Comparison of Suppressed to Nonsuppressed Conductivity Detection for the Determination of Common Inorganic Cations

INTRODUCTION
In 1975, Small and coworkers first introduced the concept of ion chromatography (IC) that allowed the sensitive detection of ions using suppressed conductivity detection. A significant portion of this work was dedicated to cation analysis. The original components described by Small et al. for the separation of cations included a low-capacity, sulfonated polystyrene/divinylbenzene (PS/DVB) column followed by a packed-bed suppressor in the hydroxide form and a conductivity detector. The primary purpose of the suppressor was to achieve sensitive detection of the ionic species by chemically modifying the eluent. This detection is accomplished by converting the mineral acid eluent to water and thereby achieving a very low background signal and low noise, while converting the analyte to its base form. Although mineral acid eluents are sufficient to elute alkali metals and ammonium, the low affinity of hydronium ions for sulfonated resins required a stronger eluting component, m-phenylenediamine, to elute the more retained alkaline earth metals. However, the concentrations of m-phenylenediamine required to separate the alkaline earth metals resulted in the alkali metals coeluting in the void volume. In addition to requiring two eluent systems for this analysis, the difficulty in converting the column from the m-phenylenediamine to the hydronium form essentially required a separate column dedicated for the analysis of alkaline earth metals. Another major drawback of this system was the requirement for periodic regeneration of the suppressor column. Today, suppressor technology has improved considerably and the chemical regeneration requirement is a distant memory. Figure 1 shows a historical timeline of suppressor development.

In 1979, a conductometric method for the determination of inorganic anions without a suppressor was first reported. This method was later commercialized and is known by various names, such as single-column IC, direct conductivity, and nonsuppressed conductivity detection. To achieve a lower background signal and therefore lower noise, nonsuppressed conductivity methods required low-capacity resins with dilute eluents. At higher conductivity levels, the influence of temperature changes become more significant, resulting in an increase in the baseline noise. Therefore, the low background requirement precludes the use of high-capacity columns that require high acid concentrations to elute the cationic species within a reasonable time. As with suppressed conductivity applications, sulfonated resins were also commonly used for nonsuppressed cation analysis, and a stronger eluting component—such as ethylenediamine—was required to separate the highly retained alkaline earth metals.

![Figure 1. Suppression timeline.](image-url)
Improved separation performance using latex-agglomerated anion-exchange columns suggested that similar performance could be achieved for cation-exchange columns. This development resulted in the first latex cation column, the IonPac® CS3, which was introduced in 1985. A layer of anion-exchange latex, functionalized with a tertiary amine, was attached to a surface-sulfonated PS/DVB substrate bead. A layer of sulfonated cation-exchange latex particles was then electrostatically attached to the positively charged surface. Due to the high mass transfer between the analytes and the latex material, a significant improvement in peak efficiencies for cations was observed. This column allowed the use of 2,3-diaminopropionic acid monohydrochloride (DAP•HCl) in combination with a mineral acid eluent for the separation of alkali and alkaline earth metals. DAP is effective for eluting alkaline earth metal ions because it can be protonated to form a divalent ion and therefore has a significantly higher selectivity for the cation-exchange resin than a monovalent eluent component. This higher selectivity allows lower eluent concentrations to be used, resulting in lower background conductivity during a gradient elution. Another advantage of using DAP with suppressed conductivity systems is that it only makes a minor contribution to the total background conductivity.

In 1987, Schomburg et al. introduced a silica-based, polymer-coated, cation-exchange column. The poly(butadiene-maleic acid) copolymer silica column was functionalized with carboxylic acid groups. The high selectivity for hydronium ions of these weak acid functional groups, in comparison to previous sulfonated resins, allowed the separation of alkali and alkaline earth metals and ammonium within a reasonable time (<20 min) using only tartaric acid, a mildly acidic complexing agent, as the eluent. This system was designed exclusively for detection with nonsuppressed conductivity. Additional eluents that are appropriate for use with these columns include dilute mineral acids, pyridine-2,6-dicarboxylic acid (PDCA), oxalic acid, and citric acid. The retention mechanism uses the unique selectivity of the carboxylate functional groups with the complexing agent in the eluent that forms complexes with divalent cations, reducing their effective positive charge. Thus, the retention times of the divalent cations are significantly reduced. However, the silica substrate only allows a relatively narrow sample and eluent pH range of 2–8. In a highly acidic environment

### Table 1. Properties of IonPac Cation-Exchange Columns Used for Suppressed IC

<table>
<thead>
<tr>
<th>Cation Exchange Column</th>
<th>Particle Diameter (µm)</th>
<th>Substrate X-Linkinga (%)</th>
<th>Latex Diameter (nm)</th>
<th>Latex X-Linkingb (%)</th>
<th>Column Capacityc (µequiv)</th>
<th>Functional Group</th>
</tr>
</thead>
<tbody>
<tr>
<td>CS3</td>
<td>10</td>
<td>2</td>
<td>300</td>
<td>5</td>
<td>100</td>
<td>Sulfonic acid</td>
</tr>
<tr>
<td>CS5Ad</td>
<td>9</td>
<td>55'</td>
<td>140</td>
<td>10</td>
<td>20</td>
<td>Sulfonic acid and</td>
</tr>
<tr>
<td>CS5Be</td>
<td>76</td>
<td>2</td>
<td>40</td>
<td></td>
<td></td>
<td>Alkyl quaternary amine</td>
</tr>
<tr>
<td>CS10</td>
<td>8.5</td>
<td>55'</td>
<td>200</td>
<td>5</td>
<td>80</td>
<td>Sulfonic acid</td>
</tr>
<tr>
<td>CS11</td>
<td>8.5</td>
<td>55'</td>
<td>200</td>
<td>5</td>
<td>35f</td>
<td>Sulfonic acid</td>
</tr>
<tr>
<td>CS12</td>
<td>8</td>
<td>55'</td>
<td>N/A</td>
<td>N/A</td>
<td>2800</td>
<td>Carboxylic acid</td>
</tr>
<tr>
<td>CS12A</td>
<td>8</td>
<td>55'</td>
<td>N/A</td>
<td>N/A</td>
<td>2800</td>
<td>Carboxylic acid and</td>
</tr>
<tr>
<td>CS14</td>
<td>8</td>
<td>55'</td>
<td>N/A</td>
<td>N/A</td>
<td>1300</td>
<td>Carboxylic acid</td>
</tr>
<tr>
<td>CS15</td>
<td>8.5</td>
<td>55'</td>
<td>N/A</td>
<td>N/A</td>
<td>2800</td>
<td>Carboxylic acid/</td>
</tr>
<tr>
<td>CS16</td>
<td>5.5</td>
<td>55'</td>
<td>N/A</td>
<td>N/A</td>
<td>8400h</td>
<td>Carboxylic acid/</td>
</tr>
<tr>
<td>CS17</td>
<td>6.5</td>
<td>55'</td>
<td>N/A</td>
<td>N/A</td>
<td>1450</td>
<td>Carboxylic acid/</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Phosphonic acid/</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Crown ether</td>
</tr>
</tbody>
</table>

aSubstrate is PS/DVB, unless otherwise noted
bCation-exchange latex is PS/DVB
cCapacity is given for 4 × 250 mm i.d. column, unless otherwise noted
dColumn designed for transition metal determination with Vis detection
eSubstrate is EVB/DVB and is solvent compatible with 100% acetonitrile, 100% acetone, and 20% tetrahydrofuran, but not alcohols (exception: CS14 and CS17 are compatible with the above solvents, including alcohols)
fCapacity is for a 2 × 250 mm i.d. column
gGrafted resin
hCapacity is for a 5 × 250 mm i.d. column
iCoated with anionic and cationic latex materials; contains both anion- and cation-exchange capacity

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(pH <2), the covalent bonds linking the functional groups become unstable, while basic conditions (pH >8) may dissolve the silica material.\textsuperscript{11}

In 1992, Dionex Corporation introduced the IonPac CS12, a polymer-based cation-exchange column with grafted carboxylate functional groups for IC with suppressed conductivity detection. This column separated the six common cations in less than 10 min using a simple isocratic acidic eluent. DAP•HCl was no longer required to separate divalent cations, which allowed the use of the Cation Self-Regenerating Suppressor\textsuperscript{9} (CSRS\textsuperscript{9}) in the recycle mode. The recycle mode requires no external base for regeneration. The CSRS improved the ease of use of the IC system, provided low baseline noise, and therefore enhanced detection sensitivity for cations. These columns are also compatible with the EG50 Eluent Generator because only a single component eluent, such as methanesulfonic acid (MSA), is required. The EG50 electrolytically generates the MSA on-line, requiring only deionized water to operate the system and therefore significantly enhances the flexibility and convenience of operation.\textsuperscript{12} Unlike previous latex columns, the grafted IonPac CS12 resin used a macroporous high-surface-area polymeric substrate to increase the exchange capacity. Following the introduction of the CS12, additional hydronium-selective carboxylate-functionalized resins that use MSA as the eluent were developed to resolve common cations and amines. Table 1 summarizes the cation-exchange columns commercially available from Dionex for suppressed conductivity eluent systems.

This application note compares suppressed to nonsuppressed conductivity detection for the determination of inorganic cations. The IonPac CS16 was used to demonstrate the capabilities of a suppressed cation system, in terms of capacity, linearity, detection limits, and typical baseline noise using a self-regenerating suppressor. A silica-based cation-exchange column, the IonPac SCS 1, was evaluated for nonsuppressed cations and the results were compared to the suppressed system.

### EQUIPMENT

#### Suppressed Cation System
Dionex ICS-2500 Reagent-Free\textsuperscript{4} Ion Chromatography (RFIC)\textsuperscript{9} System consisting of:
- GP50 Gradient Pump with vacuum degas option
- EG50 Eluent Generator
- EluGen\textsuperscript{8} EGC II MSA cartridge (Dionex P/N 058902)
- ED50A Electrochemical Detector with conductivity cell and DS3 Detector Stabilizer
- AS50 Autosampler with thermal compartment
- Chromeleon\textsuperscript{9} Chromatography Workstation

\textsuperscript{*}Any Dionex RFIC system may be used

#### Nonsuppressed Cation System
Dionex ICS-1000, ICS-1500, or ICS-2000 Ion Chromatography System consisting of:
- Dual-piston pump
- Column heater
- Digital conductivity detector
- AS50 Autosampler
- Chromeleon Chromatography Workstation

### REAGENTS AND STANDARDS
Deionized water, Type I reagent-grade, 18 MW-cm resistivity or better
- Lithium standard, 1000 mg/L (Ultra Scientific; VWR P/N ULICC 104)
- Sodium standard, 1000 mg/L (Ultra Scientific; VWR P/N ULICC 107)
- Ammonium standard, 1000 mg/L (Ultra Scientific; VWR P/N ULICC 101)
- Potassium standard, 1000 mg/L (Ultra Scientific; VWR P/N ULICC 106)
- Magnesium standard, 1000 mg/L (Ultra Scientific; VWR P/N ULICC 105)
- Calcium standard, 1000 mg/L (Ultra Scientific; VWR P/N 103)
- Lithium chloride (LiCl; Fisher L-121-100)
- Sodium chloride (NaCl; Fisher S-271)
Ammonium chloride (NH₄Cl; Fisher A-5666)
Potassium chloride (KCl; Sigma P-3911)
Magnesium chloride hexahydrate (MgCl₂ • 6H₂O; Aldrich 24,696-4)
Calcium chloride dihydrate (CaCl₂ • 2H₂O; Fisher C79-500)
Combined Six Cation Standard-II (Dionex P/N 046070)

**SUPPRESSED CATION CONDITIONS**³,¹⁴

Columns: IonPac CS16 Analytical, 5 × 250 mm (Dionex P/N 057573)
IonPac CG16 Guard, 5 × 50 mm (Dionex P/N 057574)
Eluent: 26 mM MSA
Eluent Source: EG50
Flow Rate: 1.5 mL/min
Temperature: 30 °C
Injection: 10 µL
Detection: Suppressed conductivity, CSRS ULTRA (4 mm), AutoSuppression recycle mode, current setting 100 mA
Background: <1 µS
Noise: ~0.2 nS peak-to-peak
Backpressure: ~2300 psi
Run Time: 30 min

**NONSUPPRESSED CATION CONDITIONS**

Columns: IonPac SCS 1 Analytical, 4 × 250 mm (Dionex P/N 061521)
IonPac SCG 1 Guard, 4 × 50 mm (Dionex P/N 061523)
Eluent: 3 mM MSA
Flow Rate: 1 mL/min
Temperature: 30 °C
Injection: 10 µL
Detection: Nonsuppressed conductivity
Background: ~1100 µS
Noise: ~5–10 nS peak-to-peak
Backpressure: ~2100 psi
Run Time: 35 min

**PREPARATION OF SOLUTIONS AND REAGENTS**

**Eluent Solution for Suppressed Cation System**

Generate 26 mM MSA by pumping deionized water through the EGC II MSA cartridge. Alternatively, prepare 1.0 N MSA stock solution by adding 96.10 g of methanesulfonic acid (MSA, >99%, Dionex P/N 033478) to a 1-L volumetric flask containing about 500 mL of deionized water. Dilute to the mark and mix thoroughly. Prepare 26 mM MSA by diluting 26 mL of the 1.0 N MSA stock solution to 1 L with deionized water. Degas the eluent by sonication under vacuum for 10 min or by sparging with helium. Store the eluent in a plastic eluent bottle.

**Eluent Solution for Nonsuppressed Cation System**

Prepare 3 mM MSA by diluting 3 mL of the 1.0 N MSA stock solution to 1 L with deionized water. Degas the eluent by sonication under vacuum for 10 min or by sparging with helium. Store the eluent in a plastic eluent bottle. The eluent generator is not recommended for use with the nonsuppressed cation system, because a significant increase in the baseline noise will be observed.

**Stock Standard Solutions**

Certified stock solutions may be purchased or 1000 mg/L standards may be prepared for the cations of interest. Dissolve the appropriate amounts of the required analytes in deionized water in a 100-mL plastic volumetric flask according to the amounts in Table 2. Dilute to volume with deionized water. Store in plastic containers at 4 °C. Stock standards are stable for at least three months.

**Table 2. Mass of Compound Required to Prepare 100 mL of 1000-mg/L Solution of Cation**

<table>
<thead>
<tr>
<th>Cation</th>
<th>Compound</th>
<th>Mass (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li⁺</td>
<td>Lithium (LiCl)</td>
<td>0.6108</td>
</tr>
<tr>
<td>Na⁺</td>
<td>Sodium (NaCl)</td>
<td>0.2542</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>Ammonium (NH₄Cl)</td>
<td>0.2965</td>
</tr>
<tr>
<td>K⁺</td>
<td>Potassium (KCl)</td>
<td>0.1907</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>Magnesium (MgCl₂ • 6H₂O)</td>
<td>0.8365</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>Calcium (CaCl₂ • 2H₂O)</td>
<td>1.433</td>
</tr>
</tbody>
</table>

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Working Standard Solutions

Composite working standard solutions at lower analyte concentrations are prepared by diluting the appropriate volumes of the 1000-mg/L stock standard solutions with deionized water. Prepare working standards daily if they contain less than 100 mg/L of the cations.

SYSTEM PREPARATION AND SETUP

Suppressed Cation System

Prepare the CSRS ULTRA for use by hydrating the eluent chamber. Use a disposable syringe to push approximately 3 mL of 200 mM NaOH through the “Eluent Out” port and 5 mL of 200 mM NaOH through the “Regen In” port. Allow the suppressor to sit for approximately 20 min to fully hydrate the suppressor screens and membranes. For more information on CSRS operation, see the Installation Instructions and Troubleshooting Guide for the CSRS ULTRA (Document No. 031370-07).

Install the EG50, connect it to the system, and configure it with the Chromeleon chromatography workstation. Condition the EluGen MSA cartridge as directed in the EG50 manual by setting the MSA concentration to 50 mM at a flow of 1.0 mL/min for 30 min. For instructions on EG50 installation and use, see the EluGen EGC II Quickstart Guide, (Document No. 031909).

Remove the backpressure tubing temporarily installed during conditioning of the EluGen cartridge. Install a 5 × 50 mm IonPac CG16 and a 5 × 250 mm IonPac CS16 column. Make sure the system pressure is at least 2000 psi when 26 mM MSA is delivered at 1.5 mL/min. If necessary, install backpressure coils supplied with the EG50 ship kit to bring the system pressure between 2000 and 2800 psi. Do not exceed 3000 psi.

The CS16 storage solution is 30 mM MSA; before use, equilibrate the column with 26 mM MSA eluent for 60 min. An equilibrated system has a background signal of <1 µS, and peak-to-peak noise should be between 0.2–0.5 nS. There should be no peaks eluting at the same time as the cations of interest.

Prepare a 500× dilution of the Six Cation Standard-II (Dionex P/N 046070) and make a 10-µL full-loop injection. The column is equilibrated when two consecutive injections of standard produce the same retention times. Confirm that the resulting chromatogram resembles the chromatogram in Figure 2.

Nonsuppressed Cation System

The ICS-1000, ICS-1500, or ICS-2000 integrated IC systems may be used for nonsuppressed cations. This application note describes the proper setup and system preparation for an ICS-2000. Install the 4 × 50 mm IonPac SCG 1 and 4 × 250 mm IonPac SCS 1 column in the column oven. Set the signal polarity by navigating to the dropdown menu on the LCD screen and press “DETECTOR”. In the conductivity polarity option, set the polarity to “Inverted”. For the ICS-1000 system, the polarity must be changed using Chromeleon software.

Because the ICS-2000 system contains an eluent generator cartridge, this portion of the system should be bypassed by placing a 10-32 in. union in place of the inlet and outlet fittings for the EluGen cartridge. A separate union should also be placed between the inlet and outlet fittings for the continuously regenerated trap column. Because a suppressor is not used for this system, the outlet of the conductivity detector may be connected to the tubing labeled “Regen Out” to direct the column effluent to waste. The Chromeleon program (*.pgm file) should be set for “0 mM” MSA and the suppressor should be set to “None”.

Figure 2. Separation of inorganic cations and ammonium on the IonPac CS16 column.
Equilibrate the columns with 3 mM MSA at 1 mL/min for at least 60 min. Prior to sample analysis, analyze a system blank of reagent water. An equilibrated system has a background signal of <1100 µS, and peak-to-peak noise should be <10 nS. There should be no peaks eluting at the same retention time as the cations of interest.

Prepare a 100× dilution of the Six Cation Standard-II (Dionex) and make a 10-µL full-loop injection. The column is equilibrated when two consecutive injections of standard produce the same retention times. Confirm that the resulting chromatogram is similar to the chromatogram shown in Figure 3.

RESULTS AND DISCUSSION

Conductometric detection is the major detection technique used to determine ionic species by IC. However, the measurement of conductance had some serious faults in the early attempts to apply it to IC. A major limitation was attempting to determine relatively low concentrations of an analyte in the presence of a highly conductive eluent species. This limitation was overcome when Small and coworkers introduced the concept of suppressed IC. The suppressor eliminated the highly conductive background and therefore enhanced the sensitivity of the measured analytes. In this system, an eluent species of HX (X being the anion associated with the eluent) passes through the suppressor that exchanges X– for OH– to produce a background of H2O.

In 1979, a method was reported that used IC directly coupled to a conductometric detector. A low-capacity analytical column, using dilute eluent concentrations, was required to achieve a low background signal. In this case, the background is directly proportional to the equivalent conductances of the eluent species, HX, as shown in the following equation:

\[ G = C_E(\lambda_H + \lambda_X) \]  

where \( G \) is the conductance (S•cm²/equiv), \( C_E \) is the concentration of the eluent, and \( \lambda_H \) and \( \lambda_X \) are the limiting equivalent conductances of H₃O⁺ and X–, respectively. The equivalent conductances (S•cm²/equiv) for common ions of interest in the context of this application note are: Li⁺, 38.7; Na⁺, 50.1; Mg²⁺, 53.1; Ca²⁺, 59.5; NH₄⁺, 73.5; K⁺, 73.5; H⁺, 350; OH⁻, 198. Because the conductance of hydronium is significantly greater than any other cation, analytes appear as negative peaks. Therefore, it is common to reverse the polarity of the output signal when performing cation analyses by nonsuppressed conductivity.

Suppressed and nonsuppressed conductometric methods may be differentiated in terms of sensitivity, linear range, column capacity, and the ability to perform gradient separations. Consider two identical systems with the primary difference being that the effluent first passes through a suppressor before entering the conductivity cell in the first system, whereas in the second system the effluent flows directly through the conductivity cell. In the second nonsuppressed system, the analyte signal is measured as the difference between the limiting equivalent conductance of the analyte (e.g., sodium) and the eluent cation (e.g., hydronium):

\[ \Delta G = C_{Na}(\lambda_{Na} - \lambda_H) \]  

where \( \Delta G \) is the change in conductance, \( C_{Na} \) is the concentration of sodium injected on the column, and \( \lambda_{Na} \) and \( \lambda_H \) are the limiting equivalent conductances for sodium and hydronium, respectively. If \( C_{Na} \) is neglected for this discussion, then the change in conductance for
equation 2 is –300, resulting in a negative peak. Positive peaks can be obtained by reversing the signal polarity of the detector.

In the suppressed system, the sodium analyte first passes through the suppressor, converting it to sodium hydroxide, while the acidic eluent is converted to water. Therefore, the analyte is essentially determined in a background of pure water, resulting in a positive analyte response. The response can be calculated from the following equation:

$$\Delta G = C_{Na}(\lambda_{Na} + \lambda_{OH})$$  (3)

This results in a change in conductance of +248 using suppressed conductivity detection.

In comparing the change in conductance between these two systems, the analyte response is –300 compared to +248 for the nonsuppressed and suppressed systems, respectively. It would be erroneous at this point to say the nonsuppressed system is more sensitive than the suppressed without factoring the difference in baseline noise. In this application note, the typical background conductance of a suppressed system is <1 μS compared to ~1100 μS for the nonsuppressed system. An increase in the background signal generally results in a proportional increase in baseline noise.

Therefore, in a nonsuppressed system, it is critical to use relatively dilute concentrations of acid to produce the lowest possible background signal and separate the common cations within a reasonable time. To meet this requirement, a low-capacity cation-exchange column must be used. However, column choice is not critical for suppressed systems, because high eluent concentrations may be used without any significant change in the background conductance, as long as the suppressor capacity is not exceeded. In this context, suppressed conductivity detection may easily deliver baseline noise of <0.5 nS compared to ~5–10 nS for a nonsuppressed system. Using the signals calculated from equations 2 and 3 and baseline noise of 0.4 nS for a suppressed system and 7 nS for a nonsuppressed systems, a theoretical S/N may be calculated as follows:

- Suppressed: S/N = 248/0.4 = 620
- Nonsuppressed: S/N = 300/7 = 43

Dividing equation 4 by 5 results in a S/N difference of ~14. This exercise demonstrates that the lower noise and drift generated with a suppressor results in superior sensitivity of at least an order of magnitude (i.e., factor of 10) compared with nonsuppressed detection. In addition, the calculated values agree with the experimental results determined in this application note.

The requirement of a low-capacity column for nonsuppressed detection restricts its ability to analyze high-ionic-strength matrices and lowers the dynamic range to avoid overloading the column. In addition, gradient elution is impossible because an increase in eluent strength will significantly increase the background signal and therefore preclude the detection of analytes. In contrast, columns used with suppressed systems may calibrate over four orders of magnitude in concentration due to the higher column capacity and can easily accommodate a change in eluent strength during a sample run without any significant change in the background signal. This feature allows a suppressed system to determine cations in a wide range of sample matrices. However, for analytes that form weak bases from the suppressor reaction, such as NH$_4^+$ or other amines, a nonlinear calibration curve is observed. Thus, a quadratic curve fit is typically required for acceptable correlation of the calibration curve. A linear calibration curve is observed using nonsuppressed conductivity detection.

In this application note, the IonPac CS16 and IonPac SCS 1 were used to demonstrate the capabilities of suppressed and nonsuppressed conductivity detection, respectively. The CS16 is a high-capacity cation-exchange column with 100% solvent compatibility and medium hydrophobicity. The high capacity of 8400 μeq/column is achieved by using a higher density of grafted carboxylic acid groups and a larger column format (5 × 250 mm). The higher capacity is particularly advantageous for analyzing high-ionic-strength matrices and resolving analytes at disparate concentration ratios, such as sodium and ammonium in wastewater samples.

The nonsuppressed IonPac SCS 1 is a 4.5-μm silica-based poly(butadiene-maleic acid) copolymer column functionalized with carboxylic acids. To achieve a separation of the six common cations within a reasonable time using a dilute acidic eluent, the capacity of the 4 × 250 mm SCS 1 (318 μeq/column) needs to be considerably less than that of the CS16. The SCS 1 is also 100% solvent-compatible with acetone or acetonitrile that may be used to change the selectivity or alter retention times. Figures 2 and 3 show separations of common cations using the CS16 and SCS 1, respectively. The higher-capacity CS16 column required nearly
ten times the eluent strength of the SCS 1 to achieve the separation in less than 30 min. The higher eluent strength required by the CS16, due to its higher capacity, precludes its use for nonsuppressed conductivity detection.

Because retention times vary with temperature, maintaining constant temperature is critical. Although both systems can be operated at ambient temperatures, the temperature should be controlled at 30 °C for good retention time reproducibility. However, the high stability of the polymeric CS16 column allows temperatures up to 60 °C to be used. Temperatures above 35 °C may result in irreversible damage to the silica-based SCS 1 resin and therefore should not be used.

Retention time and background signal may also vary slightly between eluent preparations for the nonsuppressed SCS 1 column. In contrast, the suppressed system can generate very reproducible retention time and peak area data by electrolytically generating the MSA on-line. This online eluent generation also significantly increases the flexibility of the suppressed cation system in comparison to manually preparing the eluents.

Tables 3 and 4 summarize the calibration data and method detection limits (MDLs) obtained for the six cations using the CS16 and SCS 1 column, respectively. The higher capacity of the CS16 column results in a calibration curve over three orders of magnitude for most cations, except for ammonium. The nonlinear dependence of peak area (or height) on concentration is common for weak bases such as ammonia that are not completely protonated at high concentrations in the suppressor. A quadratic curve fitting function extends the calibration curve for ammonium to 40 mg/L. For the nonsuppressed SCS 1 column, the calibration curve extends up to three orders of magnitude for all cations. Unlike the suppressed system, nonsuppressed detection results in a linear curve for ammonium, using a least squares fit, with a coefficient of determination ($r^2$) of 0.9999. However, sodium was calibrated up to four orders of magnitude for the suppressed system, compared to three orders of magnitude for the nonsuppressed system.

### Table 3. Linearity and MDLs Using Suppressed Conductivity Detection

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Range (mg/L)</th>
<th>Linearity ($r^2$)</th>
<th>Calculated MDL (µg/L)</th>
<th>MDL Standard (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium</td>
<td>0.05–80</td>
<td>0.9999</td>
<td>0.19</td>
<td>1</td>
</tr>
<tr>
<td>Sodium</td>
<td>0.1–1000</td>
<td>0.9999</td>
<td>1.81</td>
<td>4</td>
</tr>
<tr>
<td>Ammonium</td>
<td>0.05–40</td>
<td>0.9993</td>
<td>1.23</td>
<td>5</td>
</tr>
<tr>
<td>Potassium</td>
<td>0.05–80</td>
<td>0.9999</td>
<td>2.64</td>
<td>10</td>
</tr>
<tr>
<td>Magnesium</td>
<td>0.05–80</td>
<td>0.9999</td>
<td>1.00</td>
<td>5</td>
</tr>
<tr>
<td>Calcium</td>
<td>0.05–80</td>
<td>0.9998</td>
<td>1.09</td>
<td>5</td>
</tr>
</tbody>
</table>

Table 3. Linearity and MDLs Using Suppressed Conductivity Detection

- Lithium 0.05–50 0.9999 2.0 10
- Sodium 0.25–250 0.9999 5.8 20
- Ammonium 0.05–50 0.9999 10.9 25
- Potassium 0.2–50 0.9999 30.0 100
- Magnesium 0.2–50 0.9999 19.6 100
- Calcium 0.2–100 0.9999 36.6 150

### Table 4. Linearity and MDLs Using Nonsuppressed Conductivity Detection

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Range (mg/L)</th>
<th>Linearity ($r^2$)</th>
<th>Calculated MDL (µg/L)</th>
<th>MDL Standard (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium</td>
<td>0.05–50</td>
<td>0.9999</td>
<td>2.0</td>
<td>10</td>
</tr>
<tr>
<td>Sodium</td>
<td>0.25–250</td>
<td>0.9999</td>
<td>5.8</td>
<td>20</td>
</tr>
<tr>
<td>Ammonium</td>
<td>0.05–50</td>
<td>0.9999</td>
<td>10.9</td>
<td>25</td>
</tr>
<tr>
<td>Potassium</td>
<td>0.2–50</td>
<td>0.9999</td>
<td>30.0</td>
<td>100</td>
</tr>
<tr>
<td>Magnesium</td>
<td>0.2–50</td>
<td>0.9999</td>
<td>19.6</td>
<td>100</td>
</tr>
<tr>
<td>Calcium</td>
<td>0.2–100</td>
<td>0.9999</td>
<td>36.6</td>
<td>150</td>
</tr>
</tbody>
</table>

Table 4. Linearity and MDLs Using Nonsuppressed Conductivity Detection

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- Magnesium 0.2–50 0.9999 19.6 100
- Calcium 0.2–100 0.9999 36.6 150

* Dionex ICS-2500 system with a 10-µL injection

* CS16 can tolerate a higher upper concentration than shown

* Quadratic fit

* MDL = $\sigma t_{s,99}$, where $t_{s,99} = 3.14$ for $n = 7$
High concentrations of sodium and other cations will overload the SCS 1 due to its significantly lower capacity compared to the CS16. Overloading can cause peak splitting, especially for weakly retained analytes. This peak splitting is illustrated in Figure 4A, showing a standard injection containing 1000 ppm sodium, 40 ppm ammonium, and 100 ppm of the other common cations using the SCS 1 column. The Li⁺ peak is split and the divalent cation peaks severely tail. Figure 4B shows a chromatogram of the same standard injected on the high-capacity CS16 column with suppressed conductivity detection. Due to the significantly higher capacity of the CS16, the sample does not cause column overloading. Figure 4C shows the same standard diluted by a factor of two analyzed with the SCS 1 column. Although, the lower concentration has removed the splitting of the lithium peak, tailing is still observed for the divalent cation peaks. Therefore, analysis of high-ionic-strength matrices on the SCS 1 column requires an appropriate dilution or lower injection volume to avoid column overloading.

As previously discussed, the sensitivity for suppressed cations is significantly better than the nonsuppressed system (Tables 3 and 4). The suppressed system MDLs were lower by at least an order of magnitude for most cations compared to the nonsuppressed system. Lower detection limits may be achieved for either system by injecting a larger sample volume. The amount of sample injected onto either column depends on its ionic strength. Higher capacity columns, such as the CS16 will tolerate larger injections volumes than lower capacity columns. Although the MDLs for the suppressed system were better than the nonsuppressed system, in a truly fair comparison the column dimensions should be considered. A further improvement in detection limits than shown in Table 3 would be expected for a smaller i.d. CS16 column format, such as a $4 \times 250$ mm column. In this application note, a $4 \times 250$ mm SCS 1 column was compared to a $5 \times 250$ mm CS16 column.

An important application, particularly for environmental samples, is the ability to determine trace concentrations of ammonium in the presence of high concentrations of sodium. The high-capacity CS16 is ideal for...
Comparison of Suppressed to Nonsuppressed Conductivity Detection for the Determination of Common Inorganic Cations

this analysis by providing an improved resolution of sodium from ammonium, even in high-ionic-strength samples. Figure 5 illustrates the determination of trace-level ammonium in the presence of high sodium. The sodium to ammonium ratio shown in this chromatogram is ~6700:1. However, the CS16 is capable of tolerating ratios of up to 10,000:1. The SCS 1 is not ideal for analyzing these types of matrices due to its lower capacity. The maximum ratio determined for this column was 1000:1 sodium to ammonium (Figure 6).

The high capacity of the CS16 cation-exchange column is an advantage when injecting low pH samples, such as acidic digests, acid-preserved samples, and acidic soil extracts. These samples can contain up to 100 mM hydronium ion (pH 1) and can be injected (25 µL) without pH adjustment. However, because the functional groups are weakly acidic carboxylic acids, a sample pH <1 will impact the separation of cations on the column. The significantly lower cation-exchange capacity of the SCS 1 prevents the analysis of these types of samples without sample preparation to remove the excess hydronium ions. Therefore, samples with a pH of less than 2 (10 mM hydronium ion) should not be injected on the SCS 1 column.

Alternative cation eluents for nonsuppressed conductivity detection are weakly acidic complexing agents, such as tartaric acid and PDCA. The high affinity of PDCA for divalent metal ions, such as calcium and magnesium, causes a significant decrease in their retention. Calcium forms a particularly strong complex with PDCA, reducing its effective positive charge, and therefore causing it to elute before magnesium. Alkali metals are not affected by a change in the concentration of PDCA due to their low complexing ability. Figure 7 shows a separation of common cations using 4 mM tartaric acid and 0.75 mM PDCA. The significant increase in run times, compared to other commercially available nonsuppressed cation-exchange columns, results from the higher capacity of the SCS 1. Therefore, the optimum eluent for the SCS 1 column is 3 mM MSA, as specified under the method conditions in this application note.

Figure 5. Resolution of trace ammonium from high sodium with the IonPac CS16 column.

Figure 6. Determination of low concentrations of ammonium in high concentrations of sodium on the IonPac SCS 1 column.

Figure 7. Separation of common cations using 4 mM tartaric acid and 0.75 mM PDCA.
CONCLUSION

This application note demonstrates the capabilities of suppressed conductivity detection using the high-capacity CS16 column and nonsuppressed conductivity detection using a lower-capacity SCS 1 column for the determination of common inorganic cations. The lower noise generated with suppressed systems results in an improved S/N ratio of at least one order of magnitude compared to a nonsuppressed cation system. This improved ratio enables the determination of trace levels of cations that may otherwise prove difficult using a nonsuppressed system. The use of nonsuppressed conductivity as a detection mode requires a low-capacity column using dilute acidic eluents to achieve a low background signal. This requirement limits the linear range of common cations, prevents the use of eluent gradients limits sample pH, and prevents the possibility of analyzing high-ionic-strength matrices without overloading the column. However, nonsuppressed conductivity detection does produce linear calibration curves for ammonium and weakly basic amines.

REFERENCES

13. Dionex Corporation. Application Note 141; Sunnyvale, CA.

Figure 7. Separation of common inorganic cations using a weak acid eluent on the IonPac SCS 1 column.