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APPLICATION NOTE 157

Comparison of suppressed to nonsuppressed conductivity detection for the determination of common inorganic cations

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Ion chromatography, suppressor, suppression, Dionex IonPac CS16, Dionex IonPac SCS 1, lithium, sodium, ammonium, potassium, calcium, magnesium

Goal

To demonstrate the capabilities of suppressed conductivity detection using the high-capacity Thermo Scientific™ Dionex™ IonPac™ CS16 column and nonsuppressed conductivity detection using a lower-capacity Thermo Scientific™ Dionex™ IonPac™ SCS 1 column for the determination of common inorganic cations

Introduction

In 1975, Hamish Small and coworkers at The Dow Chemical Company first introduced the concept of ion chromatography (IC) that allowed the sensitive detection of ions using suppressed conductivity detection.[1] 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.[2] 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

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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.[3] 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.[4,5] This method was later commercialized and is known by various names, such as single-column IC, direct conductivity, and nonsuppressed conductivity detection.[6] 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.[7] 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.[6]

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 Dionex™ 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.[8] 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 makes only a minor contribution to the total background conductivity.[9]

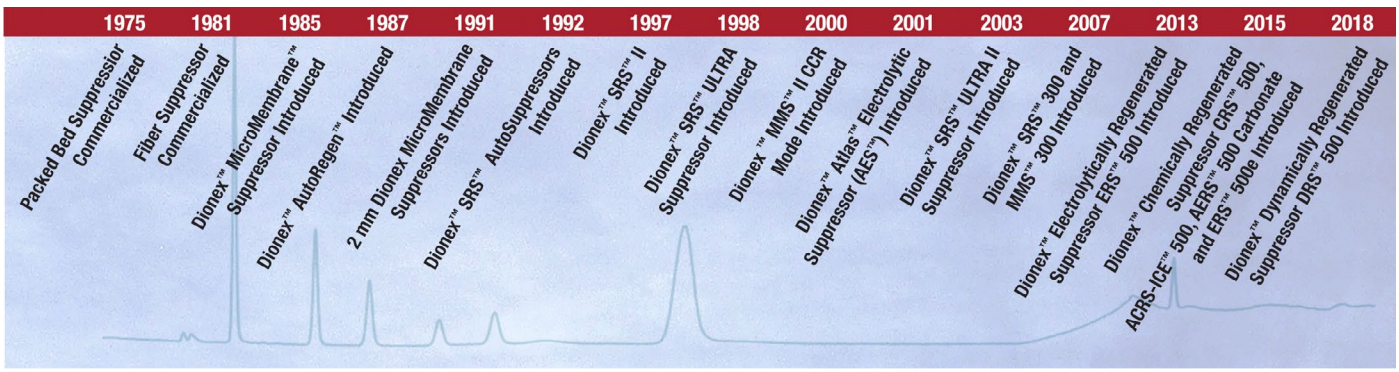

Figure 1. Thermo Scientific™ suppressor history

In 1987, Schomburg et al. introduced a silica-based, polymer-coated, cation-exchange column.[10] 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 allows only a relatively narrow sample and eluent pH range of 2–8. In a highly acidic environment (pH < 2), the covalent bonds linking the functional groups become unstable, while basic conditions (pH > 8) may dissolve the silica material.[11]

In 1992, Dionex Corporation (now part of Thermo Fisher Scientific) introduced the Dionex IonPac CS12 column, 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 Thermo Scientific™ Dionex™ CSRS™ Cation Self-Regenerating Suppressor in the recycle mode.[9] The recycle mode requires no external base for regeneration. The Dionex CSRS suppressor 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 Thermo Scientific™ Dionex™ EG50 Eluent Generator because only a single component eluent, such as methanesulfonic acid (MSA), is required. The Dionex EG50 Eluent Generator electrolytically generates the MSA online, requiring only deionized water to operate the system and therefore significantly enhancing the flexibility and convenience of operation.[12] Unlike previous latex columns, the grafted Dionex IonPac CS12 resin used a macroporous high-surface-area polymeric substrate to increase the exchange capacity. Following the introduction of the Dionex IonPac CS12 column, 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 Thermo Fisher Scientific for suppressed conductivity eluent systems.

This application note compares suppressed to nonsuppressed conductivity detection for the determination of inorganic cations. The Dionex IonPac CS16 column 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 Dionex IonPac SCS 1, was evaluated for nonsuppressed cations and the results were compared to the suppressed system. Please note that since the completion of this work, the Thermo Scientific™ Dionex™ IonPac™ CS18 column has been introduced and that column can be used with suppressed or nonsuppressed conductivity detection.

Table 1. Properties of Dionex IonPac cation-exchange columns used for suppressed IC

Cation-Exchange Column	Particle Diameter (µm)	Substrate X-Linking[a] (%)	Latex Diameter (nm)	Latex X-Linking[b] (%)	Column Capacity[c] (µequiv)	Functional Group
CS3	10	2	300	5	100	Sulfonic acid
CS5A[d]	9	55[e]	140	10	20	Sulfonic acid and
			76	2	40	Alkyl quaternary amine
CS10	8.5	55[e]	200	5	80	Sulfonic acid
CS11	8.5	55[e]	200	5	35[f]	Sulfonic acid
CS12	8	55[e]	N/A[g]	N/A[g]	2800	Carboxylic acid
CS12A	8	55[e]	N/A[g]	N/A[g]	2800	Carboxylic acid and phosphonic acid
CS14	8	55[e]	N/A[g]	N/A[g]	1300	Carboxylic acid
CS15	8.5	55[e]	N/A[g]	N/A[g]	2800	Carboxylic acid/Phosphonic acid/Crown ether
CS16	5.5	55[e]	N/A[g]	N/A[g]	8400[h]	Carboxylic acid
CS17	6.5	55[e]	N/A[g]	N/A[g]	1450	Carboxylic acid
CS18	6	55	N/A	N/A[g]	290[f]	Carboxylic Acid
CS19	4	55	N/A	N/A[g]	2410	Carboxylic Acid
CS20	5	55	N/A	N/A[g]	3000	Carboxylic Acid/Sulfonic Acid/Phosphonic Acid

[a]Substrate is PS/DVB, unless otherwise noted

[b]Cation-exchange latex is PS/DVB

[c]Capacity is given for 4 × 250 mm i.d. column, unless otherwise noted

[d]Column designed for transition metal determination with Vis detection

[e]Substrate is EVB/DVB and is solvent compatible with 100% acetonitrile, 100% acetone, and 20% tetrahydrofuran, but not alcohols (exception: Dionex IonPac CS14 and Dionex IonPac CS17 columns are compatible with the above solvents, including alcohols)

[f]Capacity is for a 2 × 250 mm i.d. column

[g]Grafted resin

[h]Capacity is for a 5 × 250 mm i.d. column

[i]Coated with anionic and cationic latex materials; contains both anion- and cation-exchange capacity

Experimental

Equipment

Suppressed cation system

- Thermo Scientific™ Dionex™ ICS-2500 Reagent-Free™ Ion Chromatography (RFIC™)* System consisting of:
  - Thermo Scientific™ Dionex™ GP50 Gradient Pump with vacuum degas option
  - Dionex EG50 Eluent Generator
  - Thermo Scientific™ Dionex™ EluGen™ EGC II MSA cartridge (P/N 058902)
  - Thermo Scientific™ Dionex™ ED50A Electrochemical Detector with conductivity cell and DS3 Detector Stabilizer
- Thermo Scientific™ Dionex™ AS50 Autosampler with thermal compartment (or any other Thermo Scientific Dionex autosampler)
- Thermo Scientific™ Chromeleon™ Chromatography Workstation

*Any Thermo Scientific Dionex RFIC system may be used, including the Thermo Scientific™ Dionex™ Integrion™ or Thermo Scientific™ Dionex™ ICS-6000 IC systems.

Nonsuppressed cation system*

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

*Any current Thermo Scientific Dionex IC system can be used for this work including the Thermo Scientific™ Dionex™ Aquion™, Dionex Integrion, or Dionex ICS-6000 IC systems. Any current Thermo Scientific Dionex autosampler could be used including a Dionex AS-DV or Dionex AS-AP.

Reagents and standards

- Deionized water, Type I reagent-grade, 18 MΩ-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 ULICC 103)
- Lithium chloride (LiCl; Fisher L-121-100)
- Sodium chloride (NaCl; Fisher S-271)
- Ammonium chloride (NH_4Cl; Fisher A-5666)
- Potassium chloride (KCl; Sigma P-3911)
- Magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$; Aldrich 24,696-4)
- Calcium chloride dihydrate ($CaCl_2 \cdot 2H_2O$; Fisher C79-500)
- Combined Six Cation Standard-II (P/N 046070)

Suppressed cation conditions[13,14]

Columns:	Dionex IonPac CS16 Analytical, 5 × 250 mm (P/N 079805) Dionex IonPac CG16 Guard, 5 × 50 mm (P/N 057574)
Eluent:	26 mM MSA
Eluent Source:	Dionex EG50
Flow Rate:	1.5 mL/min
Temperature:	30 °C
Injection:	10 µL
Detection:	Suppressed conductivity, Dionex CSRS ULTRA (4 mm) suppressor, 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:	Dionex IonPac SCS 1 Analytical, 4 × 250 mm (P/N 079809) Dionex IonPac SCG 1 Guard, 4 × 50 mm (P/N 079933)
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 (DI) water through the Dionex EGC II MSA cartridge. Alternatively, prepare 1.0 N MSA stock solution by adding 96.10 g of methanesulfonic acid (MSA, >99%, P/N 033478) to a 1 L volumetric flask containing about 500 mL of DI 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 DI water. Degas the eluent by sonicating 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 DI water. Degas the eluent by sonicating 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 DI water in a 100 mL plastic volumetric flask according to the amounts in Table 2. Dilute to volume with DI 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

Cation	Compound	Mass (g)
Li^+	Lithium (LiCl)	0.6108
Na^+	Sodium (NaCl)	0.2542
NH_4^+	Ammonium (NH_4Cl)	0.2965
K^+	Potassium (KCl)	0.1907
Mg^{2+}	Magnesium ($MgCl_2 \cdot 6\ H_2O$)	0.8365
Ca^{2+}	Calcium ($CaCl_2 \cdot 2H_2O$)	1.433

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 DI 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 Dionex CSRS ULTRA suppressor for use by hydrating the eluent chamber. Use a disposable syringe to push approximately 3 mL of 200 mN NaOH through the “Eluent Out” port and 5 mL of 200 mN NaOH through the “Regen In” port. Allow the suppressor to sit for approximately 20 min to fully hydrate the suppressor screens and membranes. Note: The Dionex CSRS ULTRA suppressor has been replaced. Please follow the start up instructions of the current cation suppressor.

Install the Dionex EG50 Eluent Generator, connect it to the system, and configure it with the Chromeleon chromatography workstation. Condition the Dionex EluGen MSA cartridge as directed in the Dionex EG50 Eluent Generator manual by setting the MSA concentration to 50 mM at a flow of 1.0 mL/min for 30 min. Note: The Dionex EluGen EGC II has been replaced. Please follow the start up instructions of the current cation eluent generation cartridge used with your Dionex IC system.

Remove the backpressure tubing temporarily installed during conditioning of the Dionex EluGen MSA cartridge. Install a 5 × 50 mm Dionex IonPac CG16 column and a 5 × 250 mm Dionex 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 Dionex EG50 Eluent Generator ship kit to bring the system pressure between 2000 and 2800 psi. Do not exceed 3000 psi.

The Dionex IonPac CS16 column 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 and 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 (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.

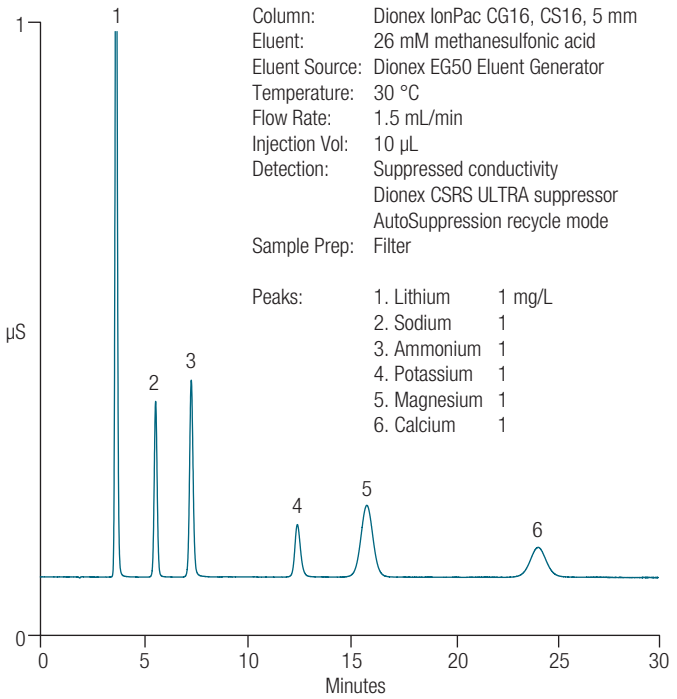

Figure 2. Separation of inorganic cations and ammonium on the Dionex IonPac CS16 column

Nonsuppressed cation system

The Dionex 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 a Dionex ICS-2000 system. Install the 4 × 50 mm Dionex IonPac SCG 1 column and 4 × 250 mm Dionex 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 Dionex ICS-1000 system, the polarity must be changed using Chromeleon CDS software.

Because the Dionex 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 Dionex 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 CDS program (*.pgm file) should be set for "0 mM" MSA and the suppressor should be set to "None".

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 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.

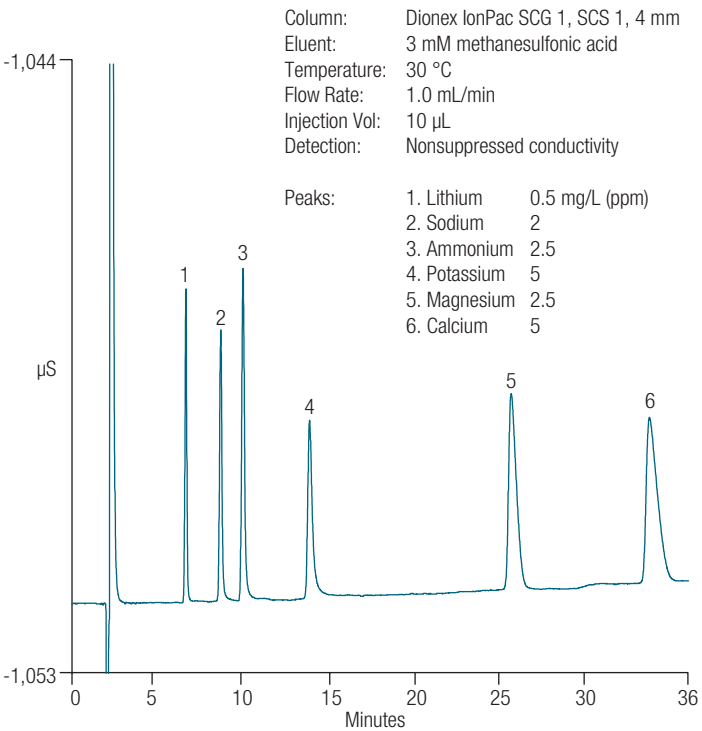

Figure 3. Separation of common inorganic cations on the Dionex IonPac SCS 1 column

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.[1] 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 H_2O. Noise is proportional to the background signal and therefore elimination of the background electrolyte lowers the noise and improves analyte sensitivity.

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:

$$G = C_E(\lambda_H + \lambda_X) \qquad (1)$$

where G is the conductance ($S \cdot cm^2/equiv$), C_E is the concentration of the eluent, and λ_H and λ_X are the limiting equivalent conductances of H_3O^+ and X^-, respectively. The equivalent conductances ($S \cdot cm^2/equiv$) for common ions of interest in the context of this application note are[15]: Li^+, 38.7; Na^+, 50.1; Mg^{2+}, 53.1, Ca^{2+}, 59.5; NH_4^+, 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):

$$\Delta G = C_{Na}(\lambda_{Na} - \lambda_H) \qquad (2)$$

where ΔG is the change in conductance, C_{Na} is the concentration of sodium injected on the column, and λ_{Na} and λ_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:

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

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, repectively. 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 (4)

Nonsuppressed: S/N = 300/7 = 43 (5)

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.[7,16] 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 Dionex IonPac CS16 and Dionex IonPac SCS 1 columns were used to demonstrate the capabilities of suppressed and nonsuppressed conductivity detection, respectively. The Dionex IonPac CS16 column 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 Dionex IonPac SCS 1 column 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 Dionex IonPac SCS 1 column (318 µeq/column) needs to be considerably less than that of the Dionex IonPac CS16 column. The Dionex IonPac SCS 1 column 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 Dionex IonPac CS16 and Dionex IonPac SCS 1 columns, respectively. The higher-capacity Dionex IonPac CS16 column required nearly ten times the eluent strength of the Dionex IonPac SCS 1 column to achieve the separation in less than 30 min. The higher eluent strength required by the Dionex IonPac CS16 column, 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 Dionex IonPac CS16 column allows temperatures up to 60 °C to be used. *Temperatures above 35 °C may result in irreversible damage to the silica-based Dionex IonPac SCS 1 resin and therefore should not be used.*

Retention time and background signal may also vary slightly between eluent preparations for the nonsuppressed Dionex IonPac SCS 1 column. In contrast, the suppressed system can generate very reproducible retention time and peak area data by electrolytically generating the MSA online. 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 Dionex IonPac CS16 and Dionex IonPac SCS 1 columns, respectively. The higher capacity of the Dionex IonPac 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.[6] A quadratic curve fitting function extends the calibration curve for ammonium to 40 mg/L. For the nonsuppressed Dionex IonPac 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.

High concentrations of sodium and other cations will overload the Dionex IonPac SCS 1 column due to its significantly lower capacity compared to the Dionex IonPac CS16 column. 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 Dionex IonPac 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 Dionex IonPac CS16 column with suppressed conductivity detection. Due to the significantly higher capacity of the Dionex IonPac CS16 column, the sample does not cause column overloading. Figure 4C shows the same standard diluted by a factor of two analyzed with the Dionex IonPac SCS 1 column. Although, the lower concentration has removed the splitting of the lithium peak, tailing is still observed for the

Table 3. Linearity and MDLs using suppressed conductivity detection[a]

Analyte	Range (mg/L)	Linearity (r^2)	Calculated MDL[b] (µg/L)	MDL Standard (µg/L)
Lithium	0.05–80	0.9999	0.19	1
Sodium	0.1–1000	0.9999	1.81	4
Ammonium[c]	0.05–40	0.9993	1.23	5
Potassium	0.05–80	0.9999	2.64	10
Magnesium	0.05–80	0.9999	1.00	5
Calcium	0.05–80	0.9998	1.09	5

[a] Dionex ICS-2500 IC system with a 10 µL injection
[b] Dionex IonPac CS16 column can tolerate a higher upper concentration than shown
[c] Quadratic fit
[d] MDL = $\sigma t_{S,99}$ where $t_{S,99}$ = 3.14 for n = 7

Table 4. Linearity and MDLs using nonsuppressed conductivity detection[a]

Analyte	Range (mg/L)	Linearity (r^2)	Calculated MDL[b] (µg/L)	MDL Standard (µg/L)
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

[a] Dionex ICS-2000 IC system with a 10 µL injection
[d] MDL = $\sigma t_{S,99}$ where $t_{S,99}$ = 3.14 for n = 7

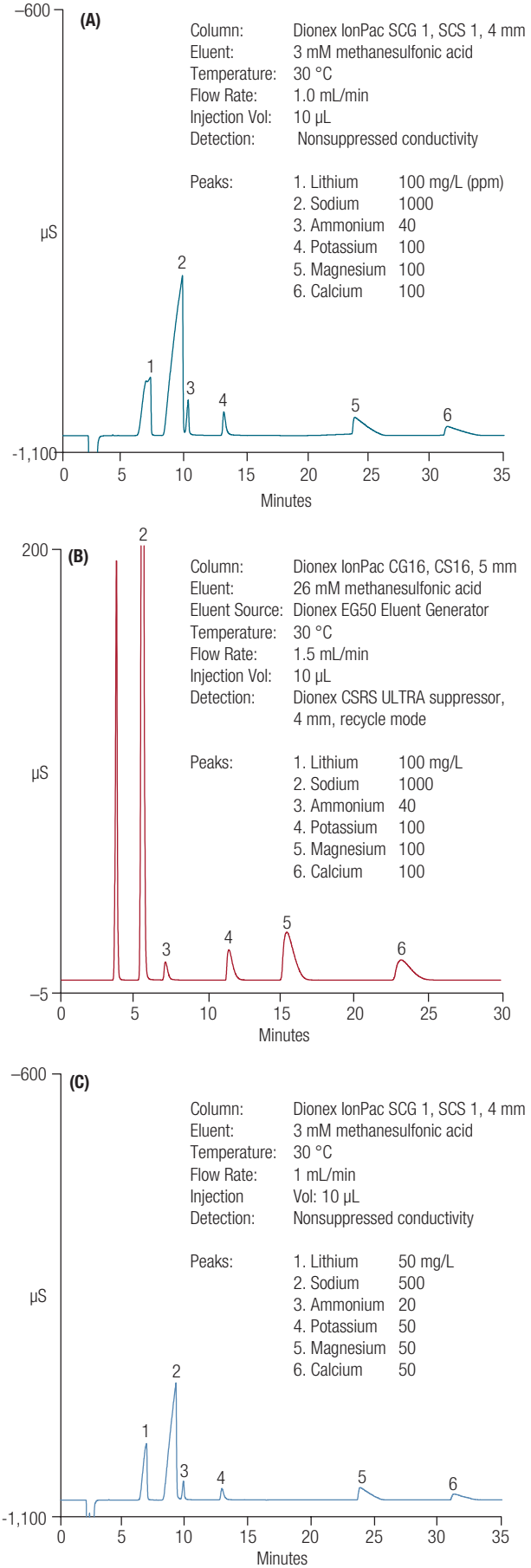

Figure 4 A–C. Separation of inorganic cations in a high-ionic strength matrix

divalent cation peaks. Therefore, analysis of high-ionic-strength matrices on the Dionex IonPac 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 Dionex IonPac CS16 column, will tolerate larger injection 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. Dionex IonPac CS16 column format, such as a 4 × 250 mm 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 Dionex IonPac CS16 column is ideal for 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 Dionex IonPac CS16 column is capable of tolerating ratios of up to 10,000:1. The Dionex IonPac SCS 1 column 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).

Column:	Dionex IonPac CG16, CS16, 5 mm
Eluent:	26 mM methanesulfonic acid
Eluent Source:	Dionex EG50 Eluent Generator
Temperature:	30 °C
Flow Rate:	1.5 mL/min
Injection Vol:	10 µL
Detection:	Suppressed conductivity Dionex CSRS ULTRA suppressor AutoSuppression recycle mode
Sample Prep:	Filter

Peaks:	1. Lithium	<0.2 mg/L
	2. Sodium	200
	3. Ammonium	0.03
	4. Potassium	0.5
	5. Magnesium	8.0
	6. Calcium	20

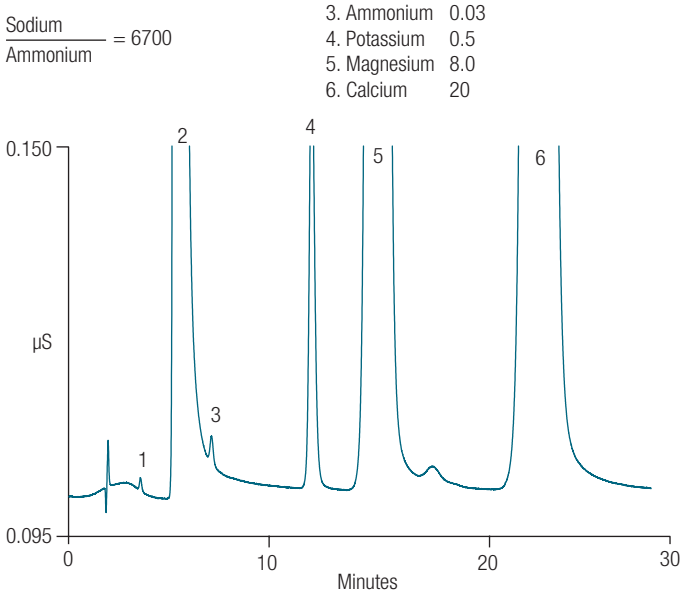

Figure 5. Resolution of trace ammonium from high sodium with the Dionex IonPac CS16 column

Column:	Dionex IonPac SCG 1, SCS 1, 4 mm
Eluent:	3 mM methanesulfonic acid
Temperature:	30 °C
Flow Rate:	1.0 mL/min
Injection Vol:	25 µL
Detection:	Nonsuppressed conductivity

Peaks:	1. Sodium	100 mg/L (ppm)
	2. Ammonium	0.1

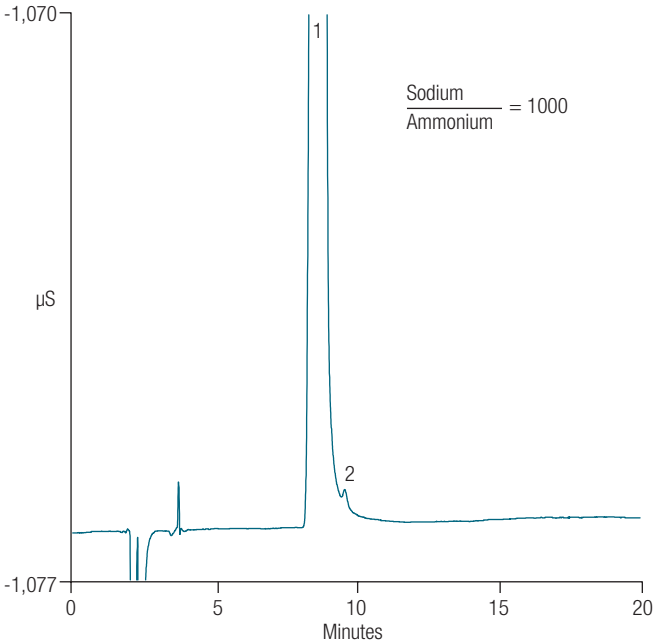

Figure 6. Determination of low concentrations of ammonium in high concentrations of sodium on the Dionex IonPac SCS 1 column

The high capacity of the Dionex IonPac 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 Dionex IonPac SCS 1 column prevents the analysis of these types of samples without sample preparation to remove the excess hydronium ions. *Therefore, samples with a pH less than 2 (10 mM hydronium ion) should not be injected on the Dionex IonPac 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 Dionex IonPac SCS 1 column. Therefore, the optimum eluent for the Dionex IonPac SCS 1 column is 3 mM MSA, as specified under the method conditions in this application note.

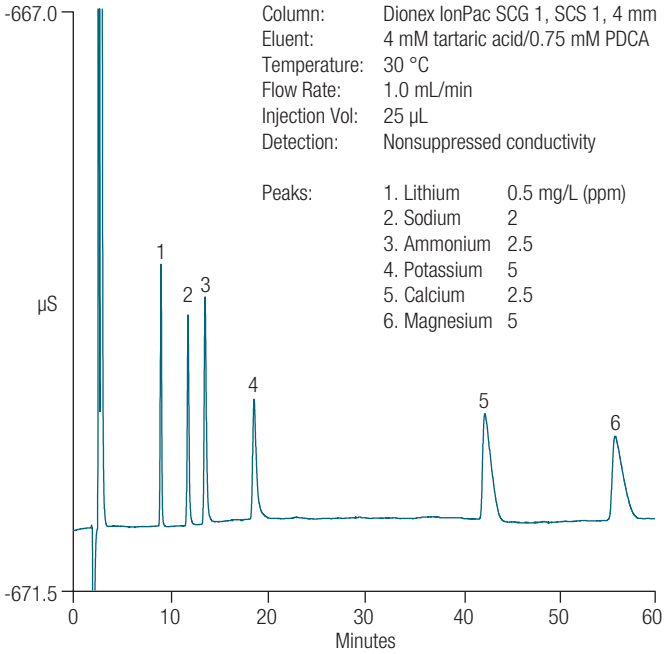

Figure 7. Separation of common inorganic cations using a weak acid eluent on the Dionex IonPac SCS 1 column

Conclusion

This application note demonstrates the capabilities of suppressed conductivity detection using the high-capacity Dionex IonPac CS16 column and nonsuppressed conductivity detection using a lower-capacity Dionex IonPac 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.

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