroMembrane Suppressor, CMMS III (2-mm or 4-mm) |
| MMS Regenerant: | 100 mN TBAOH (tetrabutylammonium hydroxide) |
| or AES Suppressor: | Cation Atlas Electrolytic Suppressor, CAES (up to 25 µeq/min) |
| Expected Background Conductivity: | ≤ 3 µS |
| Storage Solution: | Eluent |

| | Analyte | mg/L |
|---|---|---|
| 1. | $Li^+$ | 0.5 |
| 2. | $Na^+$ | 2.0 |
| 3. | $NH_4^+$ | 2.5 |
| 4. | $K^+$ | 5.0 |
| 5. | Diethylamine | 10.0 |
| 6. | $Mg^{2+}$ | 2.5 |
| 7. | $Ca^{2+}$ | 5.0 |

1 mg/L = 1 ppm

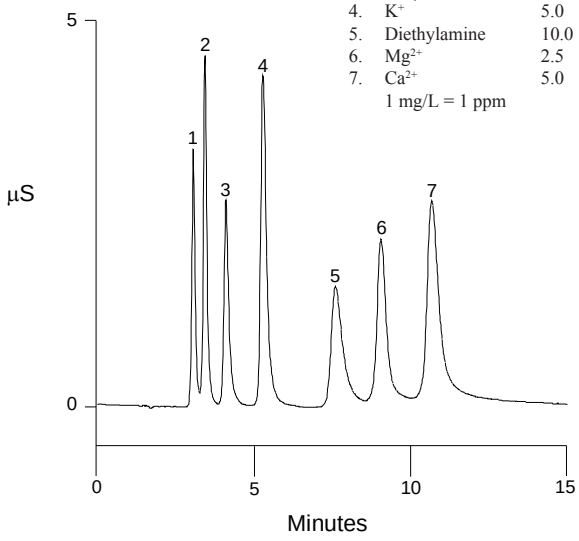



**Figure 2**
**IonPac CS14 Production Test Chromatogram**

## 5.4 Isocratic Elution of Ammonium, Group I & II Cations

Resolution of Group I and Group II Cations ($Li^+$, $Na^+$, $NH_4^+$, $K^+$, $Rb^+$, $Cs^+$, $Mg^{2+}$, $Ca^{2+}$, $Sr^{2+}$, $Ba^{2+}$) is accomplished by isocratic elution using 10 mM methanesulfonic acid (MSA).

| | |
|---|---|
| Sample Loop Volume: | 4.5 µL (2-mm), 18 µL (4-mm) |
| Analytical Column: | IonPac CS14 Analytical Column |
| Eluent: | 10 mM MSA |
| Eluent Flow Rate: | 0.25 mL/min (2-mm), 1.0 mL/min (4-mm) |
| SRS Suppressor: | Cation Self-Regenerating Suppressor, CSRS ULTRA (2-mm or 4-mm) Recycle Mode |
| or MMS Suppressor: | Cation MicroMembrane Suppressor, CMMS III (2-mm or 4-mm) |
| MMS Regenerant: | 100 mN TBAOH (tetrabutylammonium hydroxide) |
| or AES Suppressor: | Cation Atlas Electrolytic Suppressor, CAES (up to 25 µeq/min) |
| Expected Background Conductivity: | ≤ 3 µS |
| Storage Solution: | Eluent |

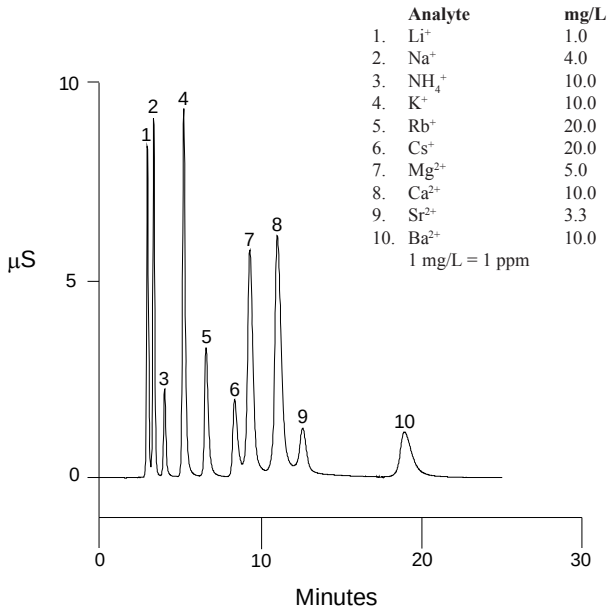



**Figure 3**
**Isocratic Elution of Ammonium, Group I & II Cations**
**($Li^+$, $Na^+$, $NH_4^+$, $K^+$, $Rb^+$, $Cs^+$, $Mg^{2+}$, $Ca^{2+}$, $Sr^{2+}$, $Ba^{2+}$)**

## 5.5 The Effect of Sample Acidity on IonPac CS14 Efficiency

The IonPac CS14 packing is functionalized with a unique carboxylate functional group that ensures long-term column stability. The column is compatible with acidic eluents and samples. The performance of the CS14 does not deteriorate with the injection of acidic samples up to approximately 20 mM in hydronium ion, thus acid digest or preserved samples can be injected without pH adjustment. In contrast, the IonPac CS12 has higher capacity and can handle samples containing up to 50 mM hydronium ion. Note that only the chromatographic separation is impaired for the particular sample. The column is not harmed in any way.

| | |
|---|---|
| Sample Loop Volume: | 6.25 µL (2-mm), 25 µL (4-mm) |
| Analytical Column: | IonPac CS14 Analytical Column |
| Eluent: | 10 mM MSA |
| Eluent Flow Rate: | 0.25 mL/min (2-mm), 1.0 mL/min (4-mm) |
| SRS Suppressor: | Cation Self-Regenerating Suppressor, CSRS ULTRA (2-mm or 4-mm) Recycle Mode |
| or MMS Suppressor: | Cation MicroMembrane Suppressor, CMMS III (2-mm or 4-mm) |
| MMS Regenerant: | 100 mN TBAOH (tetrabutylammonium hydroxide) |
| or AES Suppressor: | Cation Atlas Electrolytic Suppressor, CAES (up to 25 µeq/min) |
| Expected Background Conductivity: | ≤ 3 µS |
| Storage Solution: | Eluent |

| | Analyte | mg/L |
|---|---|---|
| 1. | $Li^+$ | 1.0 |
| 2. | $Na^+$ | 4.0 |
| 3. | $NH_4^+$ | 5.0 |
| 4. | $K^+$ | 10.0 |
| 5. | $Mg^{2+}$ | 5.0 |
| 6. | $Ca^{2+}$ | 10.0 |

1 mg/L = 1 ppm

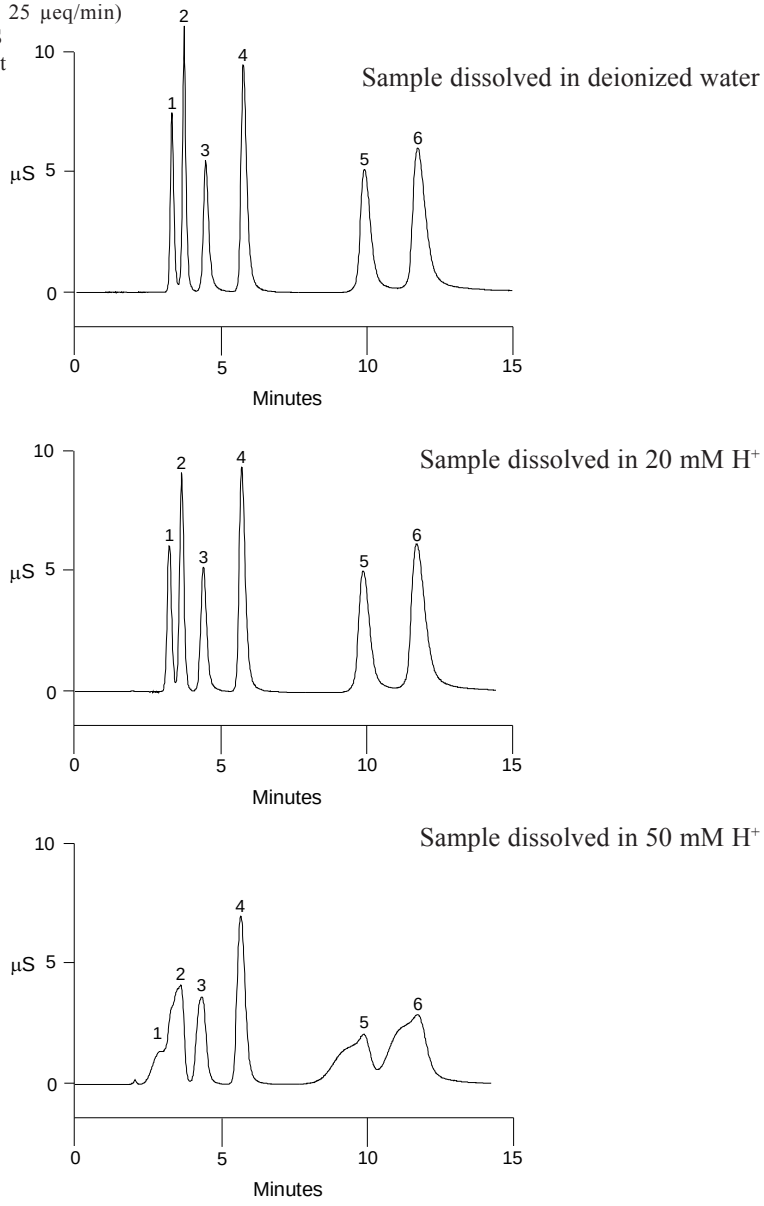



**Figure 4**
**The Effect of Sample Acidity on CS14 Efficiency**

## 5.6 Selectivity Control of Magnesium, Manganese and Calcium

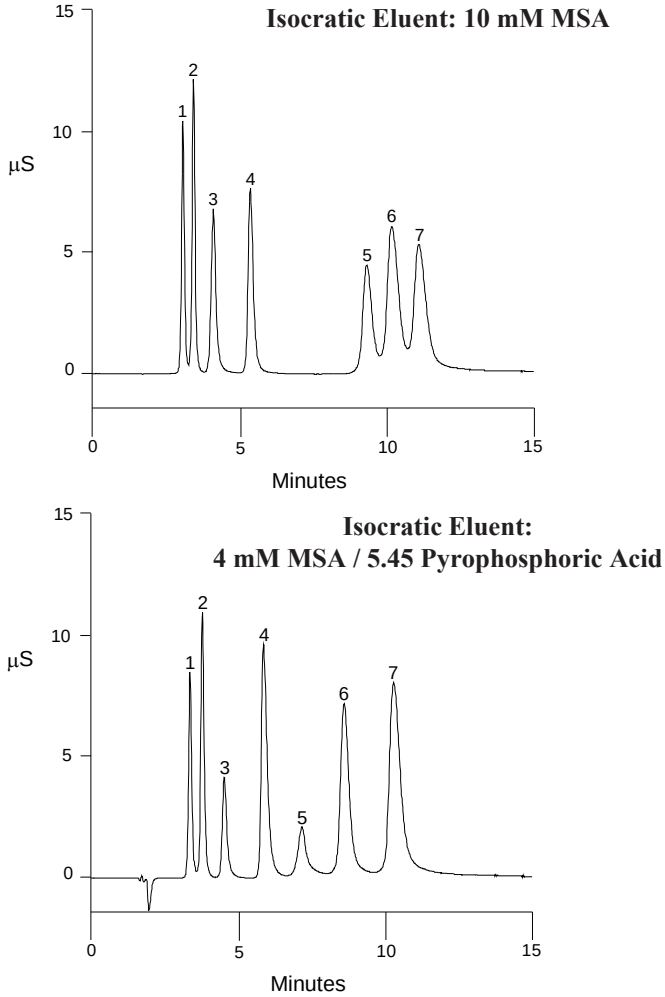
On-line monitoring of soluble manganese is a good indicator of corrosion in nuclear power plants. Manganese can be quantified in power cooling waters using the IonPac CS14. Pyrophosphoric acid is added to the methanesulfonic acid eluent to enhance the resolution of manganese from magnesium and calcium. The pyrophosphate ion complexes preferentially with the manganese, causing it to elute before magnesium. The pyrophosphoric acid concentration is critical and can be adjusted to optimize the position of manganese between potassium and magnesium. When pyrophosphoric acid is added to the eluent, the methanesulfonic acid concentration must be reduced since the pyrophosphoric acid not only complexes with manganese but also contributes hydronium ions*. This eluent can be suppressed using the AutoSuppression Recycle Mode.

The column can be quickly converted to eluents not containing pyrophosphoric acid by washing the column with 100 mM methanesulfonic acid for 30 minutes.

| | |
|---|---|
| Sample Loop Volume: | 6.25 µL (2-mm), 25 µL (4-mm) |
| Analytical Column: | IonPac CS14 Analytical Column |
| Eluent: | See Chromatogram |
| Eluent Flow Rate: | 0.25 mL/min (2-mm), 1.0 mL/min (4-mm) |
| SRS Suppressor: | Cation Self-Regenerating Suppressor, CSRS ULTRA (2-mm or 4-mm) Recycle Mode |
| or MMS Suppressor: | Cation MicroMembrane Suppressor, CMMS III (2-mm or 4-mm) |
| MMS Regenerant: | 100 mN TBAOH (tetrabutylammonium hydroxide) |
| or AES Suppressor: | Cation Atlas Electrolytic Suppressor, CAES (up to 25 µeq/min) |
| Expected Background Conductivity: | ≤ 3 µS |
| Storage Solution: | Eluent |

| | Analyte | mg/L |
|---|---|---|
| 1. | $Li^+$ | 1.0 |
| 2. | $Na^+$ | 4.0 |
| 3. | $NH_4^+$ | 5.0 |
| 4. | $K^+$ | 10.0 |
| 5. | $Mg^{2+}$ | 5.0 |
| 6. | $Mn^{2+}$ | 2.5 |
| 7. | $Ca^{2+}$ | 10.0 |

1 mg/L = 1 ppm




| | Analyte | mg/L |
|---|---|---|
| 1. | $Li^+$ | 1.0 |
| 2. | $Na^+$ | 4.0 |
| 3. | $NH_4^+$ | 5.0 |
| 4. | $K^+$ | 10.0 |
| 5. | $Mn^{2+}$ | 2.5 |
| 6. | $Mg^{2+}$ | 5.0 |
| 7. | $Ca^{2+}$ | 10.0 |

1 mg/L = 1 ppm

**Figure 5**
**Selectivity Control of Magnesium, Manganese and Calcium**

* The higher the concentration of pyrophosphoric acid in the eluent, the faster manganese will elute. Too much pyrophosphoric acid will cause manganese to co-elute with potassium

## 5.7 Isocratic Elution of Morpholine and Resolution Enhancement Addition of Solvent to Eluent

The organic solvent, acetonitrile, can be used to control the IonPac CS14 cation exchange selectivity of morpholine and methyl amines. The solvent compatibility of the IonPac CS14 permits the use of HPLC organic solvents in the eluent to modify ion exchange selectivity. The first example illustrates the use of acetonitrile in the eluent to optimize the separation of the closely eluting analyte pairs, morpholine and magnesium. The retention of the more hydrophobic member of the pair, morpholine, is decreased more by the addition of solvent, improving resolution. The acetonitrile concentration is used to optimize the positioning of morpholine between potassium and magnesium and improve the morpholine peak shape.

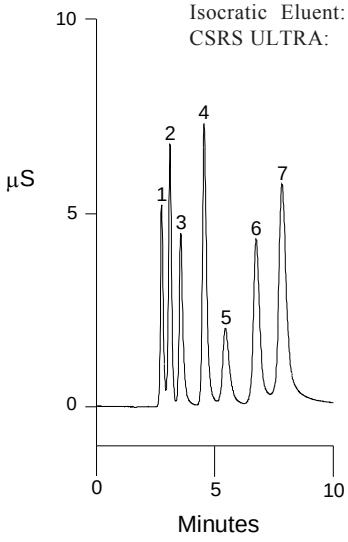
The third example illustrates the determination of trace levels of lithium, sodium, ammonium, potassium, magnesium and calcium in a high purity power plant water treated with morpholine. 1.0 mL of sample was concentrated on a CG14 guard column and then analyzed. The sample was concentrated and then run on a 2-mm system for economy of operation.

| | |
|---|---|
| Sample Loop Volume: | 6.25 µL (2-mm), 25 µL (4-mm) |
| Analytical Column: | IonPac CS14 Analytical Column |
| Eluent: | See Chromatogram |
| Eluent Flow Rate: | 0.25 mL/min (2-mm), 1.0 mL/min (4-mm) |
| SRS Suppressor: | Cation Self-Regenerating Suppressor, CSRS ULTRA (2-mm or 4-mm) Recycle Mode |
| or MMS Suppressor: | Cation MicroMembrane Suppressor, CMMS III (2-mm or 4-mm) |
| MMS Regenerant: | 100 mN TBAOH (tetrabutylammonium hydroxide) |
| Expected Background Conductivity: | $\leq$ 3 µS |
| Storage Solution: | Eluent |

| | Analyte | mg/L |
|---|---|---|
| 1. | $Li^+$ | 1.0 |
| 2. | $Na^+$ | 4.0 |
| 3. | $NH_4^+$ | 5.0 |
| 4. | $K^+$ | 10.0 |
| 5. | Morpholine | 50.0 |
| 6. | $Mg^{2+}$ | 5.0 |
| 7. | $Ca^{2+}$ | 10.0 |

1 mg/L = 1 ppm

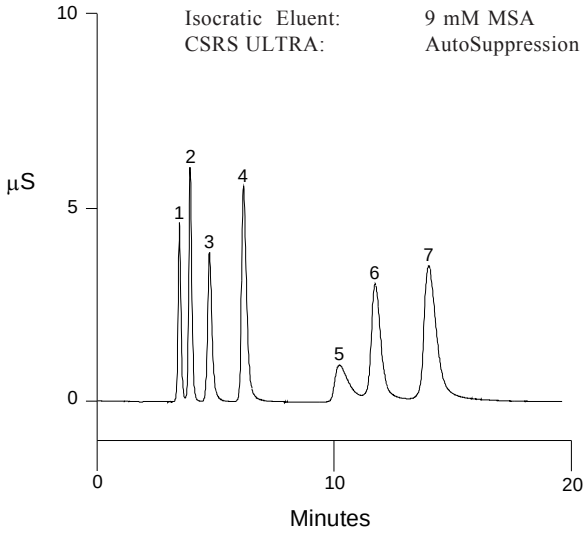
Isocratic Eluent: 10 mM MSA / 1.2% ACN
CSRS ULTRA: AutoSuppression
External Water Mode




| | Analyte | mg/L |
|---|---|---|
| 1. | $Li^+$ | 0.5 |
| 2. | $Na^+$ | 2.0 |
| 3. | $NH_4^+$ | 2.5 |
| 4. | $K^+$ | 5.0 |
| 5. | Morpholine | 25.0 |
| 6. | $Mg^{2+}$ | 2.5 |
| 7. | $Ca^{2+}$ | 5.0 |

1 mg/L = 1 ppm

Isocratic Eluent: 9 mM MSA
CSRS ULTRA: AutoSuppression Recycle Mode




System: 2-mm
Flow Rate: 0.25 mL/min
Injection: 1.0 mL concentrated on an IonPac CG14

| | Analyte | µg/L |
|---|---|---|
| 1. | $Li^+$ | 0.5 |
| 2. | $Na^+$ | 2.0 |
| 3. | $NH_4^+$ | 150.0 |
| 4. | $K^+$ | 2.0 |
| 5. | Morpholine | 2,000.0 |
| 6. | $Mg^{2+}$ | 2.0 |
| 7. | $Ca^{2+}$ | 10.0 |

1 µg/L = 1 ppb

Isocratic Eluent: 8 mM MSA / 5% ACN
CSRS ULTRA: AutoSuppression
External Water Mode

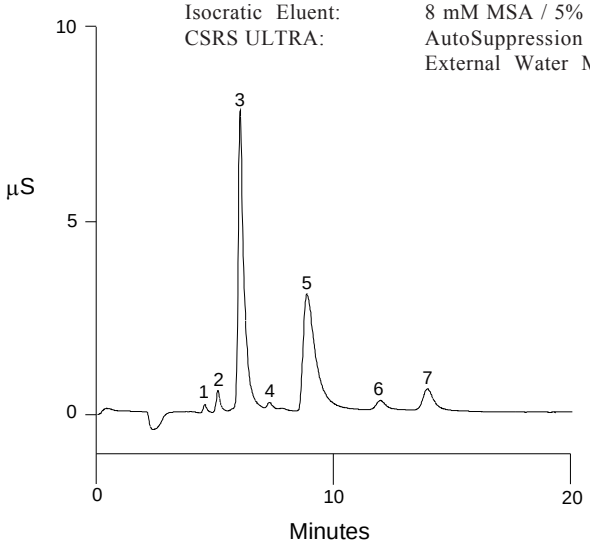



**Figure 6**
**Isocratic Elution of Morpholine and Resolution Enhancement Through the Addition of Solvent to the Eluent**

## 5.8 Elution of Morpholine with Mono-, Di- and Trimethylamines With Resolution Enhancement Through Gradient Elution

The determination of morpholine in the presence of mono-, di- and trimethylamines, ammonia, alkali and alkaline earth metals can be accomplished by isocratic elution with 10 mM MSA and 0.3% acetonitrile. Further enhancement of resolution between ammonium and methylamine and also between dimethylamine and potassium while still eluting trimethylamine rapidly and with good peak shape can be accomplished by increasing the solvent to 2.5 % acetonitrile and running a methanesulfonic acid gradient from 5 to 13 mM.

| | |
|---|---|
| Sample Loop Volume: | 6.25 µL (2-mm), 25 µL (4-mm) |
| Analytical Column: | IonPac CS14 Analytical Column |
| Eluent: | See Chromatogram |
| Eluent Flow Rate: | 0.25 mL/min (2-mm), 1.0 mL/min (4-mm) |
| SRS Suppressor: | Cation Self-Regenerating Suppressor, CSRS ULTRA (2-mm or 4-mm) External Water Mode |
| or MMS Suppressor: | Cation MicroMembrane Suppressor, CMMS III (2-mm or 4-mm) |
| MMS Regenerant: | 100 mN TBAOH (tetrabutylammonium hydroxide) |
| Expected Background Conductivity: | < 1 µS |
| Storage Solution: | Eluent |

Eluent 1: Type I DI Water
Eluent 2: 100 mM MSA
Eluent 3: 10% Acetonitrile

Eluent Flow Rate: 1.0 mL/min (4-mm System)

| TIME (min) | %E1 | %E2 | %E3 | Comments |
|---|---|---|---|---|
| Equilibration | | | | |
| 0.0 | 70 | 5 | 25 | Equilibrate to 5.0 mM MSA / 2.5% ACN |
| 7.0 | 70 | 5 | 25 | |
| Analysis | | | | |
| 0.0 | 70 | 5 | 25 | Inject, 5.0 mM MSA / 2.5% ACN |
| 0.1 | 70 | 5 | 25 | Inject Valve to Load Position |
| 7.0 | 69 | 6 | 25 | 6.0 mM MSA / 2.5% ACN |
| 12.0 | 62 | 13 | 25 | 13.0 mM MSA / 2.5% ACN |
| 18.0 | 62 | 13 | 25 | 13.0 mM MSA / 2.5% ACN |

| | Analyte | mg/L |
|---|---|---|
| 1. | $Li^+$ | 0.5 |
| 2. | $Na^+$ | 2.0 |
| 3. | $NH_4^+$ | 2.5 |
| **4.** | **Methylamine** | **10.0** |
| 5. | $K^+$ | 5.0 |
| **6.** | **Dimethylamine** | **10.0** |
| **7.** | **Trimethylamine** | **30.0** |
| **8.** | **Morpholine** | **25.0** |
| 9. | $Mg^{2+}$ | 2.5 |
| 10. | $Ca^{2+}$ | 5.0 |

1 mg/L = 1 ppm

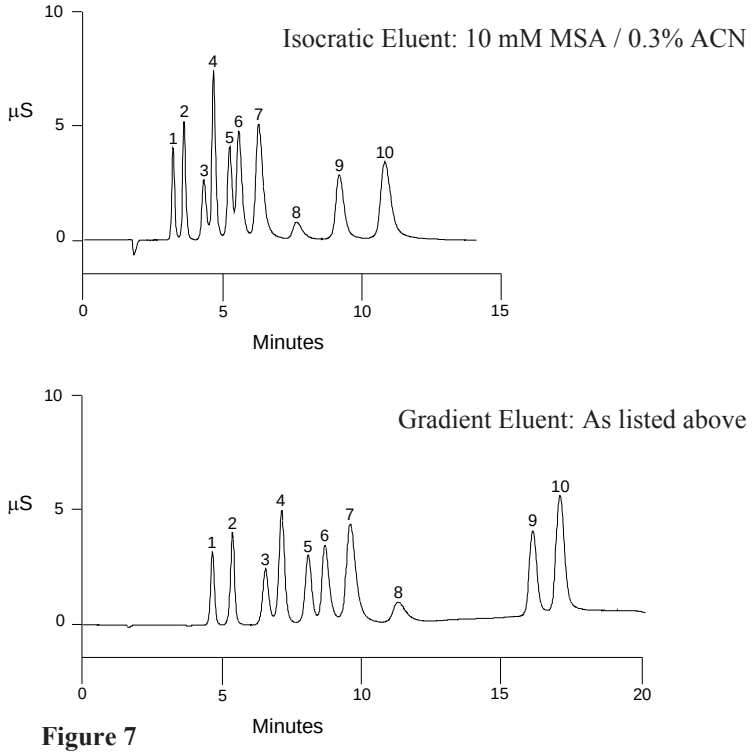



**Figure 7**
**Elution of Morpholine with Mono-, Di- and Trimethylamines, Ammonia, the Alkali and Alkaline Earth Metals**

## 5.9 Isocratic Elution of Mono-, Di- and Trimethylamines and Resolution Enhancement through Addition of Solvent to Eluent

The determination of mono-, di- and trimethylamines in the presence of ammonia, alkali (excluding potassium) and alkaline earth metals can be accomplished by isocratic elution using 10 mM methanesulfonic acid (MSA). Further enhancement of resolution to allow the determination of the methylamines with potassium present can be accomplished by the addition of a small amount of solvent to the eluent.

| | |
|---|---|
| Sample Loop Volume: | 6.25 µL (2-mm), 25 µL (4-mm) |
| Analytical Column: | IonPac CS14 Analytical Column |
| Eluent: | See Chromatogram |
| Eluent Flow Rate: | 0.25 mL/min (2-mm), 1.0 mL/min (4-mm) |
| SRS Suppressor: | Cation Self-Regenerating Suppressor, CSRS ULTRA (2-mm or 4-mm) Recycle Mode or External Water Mode |
| or MMS Suppressor: | Cation MicroMembrane Suppressor CMMS III (2-mm or 4-mm) |
| MMS Regenerant: | 100 mN TBAOH (tetrabutylammonium hydroxide) |
| Expected Background Conductivity: | < 1 µS |
| Storage Solution: | Eluent |

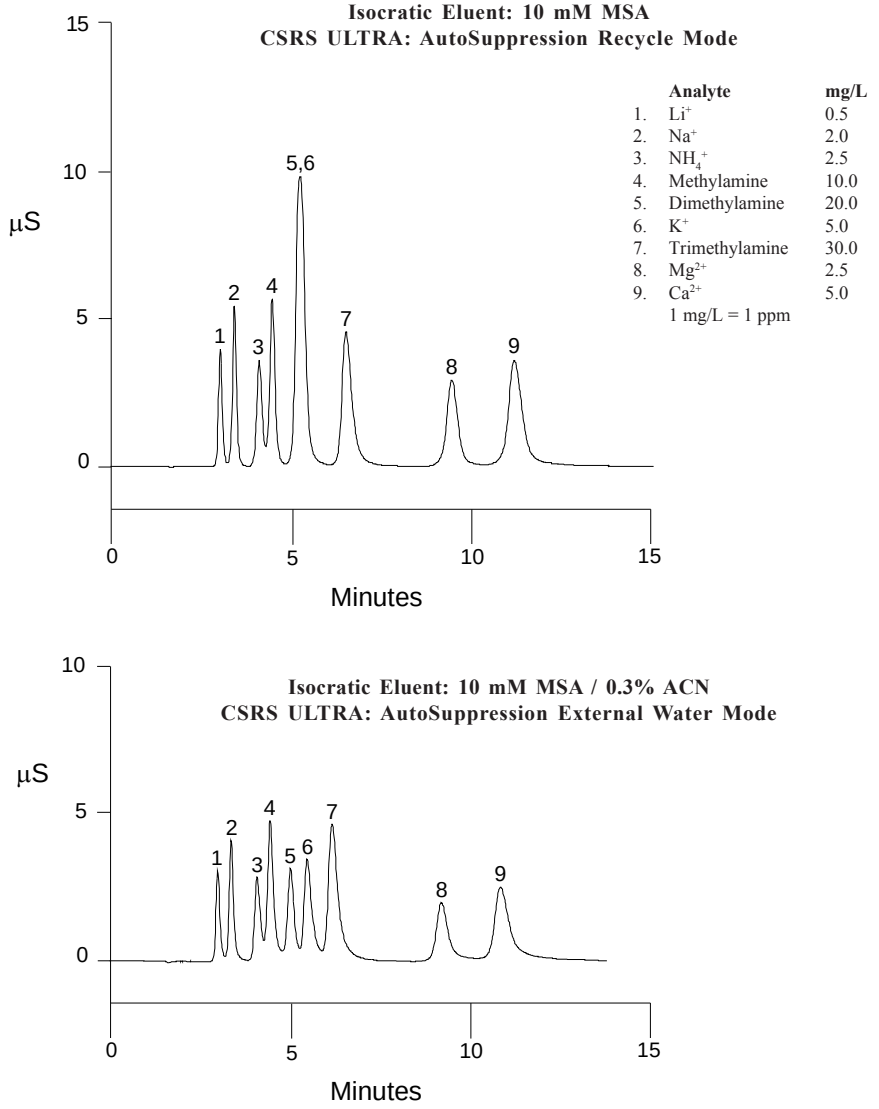



**Figure 8**
**Isocratic Elution of Mono-, Di- and Trimethylamines**

## 5.10 Elution of Mono-, Di- and Triethylamines With Resolution Enhancement Through the Addition of Solvent to the Eluent

The determination of mono-, di- and triethylamines in the presence of ammonia, alkali and alkaline earth metals can be accomplished by isocratic elution using 10 mM methanesulfonic acid (MSA). Reductions in runtimes can be accomplished by the addition of a small amount of solvent to the eluent in combination with a step gradient program.

| | |
|---|---|
| Sample Loop Volume: | 4.5 µL (2-mm), 18 µL (4-mm) |
| Analytical Column: | IonPac CS14 Analytical Column |
| Eluent: | See Chromatogram |
| Eluent Flow Rate: | 0.25 mL/min (2-mm), 1.0 mL/min (4-mm) |
| SRS Suppressor: | Cation Self-Regenerating Suppressor, CSRS ULTRA (2-mm or 4-mm) Recycle Mode or External Water Mode |
| or MMS Suppressor: | Cation MicroMembrane Suppressor, CMMS III (2-mm or 4-mm) |
| MMS Regenerant: | 100 mN TBAOH (tetrabutylammonium hydroxide) |
| Expected Background Conductivity: | < 1 µS |
| Storage Solution: | Eluent |

| | | | |
|---|---|---|---|
| Eluent 1: | Type I DI Water | Eluent Flow Rate: | 1.0 mL/min |
| Eluent 2: | 100 mM MSA | | (4-mm System) |
| Eluent 3: | 10% Acetonitrile | | |

| TIME (min) | %E1 | %E2 | %E3 | Comments |
|---|---|---|---|---|
| **Equilibration** | | | | |
| **0.0** | 86 | 9 | 5 | Equilibrate to 5.0 mM MSA / 2.5% ACN |
| **7.0** | 86 | 9 | 5 | |
| **Analysis** | | | | |
| **0.0** | 86 | 9 | 5 | Inject, 5.0 mM MSA / 2.5% ACN |
| **0.1** | 86 | 9 | 5 | Inject Valve to Load Position |
| **6.0** | 74 | 11 | 15 | 11 mM MSA / 1.5 ACN |
| **13.0** | 74 | 11 | 15 | 11 mM MSA / 1.5 ACN |

| | Analyte | mg/L |
|---|---|---|
| 1. | $Li^+$ | 0.5 |
| 2. | $Na^+$ | 2.0 |
| 3. | $NH_4^+$ | 2.5 |
| 4. | Ethylamine | 10.0 |
| 5. | $K^+$ | 5.0 |
| 6. | Diethylamine | 10.0 |
| 7. | $Mg^{2+}$ | 2.5 |
| 8. | $Ca^{2+}$ | 5.0 |
| 9. | Triethylamine | 50.0 |

1 mg/L = 1 ppm

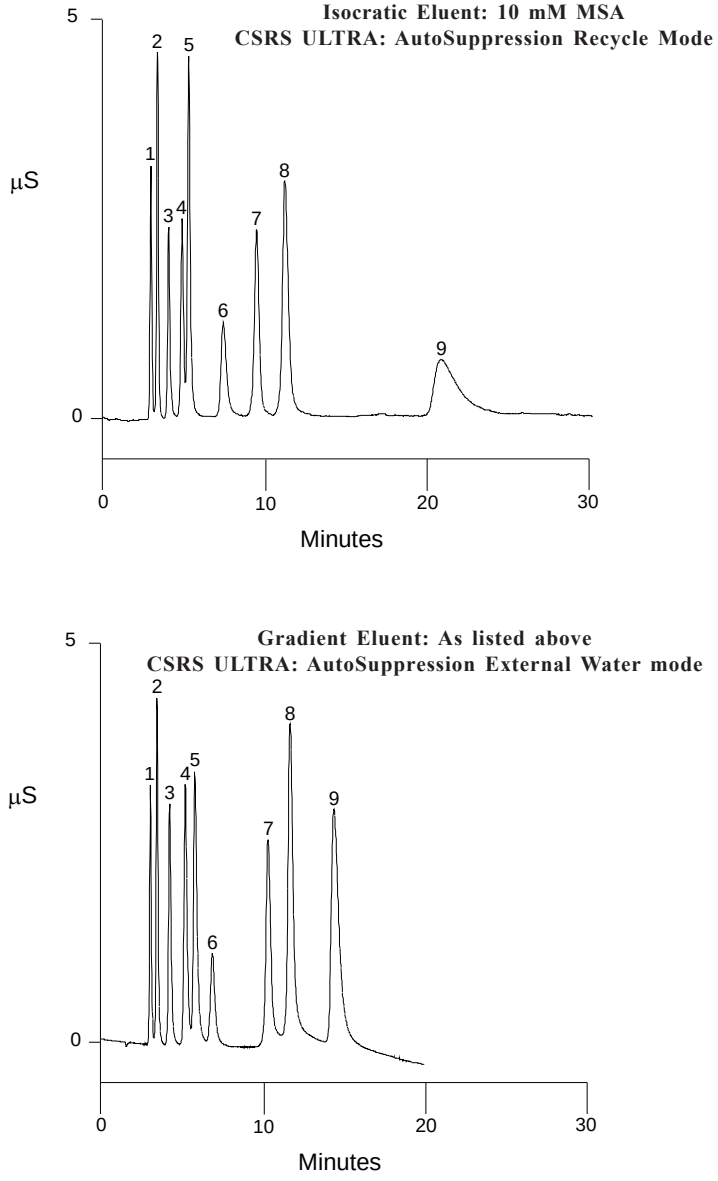



**Figure 9**
**Separation of Mono-, Di- and Triethylamines**

## 5.11 Gradient Elution of Cyclohexylamine

Power water samples are often treated with cyclohexylamine as a corrosion inhibitor. The determination of cyclohexylamine in the presence of ammonia, Group I & II cations can be accomplished by gradient elution using 9 mM methanesulfonic acid (MSA) with 5% acetonitrile (ACN) as the initial eluent and then stepping to 20 mM methanesulfonic acid (MSA) with 8% acetonitrile. The CSRS is used in the AutoSuppression External Water Mode.

| | |
|---|---|
| Sample Loop Volume: | 6.25 µL (2-mm), 25 µL (4-mm) |
| Analytical Column: | IonPac CS14 Analytical Column |
| Eluent: | See Gradient Program listed below |
| Eluent Flow Rate: | 0.25 mL/min (2-mm), 1.0 mL/min (4-mm) |
| SRS Suppressor: | Cation Self-Regenerating Suppressor, CSRS ULTRA (2-mm or 4-mm) External Water Mode |
| or MMS Suppressor: | Cation MicroMembrane Suppressor, CMMS III (2-mm or 4-mm) |
| MMS Regenerant: | 100 mN TBAOH (tetrabutylammonium hydroxide) |
| Expected Background Conductivity: | < 1 µS |
| Storage Solution: | Eluent |

| | | | |
|---|---|---|---|
| Eluent 1: | Type I DI Water | Eluent Flow Rate: | 1.0 mL/min |
| Eluent 2: | 100 mM MSA | | (4-mm System) |
| Eluent 3: | 50% Acetonitrile | | |

| TIME (min) | %E1 | %E2 | %E3 | Comments |
|---|---|---|---|---|
| **Equilibration** | | | | |
| **0.0** | 81 | 9 | 10 | Equilibrate to 9.0 mM MSA / 5.0% ACN |
| **7.0** | 81 | 9 | 10 | |
| **Analysis** | | | | |
| **0.0** | 81 | 9 | 10 | Inject, 9.0 mM MSA / 5.0% ACN |
| **0.1** | 81 | 9 | 10 | Inject Valve to Load Position |
| **7.0** | 81 | 9 | 10 | 9.0 mM MSA / 5.0% ACN, step change to |
| **7.1** | 64 | 20 | 16 | 20 mM MSA / 8.0% ACN |
| **13.0** | 64 | 20 | 16 | 20 mM MSA / 8.0% ACN |
| **13.1** | 81 | 9 | 10 | 9.0 mM MSA / 5.0% ACN |

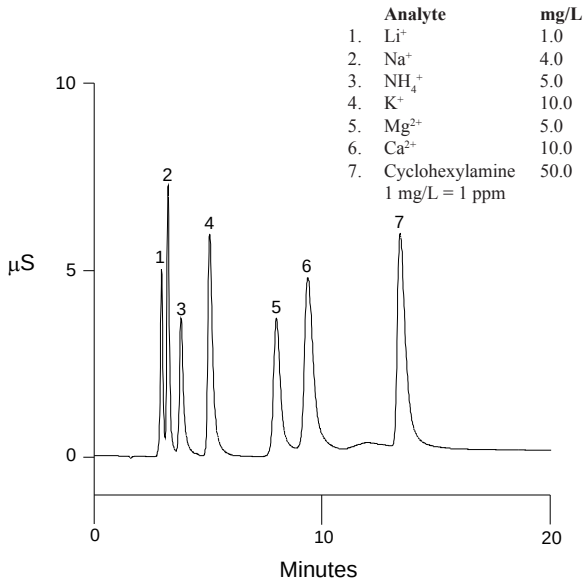



**Figure 11**
**Analysis of Cyclohexylamine**

## 5.12 Elution of Aliphatic Monoamines

The determination of aliphatic monoamines in the presence of ammonia, Group I & II cations can be accomplished by isocratic elution using 40 mM methanesulfonic acid (MSA) if complete resolution of ammonia, Group I & II cations is not required. The determination of all of the components requires a step gradient from 6 mM methanesulfonic acid (MSA) with 2% acetonitrile (ACN) to 8 mM methanesulfonic acid (MSA) with 10% acetonitrile (ACN) at 9 minutes. Note that with the addition of solvent, the amines move forward in the chromatogram relative to magnesium and calcium.

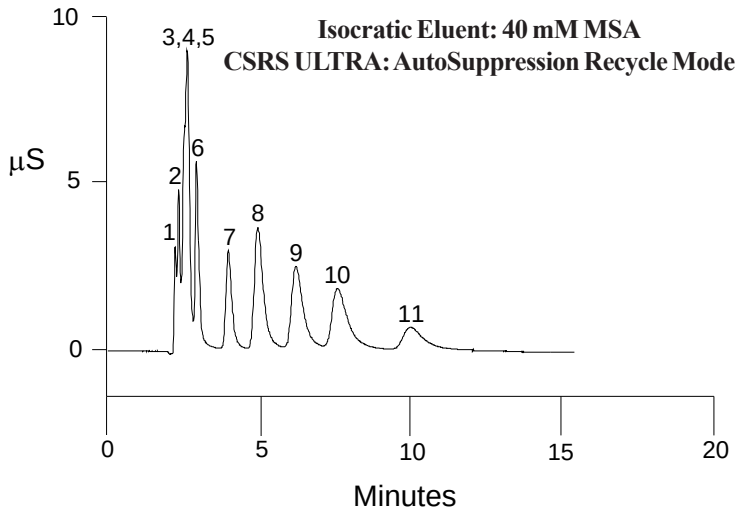
| | |
|---|---|
| Sample Loop Volume: | 6.25 µL (2-mm), 25 µL (4-mm) |
| Analytical Column: | IonPac CS14 Analytical Column |
| Eluent: | See Chromatogram |
| Eluent Flow Rate: | 0.25 mL/min (2-mm), 1.0 mL/min (4-mm) |
| SRS Suppressor: | Cation Self-Regenerating Suppressor, CSRS ULTRA (2-mm or 4-mm) Recycle Mode or External Water Mode |
| or MMS Suppressor: | Cation MicroMembrane Suppressor, CMMS III (2-mm or 4-mm) |
| MMS Regenerant: | 100 mN TBAOH (tetrabutylammonium hydroxide) |
| Expected Background Conductivity: | < 1 µS |
| Storage Solution: | Eluent |

| | | | |
|---|---|---|---|
| Eluent 1: | Type I DI Water | Eluent Flow Rate: | 1.0 mL/min |
| Eluent 2: | 100 mM MSA | | (4-mm System) |
| Eluent 3: | 20% Acetonitrile | | |

| TIME (min) | %E1 | %E2 | %E3 | Comments |
|---|---|---|---|---|
| **Equilibration** | | | | |
| **0.0** | 84 | 6 | 10 | Equilibrate to 6.0 mM MSA / 2.0% ACN |
| **7.0** | 84 | 6 | 10 | |
| **Analysis** | | | | |
| **0.0** | 84 | 6 | 10 | Inject, 6.0 mM MSA / 2.0% ACN |
| **0.1** | 84 | 6 | 10 | Inject Valve to Load Position |
| **9.0** | 84 | 6 | 10 | 6.0 mM MSA / 2.0% ACN, step change to |
| **9.1** | 42 | 8 | 50 | 8.0 mM MSA / 10% ACN |
| **20.0** | 42 | 8 | 50 | 8.0 mM MSA / 10% ACN |

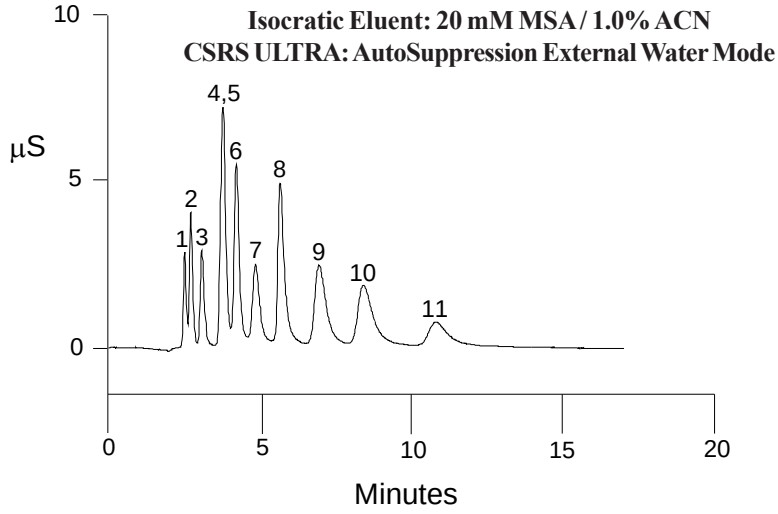
| | Analyte | mg/L |
|---|---|---|
| 1. | $Li^+$ | 0.5 |
| 2. | $Na^+$ | 2.0 |
| 3. | $NH_4^+$ | 2.5 |
| 4. | $K^+$ | 5.0 |
| 5. | $Mg^{2+}$ | 2.5 |
| 6. | $Ca^{2+}$ | 5.0 |
| 7. | n-Propylamine | 7.5 |
| 8. | tert-Butylamine | 12.5 |
| 9. | sec-Butylamine | 12.5 |
| 10. | iso-Butylamine | 12.5 |
| 11. | n-Butylamine | 37.5 |

1 mg/L = 1 ppm




| | Analyte | mg/L |
|---|---|---|
| 1. | $Li^+$ | 0.5 |
| 2. | $Na^+$ | 2.0 |
| 3. | $NH_4^+$ | 2.5 |
| 4. | $K^+$ | 5.0 |
| 5. | $Mg^{2+}$ | 2.5 |
| 6. | $Ca^{2+}$ | 5.0 |
| 7. | n-Propylamine | 7.5 |
| 8. | tert-Butylamine | 12.5 |
| 9. | sec-Butylamine | 12.5 |
| 10. | iso-Butylamine | 12.5 |
| 11. | n-Butylamine | 37.5 |

1 mg/L = 1 ppm




| | Analyte | mg/L |
|---|---|---|
| 1. | $Li^+$ | 0.5 |
| 2. | $Na^+$ | 2.0 |
| 3. | $NH_4^+$ | 2.5 |
| 4. | $K^+$ | 5.0 |
| 5. | n-Propylamine | 7.5 |
| 6. | tert-Butylamine | 12.5 |
| 7. | sec-Butylamine | 12.5 |
| 8. | iso-Butylamine | 12.5 |
| 9. | $Mg^{2+}$ | 2.5 |
| 10. | n-Butylamine | 37.5 |
| 11. | $Ca^{2+}$ | 5.0 |

1 mg/L = 1 ppm

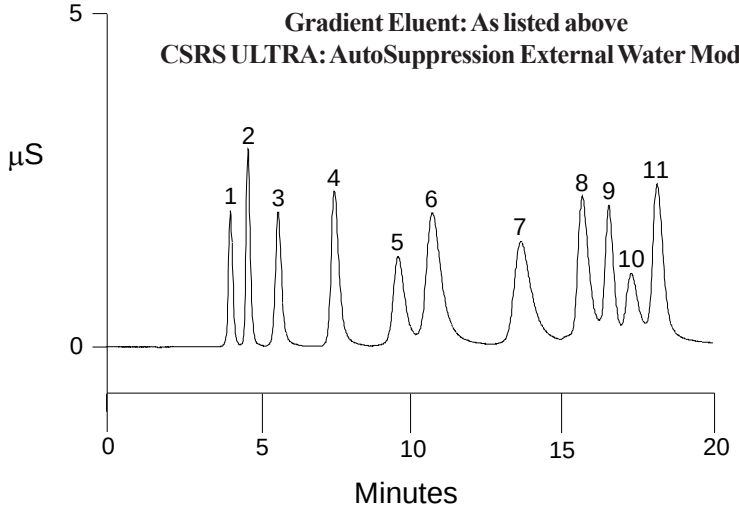



**Figure 10**
**Analysis of Aliphatic Monoamines**

## 5.13 Gradient Elution of Alkylamines, Ammonia, Group I & II Cations

The determination of many alkylamines in the presence of ammonia, Group I & II cations can be accomplished by gradient elution in which methanesulfonic acid varies from 5 mM to 20 mM and the acetonitrile varies from 2.5% to 8%. Note that in gradient analyses, increasing levels of ionic strength will increase baseline conductivity, while increasing levels of solvent will decrease baseline conductivity.

| | |
|---|---|
| Sample Loop Volume: | 6.25 µL (2-mm), 25 µL (4-mm) |
| Analytical Column: | IonPac CS14 Analytical Column |
| Eluent: | See Gradient Program listed below |
| Eluent Flow Rate: | 0.25 mL/min (2-mm), 1.0 mL/min (4-mm) |
| SRS Suppressor: | Cation Self-Regenerating Suppressor, CSRS ULTRA (2-mm or 4-mm) External Water Mode |
| or MMS Suppressor: | Cation MicroMembrane Suppressor, CMMS III (2-mm or 4-mm) |
| MMS Regenerant: | 100 mN TBAOH (tetrabutylammonium hydroxide) |
| Expected Background Conductivity: | < 1 µS |
| Storage Solution: | Eluent |

| | | | |
|---|---|---|---|
| Eluent 1: | Type I DI Water | Eluent Flow Rate: | 1.0 mL/min |
| Eluent 2: | 100 mM MSA | | (4-mm System) |
| Eluent 3: | 10% Acetonitrile | | |
| Eluent 4: | 100% Acetonitrile | | |

| TIME (min) | %E1 | %E2 | %E3 | %E4 | Comments |
|---|---|---|---|---|---|
| **Equilibration** | | | | | |
| **0.0** | 70 | 5 | 25 | 0 | Equilibrate to 5.0 mM MSA / 2.5% ACN |
| **10.0** | 70 | 5 | 25 | 0 | |
| **Analysis** | | | | | |
| **0.0** | 70 | 5 | 25 | 0 | Inject, 5.0 mM MSA / 2.5% ACN |
| **0.1** | 70 | 5 | 25 | 0 | Inject Valve to Load Position |
| **7.0** | 69 | 6 | 25 | 0 | 6.0 mM MSA / 2.5% ACN |
| **12.0** | 62 | 13 | 25 | 0 | 13.0 mM MSA / 2.5% ACN |
| **16.0** | 0 | 20 | 80 | 0 | 20.0 mM MSA / 8.0% ACN |
| **18.0** | 0 | 20 | 80 | 0 | 20.0 mM MSA / 8.0% ACN |
| **22.0** | 30 | 35 | 0 | 35 | 35.0 mM MSA / 35% ACN |
| **25.0** | 30 | 35 | 0 | 35 | 35.0 mM MSA / 35% ACN |
| **25.1** | 70 | 5 | 25 | 0 | 5.0 mM MSA / 2.5% ACN |

| | Analyte | mg/L |
|---|---|---|
| 1. | $Li^+$ | 0.5 |
| 2. | $Na^+$ | 2.0 |
| 3. | $NH_4^+$ | 2.5 |
| 4. | Methylamine | 5.0 |
| 5. | Ethylamine | 5.0 |
| 6. | Dimethylamine | 10.0 |
| 7. | $K^+$ | 5.0 |
| 8. | Trimethylamine | 20.0 |
| 9. | Propylamine | 5.0 |
| 10. | Morpholine | 25.0 |
| 11. | sec-Butylamine | 10.0 |
| 12. | iso-Butylamine | 10.0 |
| 13. | $Mg^{2+}$ | 2.5 |
| 14. | $Ca^{2+}$ | 5.0 |
| 15. | 2-Methylpiperidine | 20.0 |
| 16. | Di-n-propylamine | 20.0 |
| 17. | 3-Methylpiperidine | 20.0 |
| 18. | Cyclohexylamine | 20.0 |
| 19. | N-Methylcyclohexylamine | 20.0 |
| 20. | Tripropylamine | 20.0 |

1 mg/L = 1 ppm

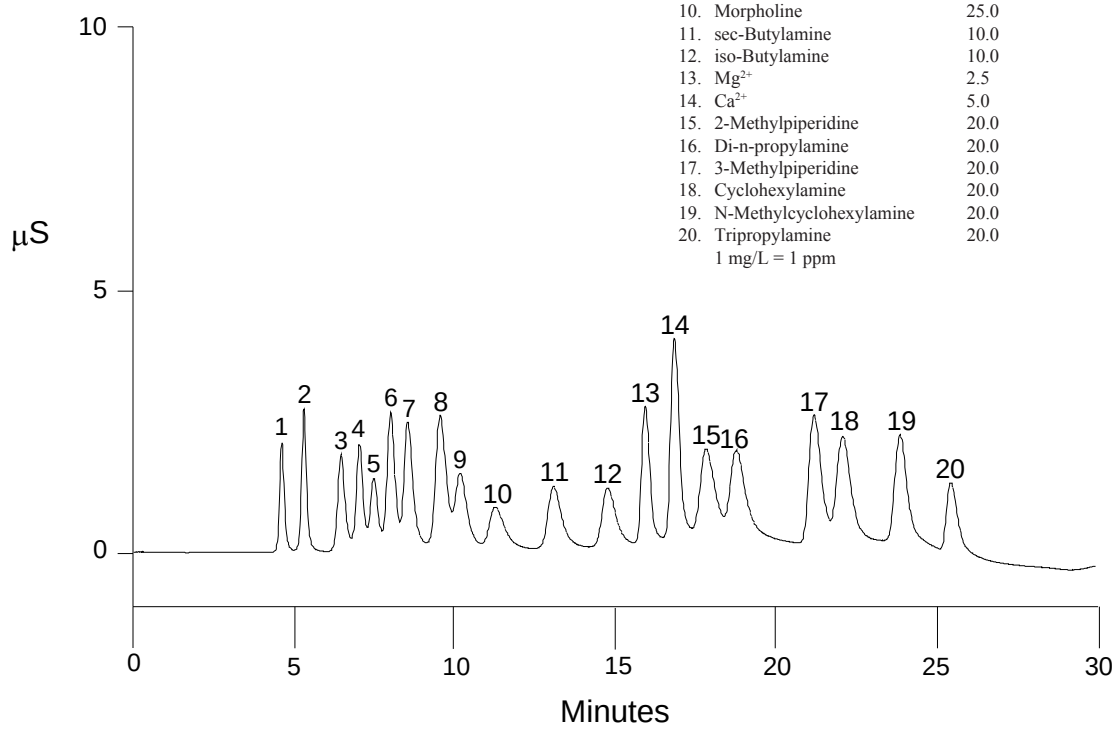



**Figure 12**
**Gradient Elution of Alkylamines, Ammonia, Group I & II Cations**

## 5.14 Elution of Di- and Triethanolamines

The determination of diethanolamine in the presence of ammonia, alkali and alkaline earth metals can be accomplished by isocratic elution using 9 mM methanesulfonic acid (MSA).

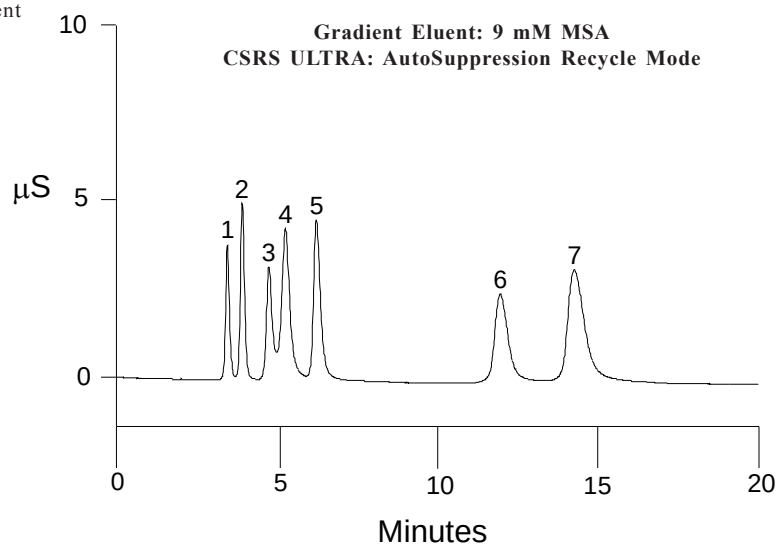
Triethanolamine is widely used in personal care products such as shampoos and industrially in scrubber solutions. The elution of triethanolamine requires the use of 10 mM methanesulfonic acid (MSA) with 1.5% acetonitrile. Either methanesulfonic acid or trifluoroacetic acid can be used with similar chromatographic results. Slightly lower concentrations of methanesulfonic acid are required to achieve identical retention times. Eluent conditions can be optimized for the specific amines of interest. Since the eluent contains solvent the Cation Self-Regenerating Suppressor is operated in the AutoSuppression External Water Mode to suppress the eluent.

| | |
|---|---|
| Sample Loop Volume: | See Chromatogram |
| Analytical Column: | IonPac CS14 Analytical Column |
| Eluent: | See Chromatogram |
| Eluent Flow Rate: | 0.25 mL/min (2-mm), 1.0 mL/min (4-mm) |
| SRS Suppressor: | Cation Self-Regenerating Suppressor, CSRS ULTRA (2-mm or 4-mm) Recycle Mode or External Water Mode |
| or MMS Suppressor: | Cation MicroMembrane Suppressor CMMS III (2-mm or 4-mm) |
| MMS Regenerant: | 100 mN TBAOH (tetrabutylammonium hydroxide) |
| Expected Background Conductivity: | < 1 µS |
| Storage Solution: | Eluent |

Injection Volume 25 µL (4-mm)

| | Analyte | mg/L |
|---|---|---|
| 1. | $Li^+$ | 0.5 |
| 2. | $Na^+$ | 2.0 |
| 3. | $NH_4^+$ | 2.5 |
| 4. | Diethanolamine | 50.0 |
| 5. | $K^+$ | 5.0 |
| 6. | $Mg^{2+}$ | 2.5 |
| 7. | $Ca^{2+}$ | 5.0 |

1 mg/L = 1 ppm




Injection Volume 18 µL (4-mm)

| | Analyte | mg/L |
|---|---|---|
| 1. | $Li^+$ | 0.5 |
| 2. | $Na^+$ | 2.0 |
| 3. | $NH_4^+$ | 2.5 |
| 4. | Triethanolamine | 400.0 |
| 5. | $K^+$ | 5.0 |
| 6. | $Mg^{2+}$ | 2.5 |
| 7. | $Ca^{2+}$ | 5.0 |

1 mg/L = 1 ppm

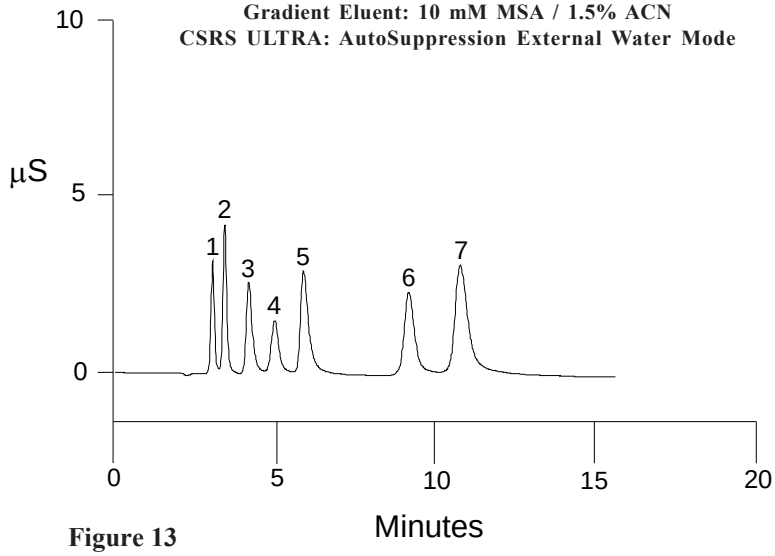



**Figure 13**
**Analysis of Substituted Di- and Triethanolamine**

## 5.15 The Isocratic Separation of Ethanolamine and the Group I & II Cations

The IonPac CS14 can be used to monitor the amine content in the quality control of chemical additives, process solutions, plating baths, and scrubber solutions.

Ethanolamine and ammonium are very difficult to resolve isocratically using methanesulfonic acid or methanesulfonic acid modified with acetonitrile. To optimize resolution, the 18-Crown-6 ether complexing agent can be added to the eluent. 18-Crown-6 forms a strong complex with monovalent cations such as potassium, ammonium and ethanolamine. This eluent can be used in the AutoSuppression Recycle Mode.

When converting the column back to eluents without 18-Crown-6 ether, the column is washed with an acetonitrile/deionized water gradient from 5% to 40% acetonitrile, held for 20 minutes and then reversed back to the new operating conditions.

| | |
|---|---|
| Sample Loop Volume: | 4.5 µL (2-mm), 18 µL (4-mm) |
| Analytical Column: | IonPac CS14 Analytical Column |
| Eluent: | 10 mM Trifluoroacetic acid/8 mM 18-Crown-6/1.2% Acetonitrile |
| Eluent Flow Rate: | 0.25 mL/min (2-mm), 1.0 mL/min (4-mm) |
| SRS Suppressor: | Cation Self-Regenerating Suppressor, CSRS ULTRA (2-mm or 4-mm) External Water Mode |
| or MMS Suppressor: | Cation MicroMembrane Suppressor, CMMS III (2-mm or 4-mm) |
| MMS Regenerant: | 100 mN TBAOH (tetrabutylammonium hydroxide) |
| Expected Background Conductivity: | ≤ 3 µS |
| Storage Solution: | Eluent |

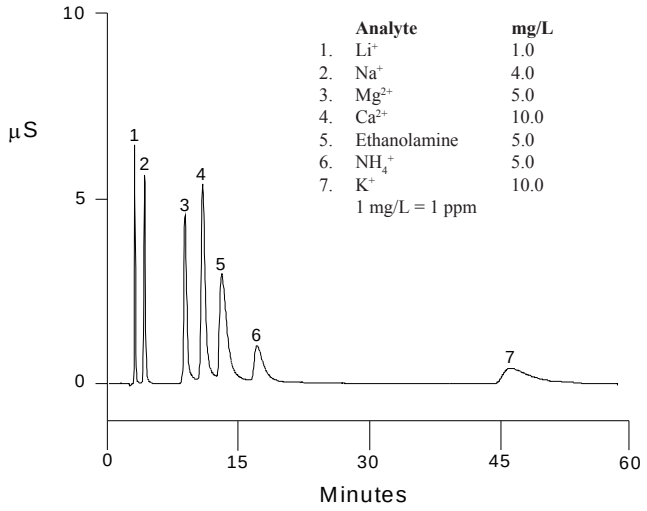
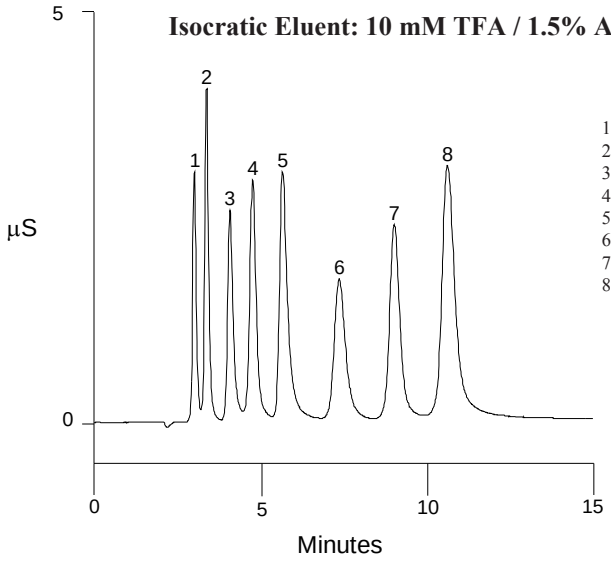



**Figure 14**
**The Isocratic Separation of Ethanolamine and the Group I & II Cations**

## 5.16 Elution of Substituted Methyl- and Ethylaminoethanols

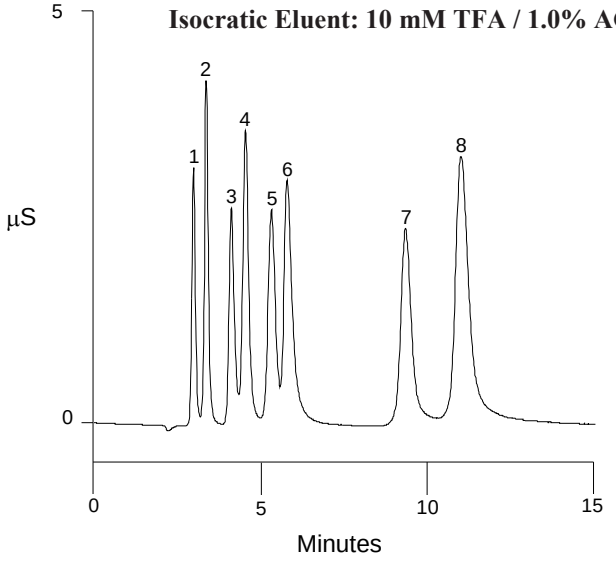
Two fairly hydrophilic amino alcohols, methylaminoethanol and ethylaminoethanol, can be determined in the presence of ammonia, Group I & II cations by isocratic elution using 10 mM trifluoroacetic acid (TFA) with 1.0 to 1.5 % acetonitrile. Trifluoroacetic acid is used in this separation instead of methanesulfonic acid as the source of hydronium ions. Since trifluoroacetic acid is a weaker acid than methanesulfonic acid, slightly higher concentrations have the equivalent eluting power of methanesulfonic acid.

| | |
|---|---|
| Sample Loop Volume: | 4.5 µL (2-mm), 18 µL (4-mm) |
| Analytical Column: | IonPac CS14 Analytical Column |
| Eluent: | See Chromatogram |
| Eluent Flow Rate: | 0.25 mL/min (2-mm), 1.0 mL/min (4-mm) |
| SRS Suppressor: | Cation Self-Regenerating Suppressor, CSRS ULTRA (2-mm or 4-mm) External Water Mode |
| or MMS Suppressor: | Cation MicroMembrane Suppressor, CMMS III (2-mm or 4-mm) |
| MMS Regenerant: | 100 mN TBAOH (tetrabutylammonium hydroxide) |
| Expected Background Conductivity: | < 1 µS |
| Storage Solution: | Eluent |




| | Analyte | mg/L |
|---|---|---|
| 1. | $Li^+$ | 0.5 |
| 2. | $Na^+$ | 2.0 |
| 3. | $NH_4^+$ | 2.5 |
| 4. | 2-Ethylaminoethanol | 10.0 |
| 5. | $K^+$ | 5.0 |
| 6. | 2-Diethylaminoethanol | 20.0 |
| 7. | $Mg^{2+}$ | 2.5 |
| 8. | $Ca^{2+}$ | 5.0 |

1 mg/L = 1 ppm




| | Analyte | mg/L |
|---|---|---|
| 1. | $Li^+$ | 0.5 |
| 2. | $Na^+$ | 2.0 |
| 3. | $NH_4^+$ | 2.5 |
| **4.** | **2-Methylaminoethanol** | **10.0** |
| **5.** | **2-Dimethylaminoethanol** | **20.0** |
| 6. | $K^+$ | 5.0 |
| 7. | $Mg^{2+}$ | 2.5 |
| 8. | $Ca^{2+}$ | 5.0 |

1 mg/L = 1 ppm

**Figure 15**
**Elution of Substituted Methyl- and Ethylaminoethanols**

## 5.17 Methanesulfonic Acid Gradient Elution of Alkanolamines with Ammonium, Group I & II Cations

The determination of alkanolamines is of great interest since these compounds are widely used in chemical and pharmaceutical industries. They are used for the production of emulsifying agents, corrosion inhibitors, laundry materials, dyes, medicines and gas purification. Alkanolamines are increasing in use as replacements for hydrocarbon-based solvents in coating and plating systems.

Alkanolamines are not normally present in waste waters. If present in the biofeed water (water entering the biopond) the bacteria will be killed, upsetting the biobalance in the biopond. NPDES discharge limits would probably be violated.

The determination of monoethanolamine, diethanolamine and other alkanolamines in the presence of ammonia, alkali and alkaline earth metals can be accomplished by gradient elution using 5 mM methanesulfonic acid (MSA) as the initial eluent and then stepping to 21 mM methanesulfonic acid (MSA) after 12 minutes. The CSRS ULTRA can be used in the AutoSuppression Recycle Mode.

| | |
|---|---|
| Sample Loop Volume: | 6.25 µL (2-mm), 25 µL (4-mm) |
| Analytical Column: | IonPac CS14 Analytical Column |
| Eluent: | See Chromatogram |
| Eluent Flow Rate: | 0.25 mL/min (2-mm), 1.0 mL/min (4-mm) |
| SRS Suppressor: | Cation Self-Regenerating Suppressor, CSRS ULTRA (2-mm or 4-mm) Recycle Mode |
| or MMS Suppressor: | Cation MicroMembrane Suppressor, CMMS III (2-mm or 4-mm) |
| MMS Regenerant: | 100 mN TBAOH (tetrabutylammonium hydroxide) |
| Expected Background Conductivity: | < 1 µS |
| Storage Solution: | Eluent |

| | | | |
|---|---|---|---|
| Eluent 1: | Type I DI Water | Eluent Flow Rate: | 1.0 mL/min |
| Eluent 2: | 10 mM MSA | | (4-mm System) |
| Eluent 3: | 100 mM MSA | | |

| TIME (min) | %E1 | %E2 | %E3 | Comments |
|---|---|---|---|---|
| **Equilibration** | | | | |
| **0.0** | 90 | 10 | 0 | Equilibrate to 1.0 mM MSA |
| **7.0** | 90 | 10 | 0 | |
| **Analysis** | | | | |
| **0.0** | 90 | 10 | 0 | Inject, 1.0 mM MSA |
| **0.1** | 90 | 10 | 0 | Inject Valve to Load Position |
| **16.0** | 70 | 30 | 0 | 3.0 mM MSA |
| **30.0** | 82 | 0 | 18 | 18.0 mM MSA |
| **30.1** | 90 | 10 | 0 | 1.0 mM MSA |

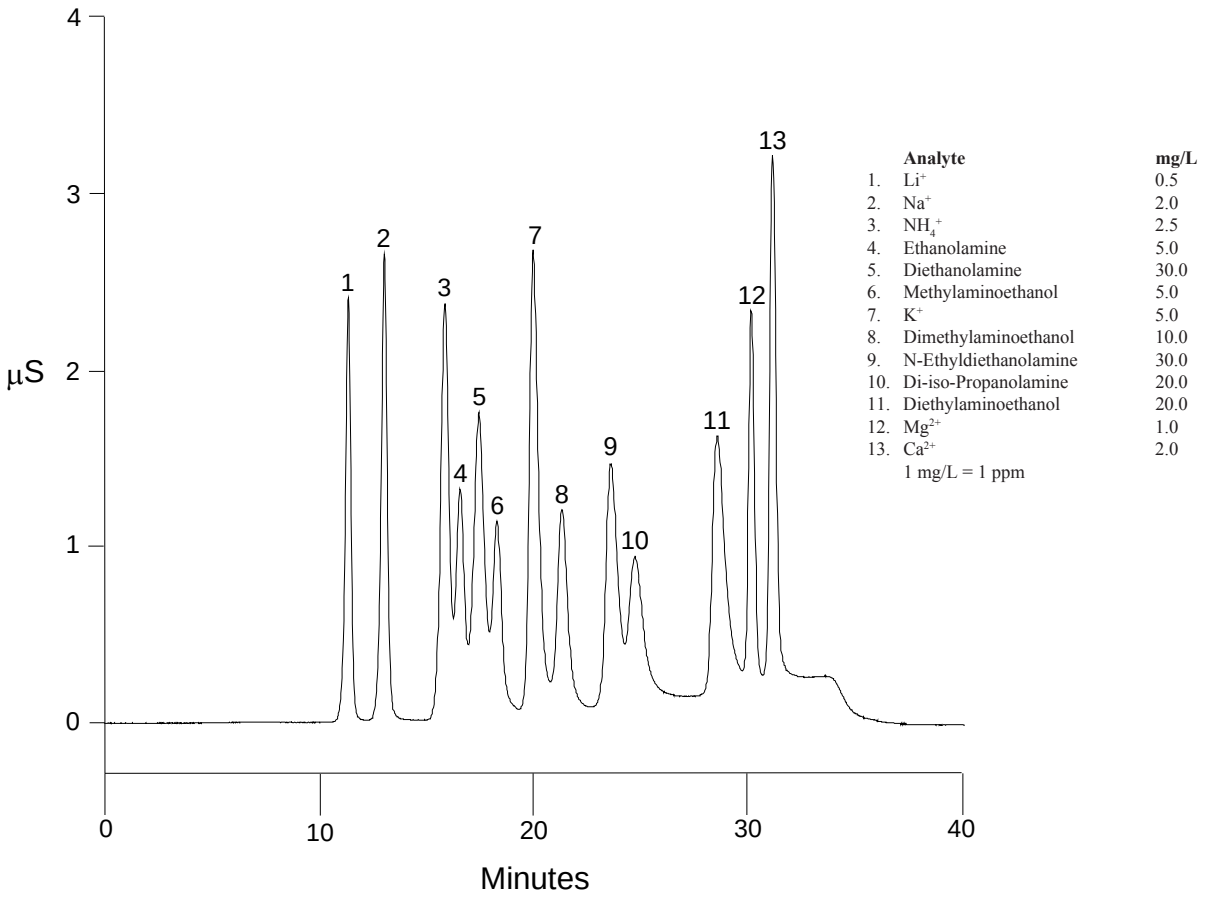



**Figure 16**
**Methanesulfonic Acid Gradient Elution of Alkanolamines with Ammonium, Group I & II Cations**

## 5.18 Methanesulfonic acid / 18-Crown-6 Gradient Elution of Alkanolamines with Group I & II Cations

The IonPac CS14 can be used to monitor the amine content in the quality control of chemical additives, process solutions, plating baths, and scrubber solutions. To optimize resolution, the 18-Crown-6 ether complexing agent can be added to the eluent as illustrated in this example. This chemical forms a strong complex with monovalent cations such as potassium, ammonium and ethanolamine. These complexes are very highly retained, increasing the retention times of these cations. Due to the differences in the degree of complexation and the selectivity of the resin for the complexes, the elution order of the ions, ethanolamine and ammonium, and ethanolamine and triethanolamine, are reversed. This technique can be useful for the determination of alkanolamines in the presence of high ammonium or potassium concentrations since these two analytes elute late.

The determination of monoethanolamine, triethanolamine and other alkanolamines in the presence of ammonia, Group I & II cations can be accomplished by gradient elution using 5 mM methanesulfonic acid (MSA) as the initial eluent and then stepping to 21 mM methanesulfonic acid (MSA) after 12 minutes.

This eluent can be suppressed using the AutoSuppression Recycle Mode. To convert the column back to eluents without 18-Crown-6 ether, wash the column with an acetonitrile/DI water gradient from 5% to 40% acetonitrile, hold for 20 minutes, and then equilibrate to the new operating conditions. Carefully flush all lines and fittings used with the 18-Crown-6 eluent.

| | |
|---|---|
| Sample Loop Volume: | 6.25 µL (2-mm), 25 µL (4-mm) |
| Analytical Column: | IonPac CS14 Analytical Column |
| Eluent: | See Chromatogram |
| Eluent Flow Rate: | 0.25 mL/min (2-mm), 1.0 mL/min (4-mm) |
| SRS Suppressor: | Cation Self-Regenerating Suppressor, CSRS ULTRA (2-mm or 4-mm) Recycle Mode |
| or MMS Suppressor: | Cation MicroMembrane Suppressor, CMMS III (2-mm or 4-mm) |
| MMS Regenerant: | 100 mN TBAOH (tetrabutylammonium hydroxide) |
| Expected Background Conductivity: | < 1 µS |
| Storage Solution: | Eluent |

| | | | |
|---|---|---|---|
| Eluent 1: | Type I DI Water | Eluent Flow Rate: | 1.0 mL/min |
| Eluent 2: | 10 mM MSA | | (4-mm System) |
| Eluent 3: | 100 mM MSA | | |
| Eluent 4: | 10 mM 18-Crown-6 | | |

| TIME (min) | %E1 | %E2 | %E3 | %E4 | Comments |
|---|---|---|---|---|---|
| **Equilibration** | | | | | |
| **0.0** | 45 | 30 | 0 | 25 | Equilibrate to 3.0 mM MSA / 2.5 mM 18-Crown-6 |
| **10.0** | 45 | 30 | 0 | 25 | |
| **Analysis** | | | | | |
| **0.0** | 45 | 30 | 0 | 25 | Inject, 3.0 mM MSA / 2.5 mM 18-Crown-6 |
| **0.1** | 45 | 30 | 0 | 25 | Inject Valve to Load Position |
| **10.0** | 45 | 30 | 0 | 25 | 3.0 mM MSA / 2.5 mM 18-Crown-6 |
| **15.0** | 35 | 0 | 40 | 25 | 40 mM MSA / 2.5 mM 18-Crown-6 |
| **35.0** | 35 | 0 | 40 | 25 | 40 mM MSA / 2.5 mM 18-Crown-6 |
| **35.1** | 45 | 30 | 0 | 25 | 3.0 mM MSA / 2.5 mM 18-Crown-6 |

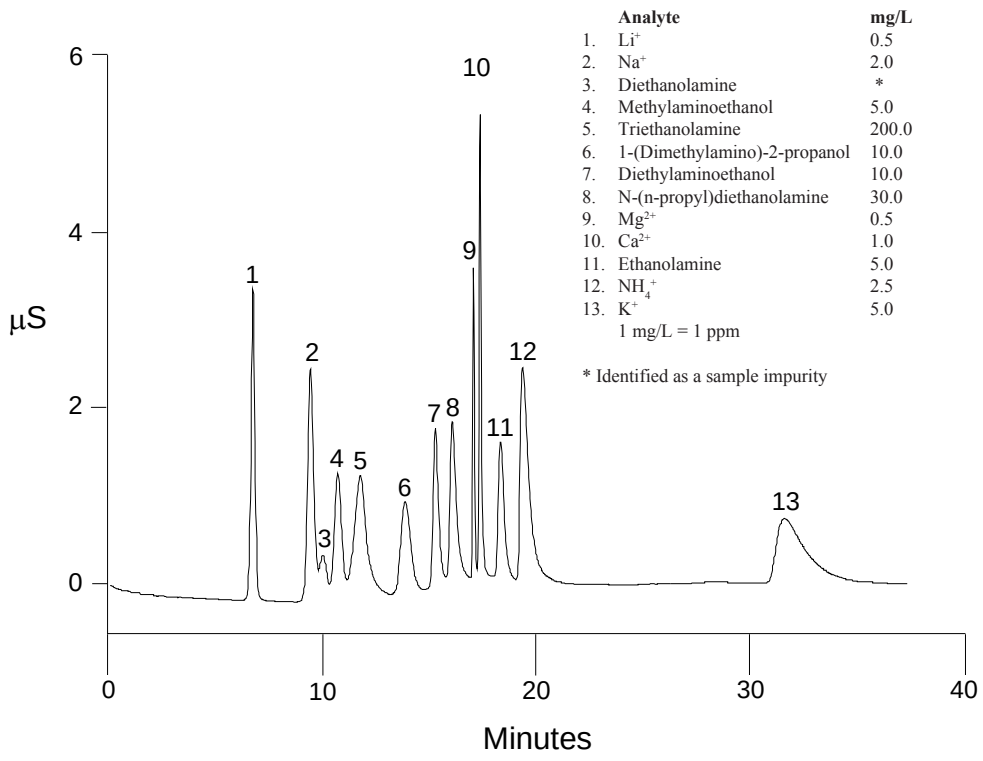



**Figure 17**
**Methanesulfonic Acid / 18-Crown-6 Gradient Elution of Alkanolamines, Group I & II Cations**

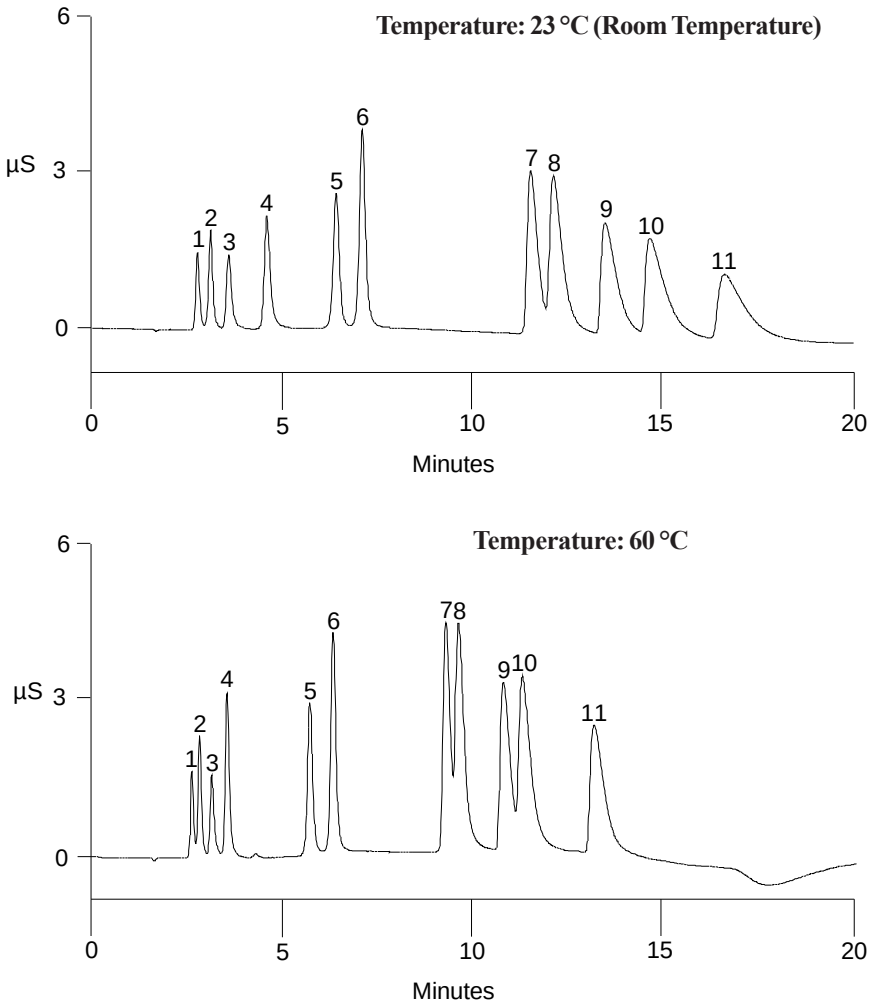
## 5.19 The Effect of Temperature on the Gradient Elution of Diamines with Ammonia, Group I & II Cations

The determination of many diamines in the presence of ammonia, Group I & II cations can be accomplished by gradient elution in which methanesulfonic acid varies from 10 mM to 20 mM and the acetonitrile varies from 5% to 15%. The following two applications demonstrate the effect of temperature on the separation. The efficiency of the peaks is significantly improved by increasing the column temperature to 60°C centigrade. Note that in gradient analyses, increasing levels of ionic strength will increase baseline conductivity, while increasing levels of solvent will decrease baseline conductivity.

| | |
|---|---|
| Sample Loop Volume: | 6.25 µL (2-mm), 25 µL (4-mm) |
| Analytical Column: | IonPac CS14 Analytical Column |
| Eluent: | See Gradient Program listed below |
| Eluent Flow Rate: | 0.25 mL/min (2-mm), 1.0 mL/min (4-mm) |
| SRS Suppressor: | Cation Self-Regenerating Suppressor, CSRS ULTRA (2-mm or 4-mm) External Water Mode |
| or MMS Suppressor: | Cation MicroMembrane Suppressor, CMMS III (2-mm or 4-mm) |
| MMS Regenerant: | 100 mN TBAOH (tetrabutylammonium hydroxide) |
| Expected Background Conductivity: | < 1 µS |
| Storage Solution: | Eluent |

| | | | |
|---|---|---|---|
| Eluent 1: | Type I DI Water | Eluent Flow Rate: | 1.0 mL/min |
| Eluent 2: | 100 mM MSA | | (4-mm System) |
| Eluent 3: | 50% Acetonitrile | | |

| TIME (min) | %E1 | %E2 | %E3 | Comments |
|---|---|---|---|---|
| **Equilibration** | | | | |
| **0.0** | 80 | 10 | 10 | Equilibrate to 10 mM MSA / 5.0% ACN |
| **7.0** | 80 | 10 | 10 | |
| **Analysis** | | | | |
| **0.0** | 80 | 10 | 10 | Inject, 10 mM MSA / 5.0% ACN |
| **0.1** | 80 | 10 | 10 | Inject Valve to Load Position |
| **10.0** | 50 | 20 | 30 | 20 mM MSA / 15% ACN |
| **20.0** | 50 | 20 | 30 | 20 mM MSA / 15% ACN |
| **20.1** | 80 | 10 | 10 | 10 mM MSA / 5.0% ACN |




| | Analyte | mg/L |
|---|---|---|
| 1. | $Li^+$ | 0.5 |
| 2. | $Na^+$ | 2.0 |
| 3. | $NH_4^+$ | 2.5 |
| 4. | $K^+$ | 5.0 |
| 5. | $Mg^{2+}$ | 2.5 |
| 6. | $Ca^{2+}$ | 5.0 |
| 7. | Cadaverine | 50.0 |
| 8. | Putrescine | 50.0 |
| 9. | 1,2-Propanediamine | 50.0 |
| 10. | Ethylenediamine | 50.0 |
| 11. | N,N-Diethylethylenediamine | 100.0 |

1 mg/L = 1 ppm

**Figure 18**
**The Effect of Temperature on the Gradient Elution of Diamines with Ammonia, Group I & II Cations**

**CAUTION**

**The CSRS ULTRA should be placed outside of the oven for oven temperatures > 40 °C. Minimize tubing lengths between the column, the CSRS-ULTRA and the cell. Use the AutoSuppression External Water Mode to ensure proper cooling of the CSRS-ULTRA.**

# SECTION 6 - TROUBLESHOOTING GUIDE

The purpose of the Troubleshooting Guide is to help you solve operating problems that may arise while using IonPac CS14 columns. For more information on problems that originate with the Ion Chromatograph (IC) or the suppressor, refer to the Troubleshooting Guide in the appropriate operator's manual. If you cannot solve the problem on your own, call the nearest Dionex Office (see, "Dionex Worldwide Offices").

**Table 8**
**CS14/CG14 Troubleshooting Summary**

| Observation | Cause | Action | Reference Section |
|---|---|---|---|
| **High Back Pressure** | Unknown Component | Isolate Blockage | 6.1.1 |
| | Plugged Column Bed Supports | Replace Bed Supports | 6.1.2 |
| | Plugged System Hardware | Unplug, Replace | Component Manual |
| **High Background Conductivity** | | | |
| **Improper Suppressor Operation** | CSRS Not Suppressing | Check Current | 6.5.A, Component Manual |
| | | Check "REGEN OUT" Flow | 6.5.D, Component Manual |
| | | Check for leaks | 6.5.B, Component Manual |
| | CAES Not Suppressing | Check Current | Component Manual |
| | CMMS Not Suppressing | Check Regenerant | Component Manual |
| | | Check AutoRegen Cartridge | Component Manual |
| **Contamination** | Bad Eluents | Remake Eluents | 6.2, 6.4 |
| | Contaminated Column | Clean Column | 6.3, Column Care |
| | Contaminated CSRS, CAES, or CMMS | Clean Suppressor | 6.5, Component Manual |
| **Hardware Operation** | | | |
| | Proportioning Valve | Service Valve | Component Manual |
| **Poor Peak Resolution** | | | |
| **Poor Efficiency** | Large System Void Volumes | Replumb System | 6.6.3.C, Component Manual |
| | Sluggish Injection Valve | Service Valve | 6.6.3.B, Component Manual |
| | Column Headspace | Replace Column | 6.6.1.A |
| | Column Overloading | Reduce Sample Size | 6.6.1.C, 3.3.1, 3.3.2 |
| **Fronting Peaks** | Column Overloading | Reduce Sample Size | 6.6.1.C, 3.3.1, 3.3.2 |
| **Tailing Peaks** | Contaminated CSRS, CAES, or CMMS | Clean Suppressor | 6.5, Component Manual |
| **Short Retention Times** | | | |
| | Flow Rate Too Fast | Recalibrate Pump | 6.6.2.A |
| | First Peaks Elute Too Fast | Equilibrate to First Eluent | 6.6.3.A |
| | Bad Eluents | Remake Eluents | 6.6.2.B |
| | Column Contamination | Clean Column | 6.6.2.C |
| **Spurious Peaks** | | | |
| | Column Contamination | Pretreat Samples | 6.3, 6.7.A, 6.7.B, |
| | Sluggish Injection Valve | Service Valve | 6.7.C, Component Manual |

## 6.1 High Back Pressure

### 6.1.1 Finding the Source of High System Pressure

Total system pressure for the IonPac CG14 (4-mm) Guard Column plus the CS14 (4-mm) Analytical Column when using the test chromatogram conditions should be equal or less than 1,650 psi (11.37 MPa). If the system pressure is higher than 1,750 psi (12.06 MPa), it is advisable to determine the cause of the high system pressure. The system should be operated with a High-Pressure In-Line Filter (P/N 044105) which is positioned between the Gradient Pump pressure transducer and the injection valve. Make sure you have one in place and that it is not contaminated.

**A. Make sure that the pump is set to the correct eluent flow rate.** Higher than recommended eluent flow rates will cause higher pressure. Measure the pump flow rate if necessary with a stop watch and graduated cylinder.

**B. Determine which part of the system is causing the high pressure.** High pressure could be due to a plugged tubing or tubing with collapsed walls, an injection valve with a clogged port, a column with particulates clogging the bed support, a clogged High-Pressure In-Line Filter, the suppressor or the detector cell.

To determine which part of the chromatographic system is causing the problem, disconnect the pump eluent line from the injection valve and turn the pump on. Watch the pressure; it should not exceed 50 psi (0.34 MPa). Continue adding system components (injection valve, column(s), suppressor and detector) one by one, while monitoring the system pressure. The pressure should increase up to a maximum when the Guard and Analytical columns are connected (see Table 9, "Typical CS14/CG14 Operating Back Pressures").

The Cation Self-Regenerating Suppressor ULTRA may add up to 100 psi (0.69 MPa). No other components should add more than 100 psi (0.69 MPa) of pressure. Refer to the appropriate manual for cleanup or replacement of the problem component.

**Table 9**
**Typical CS14/CG14 Operating Back Pressures**

| Column | Typical Back Pressure psi (MPa) | Flow Rate mL/min |
|---|---|---|
| CS14 4-mm Analytical | ≤ 1,200 (8.27) | 1.0 |
| CG14 4-mm Guard | ≤ 450 (3.10) | 1.0 |
| **CS14 + CG14 4-mm columns** | **≤ 1,650 (11.37)** | **1.0** |
| CS14 2-mm Analytical | ≤ 1,200 (8.27) | 0.25 |
| CG14 2-mm Guard | ≤ 450 (3.10) | 0.25 |
| **CS14 + CG14 2-mm columns** | **≤ 1,650 (11.37)** | **0.25** |

### 6.1.2 Replacing Column Bed Support Assemblies

If the column inlet bed support is determined to be the cause of the high back pressure, it should be replaced. To change the inlet bed support assembly, refer to the following instructions, using one of the two spare inlet bed support assemblies included in the Ship Kit.

**A. Disconnect the column from the system.**

**B. Carefully unscrew the inlet (top) column fitting.** Use two open-end wrenches.

**C. Remove the bed support.** Turn the end fitting over and tap it against a benchtop or other hard, flat surface to remove the bed support and seal assembly. If the bed support must be pried out of the end fitting, use a sharp pointed object such as a pair of tweezers, but be careful that you **do not scratch the walls of the end fitting.** Discard the old bed support assembly.

**D. Place a new bed support assembly into the end fitting.** Make sure that the end of the column tube is clean and free of any particulate matter so that it will properly seal against the bed support assembly. Use the end of the column to carefully start the bed support assembly into the end fitting.

| Part | 4-mm Columns (P/N) | 2-mm Columns (P/N) |
|---|---|---|
| Analytical Column | 044123 | 044121 |
| Guard Column | 044124 | 044122 |
| Bed Support Assembly | 042955 | 044689 |
| End Fitting | 052809 | 043278 |

**CAUTION**

**If the column tube end is not clean when inserted into the end fitting, particulate matter may obstruct a proper seal between the end of the column tube and the bed support assembly. If this is the case, additional tightening may not seal the column but instead damage the column tube or the end fitting.**

**E. Screw the end fitting back onto the column.** Tighten it fingertight, then an additional 1/4 turn (25 in x lb). Tighten further only if leaks are observed.

**F. Reconnect the column to the system and resume operation.**

**CAUTION**

**Replace the outlet bed support ONLY if high pressure persists after replacement of the inlet fitting.**

## 6.2 Preparation of Eluents

**A. Make sure that the eluents and regenerant are made correctly.**

**B. Make sure that the eluents are made from chemicals with the recommended purity.**

**C. Make sure that the deionized water used to prepare the reagents has a specific resistance of 18.2 megohm-cm.**

## 6.3 A Contaminated Guard or Analytical Column

**Determine if the column is contaminated.** Column contamination can lead to a loss of column capacity since all of the cation exchange sites will no longer be available for the sample ions. Polyvalent cations may be concentrating on the column over a series of runs. Remove the IonPac CG14 Guard and CS14 Analytical Columns from the system. If the background conductivity decreases, the column(s) is (are) the cause of the high background conductivity. Clean or replace the CG14 at the first sign of column performance degradation (compared to the original test chromatogram) to eliminate downtime. Clean the column(s) as instructed in "Column Care." To make sure that contaminated hardware is not causing the high background, use deionized water with a specific resistance of 18.2 megohm-cm as eluent. The background should be less than 1 µS. If it is not, check the detector/conductivity cell calibration by injecting deionized water directly into it. See the appropriate manual for details.

**A. Check for a contaminated Gradient Mixer.** Gradient Mixers (GM-2) in the Gradient Pump Module should be flushed thoroughly to remove eluents containing DL-2,3-diaminopropionic acid monohydrochloride (DAP·HCl). Chloride containing eluents should not be pumped through the CSRS ULTRA.

**B. Use chemicals and deionized water of the proper purity.** Be especially careful to make sure that the recommended chemicals are used. The deionized water should have a specific resistance of 18.2 megohm-cm.

**C. The system should be as metal-free as possible.** Gripper tubing fittings in the system are a potential source for metal contamination of the column. The new Dionex ThermoFlare or PEEK ferrule fittings are preferred. Inspect the eluent pumps periodically for any signs of leakage.

**D. Glass eluent reservoirs can be a source of sodium contamination in the eluent.** Two-liter polyethylene eluent reservoirs (P/N 039163) are preferred.

**E. Install an IonPac Cation Trap Column (CTC-1, P/N 040192).** It should be positioned between the pump and the injection valve. It is highly recommended for all cation gradient analyses. The CTC-1 strips the eluent of cation contaminants that will bind strongly to the analytical column resulting in the loss of column capacity and potentially interfering with the desired cation analyses. The CTC-1 minimizes baseline changes when performing gradient anlyses. The CTC (2-mm), P/N 043132, should be used in 2-mm systems.

## 6.4 High Background or Noise

In a properly working system, the background conductivity using the operating conditions described in Section 4, "Operation," should be < 1 µS with a CSRS ULTRA.

A system with a high background (> 3 µS) will probably also have high noise, resulting in increased detection limits.

**A. Make sure that the eluents and regenerant are prepared correctly (see Section 5.2, "Eluent Preparation").**

**B. Determine if the columns or system are contaminated (see Section 6.3, "A Contaminated Guard or Analytical Column").**

**C. Determine if the Suppressor is the cause of the high background and/or noise.** If the above items have been checked and the problem still persists, the suppression system is causing the problem. See Section 6.5, "A Suppressor that Does Not Suppress Properly."

Typical background conductivity levels, in a properly working system, are shown below:

| ELUENT | EXPECTED BACKGROUND CONDUCTIVITY |
|---|---|
| 20 mN Methanesulfonic acid | < 1 µS |
| 50 mN Methanesulfonic acid | < 2 µS |

## 6.5 A Suppressor Not Suppressing Properly

If the Cation Self-Regenerating Suppressor or the Cation MicroMembrane Suppressor is causing the problem, refer to Cation Self-Regenerating Suppressor ULTRA Product Manual (Document No.031370), to the Cation Atlas Electrolytic Suppressor Product Manual (Document No. 031770), or to the Cation MicroMembrane Suppressor Product Manual (Document No. 031728) for detailed troubleshooting assistance.

**A. Check that the CSRS ULTRA is not in an alarm state.**

**B. Check for CSRS ULTRA leaks.**

**C. Make sure that the back pressure tubing is properly installed in the CSRS ULTRA.**

**D. Check the regenerant flow rate at the REGEN OUT port of the CSRS.** Turn the power to the CSRS off. Measure the regenerant flow rate. If it is being used in the recycle mode, it should be the same flow rate as the eluent (typically 1 mL/min for 4-mm operation). If it is used in the AutoSuppression External Water Mode, it should be approximately 5 mL/min for non-solvent containing eluents. When solvents are used in the eluent, the regenerant flow rate should be approximately 8 mL/min.

**E. Check the eluent flow rate.** See if the eluent flow rate is equivalent to the flow rate specified by the analytical protocol. Measure the eluent flow rate after the column using a stopwatch and graduated cylinder. Refer to the Cation Self-Regenerating Suppressor ULTRA Product Manual (Document No. 031370) or to the Cation MicroMembrane Suppressor III Product Manual (Document No. 031728) for assistance in determining if the eluent is within suppressible limits.

**F. If you are using an AutoRegen Accessory with the CSRS (in the Chemical Suppression Mode) or the CMMS, prepare fresh regenerant solution.** Test both the suppressor and the AutoRegen Regenerant Cartridge for contamination.

**1. If the background conductivity is high after preparing fresh regenerant and bypassing the AutoRegen Regenerant Cartridge, you probably need to clean or replace your CSRS or CMMS.**

**2. If the background conductivity is low when freshly prepared regenerant is run through the CSRS or CMMS without an AutoRegen Accessory in-line, test the AutoRegen Regenerant Cartridge to see if it is expended.** Connect the freshly prepared regenerant to the AutoRegen Regenerant Cartridge. Pump approximately 200 mL of regenerant through the AutoRegen Regenerant Cartridge to waste before recycling the regenerant back to the regenerant reservoir. If the background conductivity is high after placing the AutoRegen Accessory in-line, you probably need to replace the AutoRegen Regenerant Cartridge. Refer to the "AutoRegen Regenerant Cartridge Refill Product Manual" (Document No. 032852) for assistance.

**CAUTION** **Do not recycle the regenerant through the Cation Regenerant Cartridge if the eluent contains acetonitrile.**

**G. Non-linear response or loss of sensitivity**

Indications of carbonate contamination are:

1. A higher ammonium peak than should be expected.

2. Dips on either side of an analyte peak's base.

Non-linear response or loss of sensitivity may occur when the suppressor is contaminated with carbonate. This contamination is possibly from dissolved carbon dioxide in the DI water. Degassing will help minimize the presence of carbon dioxide in acidic eluents or in DI water. Note, when pressurizing eluent reservoirs on the system use inert gases such as nitrogen (aqueous applications) or helium (aqueous or solvent applications).

When the CSRS suppressor is contaminated with carbonate the following treatment is recommended.

1. Push 5 mL of 2 M NaOH (freshly prepared) through the **ELUENT IN** port and divert a line from the **ELUENT OUT** port to waste.

2. Push 10 mL of 2 M NaOH (freshly prepared) through the **REGEN IN** port and divert a line out from the **REGEN OUT** port to waste.

3. Allow the suppressor to equilibrate for 20 minutes.

4. Repeat steps 1 and 2 with degassed DI water and reinstall the unit on the system.

5. If problem persists repeat steps 1–4.

## 6.6 Poor Peak Resolution

Poor peak resolution can be due any or all of the following factors.

### 6.6.1 Loss of Peak Efficiency throughout the Chromatogram

**A. Check to see if headspace has developed in the guard or analytical column.** This is usually due to improper use of the column such as submitting it to high pressures. Remove the column's top end fitting (see Section 6.1.2, "Replacing Column Bed Support Assemblies"). If the resin does not fill the column body all the way to the top, it means that the resin bed has collapsed, creating a headspace. The column must be replaced.

**B. Extra-column effects can result in sample band dispersion, making the peaks' elution less efficient.** Make sure you are using PEEK tubing with an i.d. of no greater than 0.010" for 4-mm systems or no greater than 0.005" for 2-mm systems to make all eluent liquid line connections between the injection valve and the detector cell inlet. Cut the tubing lengths as short as possible. Check for leaks.

**C. Check the sample for column overloading.** Overloading the column and/or injecting samples in very acidic matrices (>50 mM $H^+$) can cause poor efficiencies.

### 6.6.2 Loss of Resolution Throughout the Chromatogram Due to Shortened Retention Times

Even with adequate system and column efficiency, resolution of peaks will be compromised if analytes elute too fast.

**A. Check the flow rate.** See if the eluent flow rate is equivalent to the flow rate specified by the analytical protocol. Measure the eluent flow rate after the column using a stopwatch and graduated cylinder.

**B. Check to see if the eluent compositions and concentrations are correct.** An eluent that is too concentrated will cause the peaks to elute faster. Prepare fresh eluent. If you are using a gradient pump to proportion the eluent, components from two or three different eluent reservoirs, the resulting eluent composition may not be accurate enough for the application. Use one reservoir containing the correct eluent composition to see if this is the problem. This may be a problem when one of the proportioned eluents is less than 5%.

**C. Column contamination can lead to a loss of column capacity.** This is because all of the cation exchange sites will no longer be available for the sample ions. For example, polyvalent cations from the sample or metals may concentrate on the column. Refer to "Column Care," for recommended column cleanup procedures.

Possible sources of column contamination are impurities in chemicals and in the deionized water used for eluents or components of the sample matrix. Be especially careful to make sure that the recommended chemicals are used. The deionized water should have a specific resistance of 18.2 megohm-cm.

**D. Diluting the eluent will improve peak resolution, but will also increase the analytes' retention times.** If a 10% dilution of the eluent is not sufficient to obtain the desired peak resolution, or if the resulting increase in retention times is unacceptable, clean the column (see "Column Care").

After cleaning the column, reinstall it in the system and let it equilibrate with eluent for about 30 minutes. No water wash is necessary. The column is equilibrated when consecutive injections of the standard give reproducible retention times. The original column capacity should be restored by this treatment, since the contaminants should be eluted from the column. If you need assistance in solving resolution problems, contact the nearest Dionex Office (see, "Dionex Worldwide Offices")

### 6.6.3 Loss of Early Eluting Peak Resolution

Lack of equilibration to the initial eluent, improper system operation or improperly swept out void volumes are usually the cause of poor resolution or efficiency of peaks eluting near the system void volume compared to the later eluting peaks.

**A. Be sure that the column is equilibrated to the initial eluent.** Typically gradient applications require approximately 10 minutes to equilibrate to the initial eluent. The minimum equilibration time can be determined by making successive runs with increasing equilibration times. The column is equilibrated to the initial eluent when additional equilibration time does not increase the runtime of the first eluting peaks.

**B. Sluggish operation of the injection valve may be the problem.** Check the air pressure and make sure there are no gas leaks or partially plugged port faces. Refer to the valve manual for instructions.

**C. Improperly swept out volumes anywhere in the system prior to the guard and analytical columns may be the problem.** Swap components, one at a time, in the system prior to the analytical column and test for front-end resolution after every system change.

## 6.7 Spurious Peaks

**A. Eluents made with chemicals lacking the required purity will contaminate columns rapidly.** Remake all stock solutions and eluents using chemicals that meet the chemical requirements specified in Section 4.3, "Chemical Purity Requirements." Clean the column as indicated in "Column Care."

**B. Spurious peaks may be due to column contamination.** If the samples contain an appreciable level of polyvalent cations, polyvalent cations may contaminate the column. As a result, the retention times for the analytes will decrease, and spurious, inefficient peaks can show up at unexpected times. This problem may be solved by increasing the time between analyses or by adding a regeneration step between successive runs to elute polyvalent cationic contaminants off the column before the next sample injection takes place.

**C. An injection valve that needs service may produce baseline upsets.** This baseline upset can show up as one or multiple peaks of varying size(s) and shape(s). Typically this will occur when the particular valve needs to be cleaned or torqued (see the system manual). Small baseline disturbances at the beginning or at the end of the chromatogram can be overlooked as long as they do not interfere with the quantification of the peaks of interest.

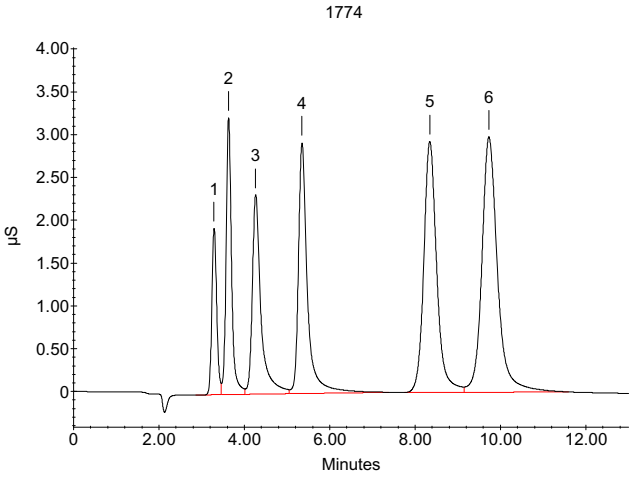
# APPENDIX A - QUALITY ASSURANCE REPORT

**Quality Assurance Report - IonPac CS14 Analytical Column - 2 x 250 mm**

**Quality Assurance Report - IonPac CS14 Analytical Column - 4 x 250 mm**

# IonPac® CS14
# Analytical (2 x 250 mm)
# Product No. 44121

**Serial No. : 1774** **Pressure (PSI) : 940** **Date : 5/13/02 4:08:31 PM**




**Eluent:** 10.0 mM methanesulfonic acid

**Eluent Flow Rate:** 0.25 mL/min

**Detection:** Suppressed Conductivity
**CSRS®-ULTRA, 2-mm**
AutoSuppression® Recycle Mode

**Injection Volume:** 2.5 µL

**Storage Solution:** Eluent

Peak Information : Found Components

| Peak No. | Retention Time | Name | (mg/L) | Efficiency | Asymmetry (10%) | Resolution |
|---|---|---|---|---|---|---|
| 1 | 3.29 | Lithium | 0.5 | 3942 | 1.4 | 1.58 |
| 2 | 3.63 | Sodium | 2.0 | 4320 | 1.3 | 2.32 |
| 3 | 4.26 | Ammonium | 2.5 | 2785 | 2.1 | 3.33 |
| 4 | 5.35 | Potassium | 5.0 | 4100 | 1.8 | 6.96 |
| 5 | 8.34 | Magnesium | 2.5 | 4010 | 1.3 | 2.44 |
| 6 | 9.73 | Calcium | 5.0 | 3973 | 1.3 | n/a |

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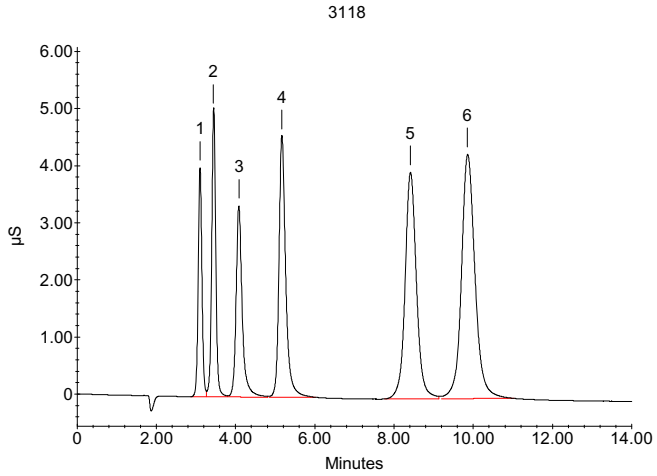
# IonPac® CS14
# Analytical (4 x 250 mm)
# Product No. 44123

**Serial No. : 3118** **Pressure (PSI) : 1100** **Date : 3/3/00 9:47:05 AM**




**Eluent:** 10.0 mM methanesulfonic acid

**Detection:** Suppressed Conductivity
**CSRS®-ULTRA**
AutoSuppression® Recycle Mode

**Plot Scale:** Autoscale

**Injection Volume:** 25 µL

**Storage Solution:** Eluent

Peak Information : Found Components

| Peak No. | Retention Time | Name | (mg/L) | Efficiency | Asymmetry (10%) | Resolution |
|---|---|---|---|---|---|---|
| 1 | 3.10 | Lithium | 0.5 | 4986 | 1.1 | 1.88 |
| 2 | 3.44 | Sodium | 2.0 | 5418 | 1.2 | 2.90 |
| 3 | 4.08 | Ammonium | 2.5 | 4099 | 1.4 | 3.98 |
| 4 | 5.16 | Potassium | 5.0 | 5104 | 1.6 | 8.22 |
| 5 | 8.41 | Magnesium | 2.5 | 4452 | 1.2 | 2.63 |
| 6 | 9.85 | Calcium | 5.0 | 4388 | 1.3 | n/a |

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# APPENDIX B - COLUMN CARE

## Recommended Operating Pressures

Operating a column above its recommended pressure limit can cause irreversible loss of column performance. The maximum recommended operating pressure for the IonPac CS14 Analytical or Guard Column is 4,000 psi (27.57 MPa).

**CAUTION** **Formation of esters will occur in the column packing. This can significantly reduce the column capacity for cation exchange. Do not use the CS14 column with basic eluents.**

## Column Start-Up

The column is shipped with eluent as the storage solution. This eluent is the same one shown in the test chromatogram. If you plan to use an eluent other than the test eluent, first equilibrate the column with the desired eluent for 30 to 60 minutes. The column is equilibrated when two consecutive injections of the standard produce the same retention times.

## Column Storage

The column's storage solution should be the eluent used for the particular application. If the column will not be used for one week or more, prepare it for long term storage by flushing the column for a few minutes with the eluent. Cap both ends securely, using the plugs supplied with the column.

## Column Conditioning

For sample matrices that contain organic solvent content, it is recommended to condition the column with the following procedure:

A. Disconnet the column and direct the column effluent to a waste container.

B. Rinse the column for 90 minutes with 0.5 mN sulfuric acid and 10% acetonitrile.

C. Rinse the column for 30 minutes with eluent.

D. Reconnect the column to the suppressor.

## Column Cleanup

The following column cleanup protocols have been divided into two general isocratic protocols:

A. Acid soluble contaminants

B. Hydrophobic cations and organic contaminants.

Always ensure that the cleanup protocol used does not switch between eluents which may create high pressure eluent interface zones in the column. High pressure zones can disrupt the uniformity of the packing of the column bed and irreversibly damage the performance of the column. High pressure zones in the column can be created by pumping successive eluents through the column that are not miscible, that have eluent components in one eluent that will precipitate out in the other eluent or by using an acid eluent followed by a base eluent which may create a neutralization pressure band. The precipitation of the salts in solvents during column rinses can result in very high pressure zones. High viscosity mixing zones can be created between two eluents having solvents with a very high energy of mixing.

When in doubt, always include short column rinse steps to reduce the solvent content of the eluent to < 5% levels and the ionic strength of the eluent to < 50 mM levels. This intermediate low concentration step will prevent precipitation or high viscosity zones. Avoid creating high pressure zones in the column that may disrupt the uniformity of the column packing.

### Column Cleanup Procedure for Polyvalent Cations and Acid-Soluble Contaminants or Transition Metals

A. Prepare 500 mL of 1 M HCl for the cleanup solution. Alternatively prepare 500 mM oxalic acid to remove transition metals such as iron or aluminum contamination.

**NOTE**

**Nitric acid should not be used instead of hydrochloric acid since nitric acid will not effectively remove iron contaminants. Do not clean the column with alcohols or with basic eluents.**

B. Disconnect the suppressor from the IonPac CS12 Analytical Column. If your system is configured with both a guard column and an analytical column, place the guard behind the analytical column in the eluent flow path. Double check that the eluent flows in the direction designated on each of the column labels.

**CAUTION**

**When cleaning an analytical column and a guard column in series, ensure that the guard column is placed after the analytical column in the eluent flow path. Contaminants that have accumulated on the guard column can be eluted onto the analytical column and irreversibly damage it. If in doubt, clean each column separately.**

C. Set the pump flow rate to 1.0 mL/min for a CS12 4-mm Analytical or Guard Column or set the pump flow rate to 0.25 mL/min for a CS12 2-mm Analytical or Guard Column.

D. Rinse the column for 15 minutes with 10 mM HCl before pumping the chosen cleanup solution over the column.

E. Pump the cleanup solution (1 M HCl or 500 mM oxalic acid) through the column for 60 minutes.

F. Rinse the column for 15 minutes with 10 mM HCl before pumping eluent over the column.

G. Equilibrate the column(s) with eluent before resuming normal operation for at least 30 minutes.

H. Reconnect the suppressor to the CS12 Analytical Column and place the guard column in line between the injection valve and the analytical column if your system was originally configured with a guard column.

**CAUTION**

**Do not pump HCl through the CSRS ULTRA when used in the electrolytic mode.**

### Hydrophobic Cations and Organic Contaminants

A. Disconnect the analytical column from the injection valve and the suppressor. Disconnect the Gradient Mixer or the Cation Trap Column (CTC-1) from the gradient pump. Connect the IonPac CS12 2-mm or 4-mm Analytical Column directly to the gradient pump. Direct the effluent from the analytical column directly to a waste container.

B. Set the flow rate to 1 mL/min on 4-mm systems or 0.25 mL/min on 2-mm systems.

C. Use the following gradient program to remove hydrophobic cations and organic contaminants.

Eluent 1: 100 mM HCl
Eluent 2: 90% Acetonitrile in deionized water

| Time (min) | % E1 | % E2 |
|---|---|---|
| 0.0 | 100 | 0 |
| 20.0 | 0 | 100 |
| 25.0 | 0 | 100 |
| 45.0 | 100 | 0 |
| 55.0 | 100 | 0 |

D. Rinse the column for 15 minutes with 10 mM HCl before pumping eluent over the column.

E. Equilibrate the column(s) with eluent before resuming normal operation for at least 30 minutes.

F. Reconnect the IonPac CS14 Analytical Column outlet to the suppressor, and the inlet to either the IonPac CG14 2-mm or 4-mm Guard Column, or the gradient pump.

G. Equilibrate the system with eluent before resuming normal operation.