

Technical Report

Using the ICDS™-Ci High-Performance Suppressor for Highly Sensitive Cation Analysis

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Abstract:

In ion chromatography, the suppressor method is widely used for highly sensitive ion analysis. The suppressor works by replacing ions present in the eluent, which reduces the baseline signal at detection and suppresses noise at the detector, thereby enabling the detection and quantitative analysis of ions at trace levels. The ICDS-Ci electrodialytic suppressor for cation analysis adopts a folded membrane dialysis design, reducing internal volume and suppressing peak dispersion. It features a continuously regenerating design that requires no regenerant, allowing measurements over extended periods with a stable baseline. This article describes the principles of suppression, the features of the ICDS-Ci, and an evaluation of cation analysis using the ICDS-Ci suppressor.

Keywords: Ion chromatograph, cation analysis, ICDS-Ci, Nexera™ IC, suppressor method, electrodiolysis, membrane dialysis-type suppressor

1. Introduction to the Suppressor Method

Ion chromatography is an analytical technique that combines separation in ion-exchange mode with conductivity detection to analyze ions in a sample. In this method, ions present in the eluent are continuously detected by conductivity as a constant baseline signal, and noise in this baseline can obstruct detection of the target ions. Therefore, a suppressor is used to reduce baseline noise. The suppressor is a device that replaces ions in the eluate after column separation and thereby reduces the background conductivity derived from the eluent. This lowers the baseline signal, suppresses noise, and allows target ions to be detected with high sensitivity.

2. Fundamentals of a Cation Suppressor

This section explains the fundamentals of a cation suppressor using an example of cation analysis with an aqueous methanesulfonic acid eluent. A flow diagram of the suppressor method is shown in Figure 1. Located just before the conductivity detector, the suppressor method exchanges methanesulfonate ions in the eluent for hydroxide ions, thereby converting methanesulfonic acid to water (H₂O). Water has a low degree of ionization, giving it a low level of conductivity and substantially reducing the amount of baseline noise (Figure 2).

With an ion chromatograph, the peak intensity is the difference between the baseline conductivity of the eluent and the conductivity of the target peak. In cation analysis, this difference in conductivity is larger when there is no cation suppressor, so peak intensity is reduced when a suppressor is used. However, baseline noise is reduced to an even greater extent, resulting in an improved S/N ratio.

One note of caution regarding suppressor use is that the dissociation state of ions can vary depending on concentration, causing the calibration curve to become nonlinear (Figure 3). After passing through the suppressor, the concentration of methanesulfonic acid decreases, and the solution becomes more susceptible to pH changes. As a result, the pH varies depending on the concentration of the eluted ions, and the dissociated state of the ions changes accordingly. In particular, ammonia is a weak base and

is in an equilibrium state in the eluent, so its degree of dissociation changes depending on concentration. For the equilibrium $\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$, the peak intensity of ammonia is known to vary non-proportionally with concentration, resulting in a non-linear calibration curve. Therefore, a linear approximation is not suitable, and a calibration curve approximated by a quadratic function is recommended.

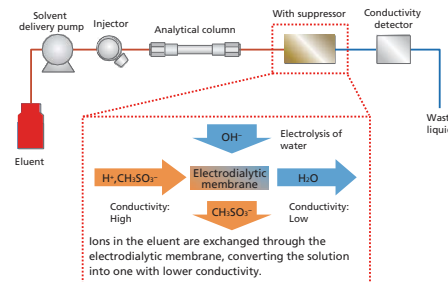
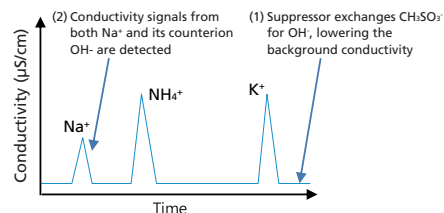


Figure 1: Analysis Flow Path in the Suppressor Method



- (1) In the suppressor method, methanesulfonate ions are exchanged for OH⁻. The low degree of dissociation of H₂O results in low conductivity.
- (2) The counterion to the target ion is also exchanged for OH⁻. At the peak elution position, the sum of the conductivity of the target ion and its counterion is detected.

Figure 2: Example Chromatogram in the Suppressor Method

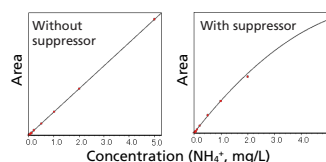


Figure 3: Example Calibration Curves with and without a Suppressor

3. Fundamentals of Analysis without a Suppressor

This section also explains the fundamentals of cation analysis without a suppressor (Figures 4 and 5). Without a suppressor, the ions in the eluent pass unimpeded into the detector, so analysis is performed with a high baseline signal. This high baseline increases the amount of noise during analysis, hiding small ion peaks and making it difficult to detect trace ion components.

During cation analysis without a suppressor, hydrogen ions in the eluent have a higher conductivity than target ions (Table 1), creating a relative reduction in conductivity upon target ion elution that is detected as a negative peak (Figure 5). Therefore, in actual analysis, the signal is inverted so that the negative peaks can be detected as positive peaks. Compared with the suppressor method, analysis without a suppressor gives a greater difference between the conductivity of the eluent and the eluted target peak, resulting in a higher peak intensity. However, not using a suppressor also results in more baseline noise and a lower S/N ratio.

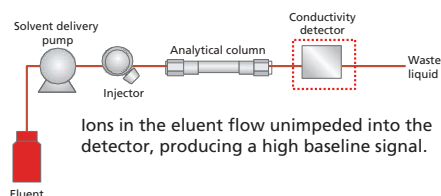
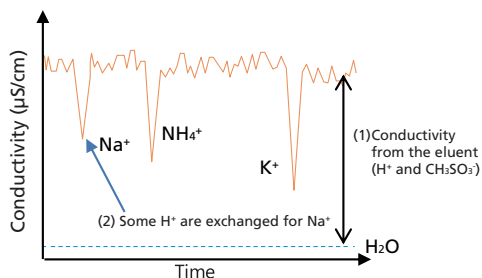


Figure 4: Analysis Flow Path without a Suppressor



- (1) Without a suppressor, methanesulfonate ions and hydrogen ions in the eluent are continuously introduced into the detector, so the conductivity derived from these ions is observed as the baseline.
- (2) When a target ion passes through the detector, some of the hydrogen ions are replaced by the target ions, lowering the conductivity. This reduction in conductivity is detected as a negative peak.

Figure 5: Example Chromatogram without a Suppressor

Table 1: Limiting Molar Conductivity of Example Ions

Ion	Limiting Molar Conductivity in Water ($S\ cm^2\ mol^{-1}$)
H^+	349.7
Na^+	50.1
NH_4^+	73.5
K^+	73.5

4. Comparing Analysis with and without a Suppressor

The suppressor method ensures that baseline noise is low, creating the best conditions for highly sensitive analysis. However, the pH may vary depending on the concentration of the target ions, changing their dissociation state accordingly. In such cases, a calibration curve cannot be approximated by a linear equation and is instead fitted with a quadratic equation.

Without a suppressor, while background noise is high, the dissociated state of target ions is less likely to change based on concentration, and the calibration curve can be approximated with a linear equation.

Sensitivity, accuracy, and other factors must be taken into account when deciding whether to use a suppressor.

5. Key Features of the ICDS-Ci Suppressor

The ICDS-Ci cation suppressor utilizes a membrane dialysis type and features an internal layout designed especially for improved ion removal efficiency.

5.1 What is a Membrane Dialysis-Type Suppressor?

A membrane dialysis-type suppressor passes eluent through one side of two flow paths separated by an ion exchange membrane while regenerant is passed along the other channel, and ions in the eluent pass into the regenerant by either chemical or electro dialysis for subsequent removal.

A membrane dialysis-type suppressor removes ions and performs regeneration continuously and simultaneously, offering stable baselines over extended periods of analysis.

5.2. ICDS-Ci Features and Suppressor Operation

The ICDS-Ci cation suppressor is designed to reduce noise by efficiently removing anions from the eluent, and employs electro dialysis with an internal eluent flow path arranged in a folded configuration (patented). This design allows the ICDS-Ci to perform highly efficient dialysis despite a low internal volume, resulting in stable electro dialysis and low noise, and improving the quantitative accuracy of trace component analysis. (Figure 6)

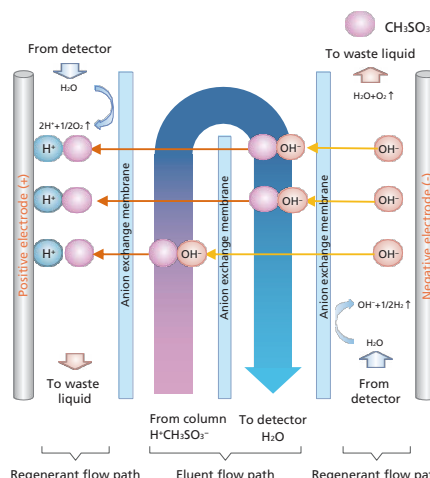


Figure 6: ICDS-Ci Structure and Suppressor Operation

When a direct current is applied across the electrodes, water undergoes electrolysis, generating hydrogen ions at the positive electrode and hydroxide ions at the negative electrode, and ion removal from the solution is achieved by controlling the movement of these ions with an ion exchange membrane. This process is explained in detail below.

- (1) Hydroxide ions, generated at the negative electrode by electrolysis and driven by the applied voltage, move toward the positive electrode together with methanesulfonate ions from the eluent.
- (2) Hydroxide ions pass through the anion-exchange membrane, which permits only anions to pass, and permeate into the eluent flow path. As a result, anions in the eluent are discharged through the anion-exchange membrane toward the anode by electro dialysis. The ICDS-Ci suppressor uses a folded flow path layout that allows dialysis to take place twice along the same eluent flow path.
- (3) The anions discharged toward the anode combine with hydrogen ions generated by electrolysis at the anode to form water or salt, which is then discharged from the suppressor.

Notably, the ICDS-Ci suppressor reuses the liquid that exits the detector as regenerant.

6. Example Analysis with a Suppressor

This section describes an example analysis performed using a cation suppressor.

6.1 Analysis Conditions

The cation analysis was performed using the Nexera IC ion chromatograph (Figure 7). A cation suppressor is optionally available and can be installed inside the main unit of the Nexera IC ion chromatograph.



Figure 7: Nexera IC Cation Analysis System

Table 2: Analysis Conditions

Cation

Column : Shim-pack™ IC-C4 (150 mm × 4.6 mm I.D., 7 μm)^{*1}
 Guard Column: Shim-pack IC-GC4 (10 mm × 4.6 mm I.D., 7 μm)^{*2}
 Mobile phase : 2.5 mmol/L Methanesulfonic acid
 Flow rate : 1.0 mL/min
 Injection vol. : 50 μL
 Column temp.: 40 °C
 Detection : Conductivity

^{*1} P/N : 228-41616-91 ^{*2} P/N : 228-59900-91

6.2. Precautions for Sample and Eluent Preparation

When performing quantitative analysis on the order of 10 μg/L, care must be taken because the ion concentration in the sample is low and the sample is highly susceptible to contamination. Many causes of contamination must be considered, including contamination from the surroundings, and contamination from the apparatus and containers used to prepare and hold the sample and eluent.

To prevent this contamination, apparatus and containers must be cleaned thoroughly, and the environment must be properly managed.

6.3 Highly Sensitive Quantitative Analysis Using ICDS-Ci

Calibration curves were prepared in the range of 10 to 200 μg/L (Figure 8). All calibration curves resulted in a coefficient of determination (R^2) of at least 0.999 in the measured range. As shown, using the ICDS-Ci suppressor allows for highly sensitive analysis of trace ions at concentrations on the order of 10 μg/L.

Table 3: Calibration Curve Range and R^2 for Target Ions

Ion	Calibration Curve Range	Coefficient of Determination (R^2)
Na ⁺	10-200 μg/L	0.999 or more
NH ₄ ⁺ *	10-200 μg/L	0.999 or more
K ⁺	10-200 μg/L	0.999 or more
Mg ²⁺	10-200 μg/L	0.999 or more
Ca ²⁺	10-200 μg/L	0.999 or more

* Because the dissociation state of NH₄⁺ varies depending on concentration, a calibration curve was prepared using a quadratic curve to correct for this behavior.

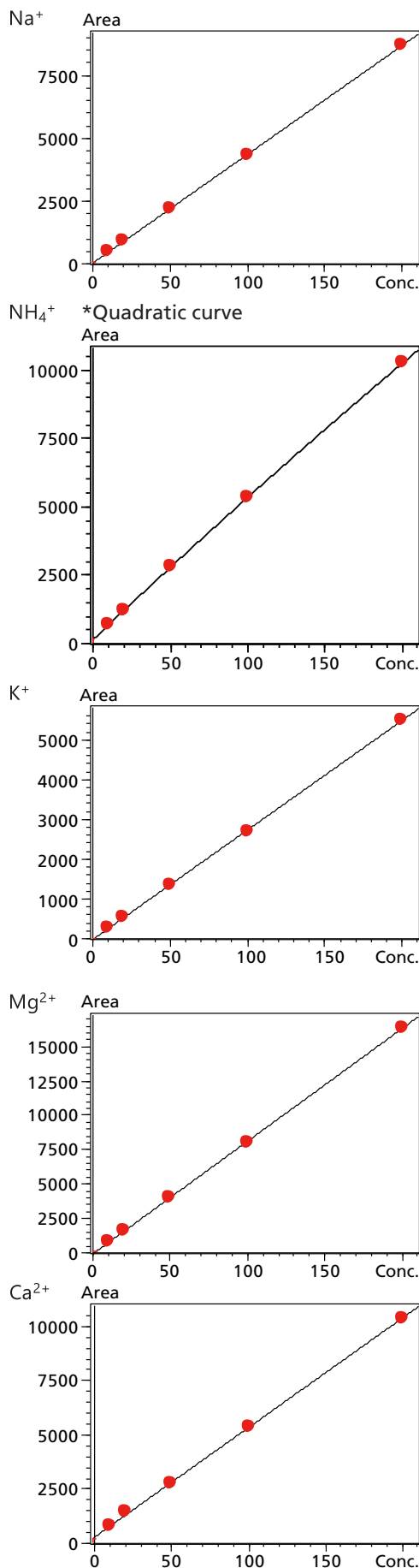


Figure 8: Calibration Curves in the Range of 10-200 μg/L

6.4 Peak Area Reproducibility

The peak area reproducibility for each target ion at 100 µg/L is shown in Table 4, and corresponding chromatograms are shown in Figure 9. The peak area reproducibility with a suppressor is superior compared to without a suppressor. This improvement in reproducibility is believed to be due to the reduction in baseline noise and the reduction in peak area and peak height variability achieved by using the cation suppressor (Figure 10).

Table 4: Peak Area Reproducibility of Target Ions (%RSD)

	Peak Area %RSD at 100 µg/L (n = 6)				
	Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺
With suppressor	0.023	0.128	0.056	0.239	0.268
Without suppressor	0.459	0.447	0.782	1.770	4.315

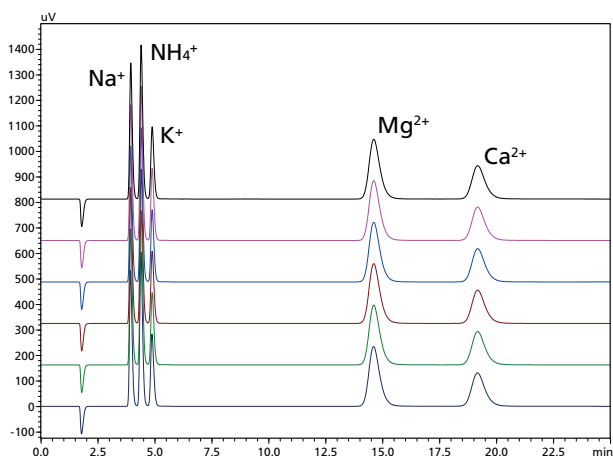
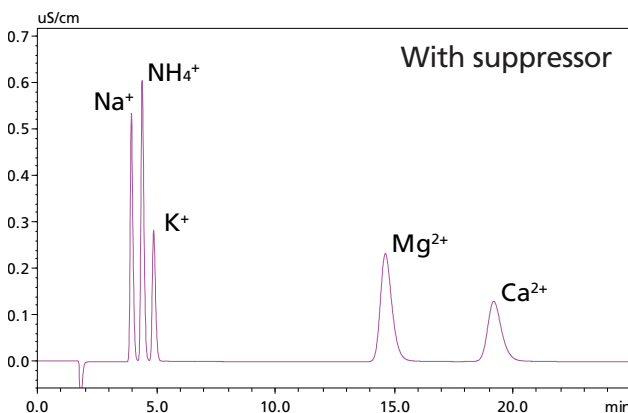


Figure 9: Chromatograms of 100 µg/L Five-Component Cation Standard with a Suppressor



7. Conclusions

- A cation suppressor suppresses the baseline signal during detection by replacing ions present in the eluent. This reduces background noise and enables trace analysis.
- The ICDS-Ci cation suppressor, an optional unit for the Nexera IC system, adopts an electrochemical design with an internal eluent flow path arranged in a folded layout. These features provide high dialysis efficiency despite the low internal volume, enable stable electrochemical dialysis, and reduce noise.
- Evaluation using the Nexera IC confirmed that highly sensitive quantitative analysis on the order of 10 µg/L is possible. It also demonstrated excellent quantitative performance and good reproducibility even in the low-concentration range.

References

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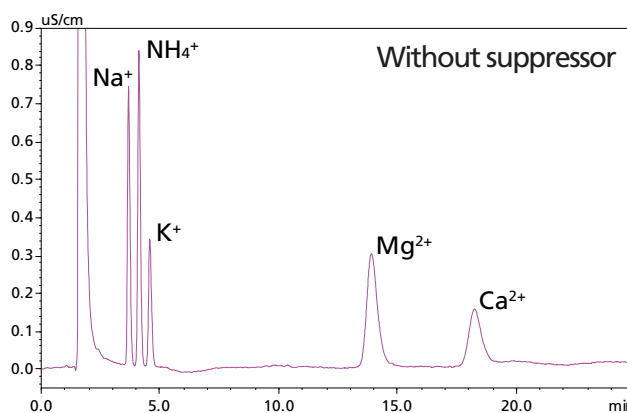


Figure 10: Chromatograms of 100 µg/L Five-Component Cation Standard with and without a Suppressor

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