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Conductivity Detection in Cation Chromatography—Advantages and Disadvantages of Suppression

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Executive Summary

The need for suppression in cation-exchange chromatography has been discussed for the last 20 years. Some believe that nonsuppressed conductivity detection for cation analysis is more sensitive than suppressed conductivity detection. Here we examine this subject in a nonbiased, scientific manner.

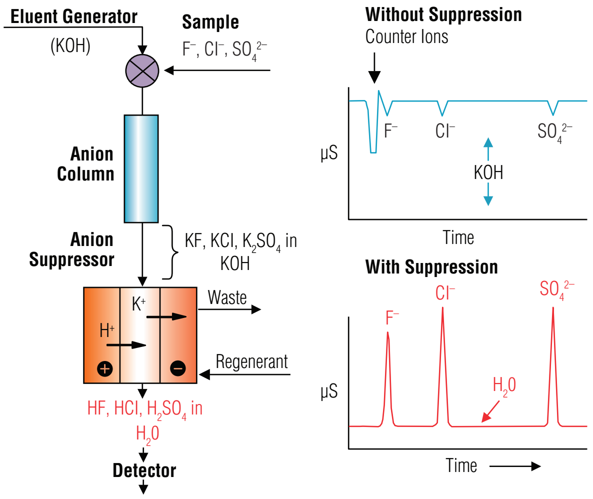

Figure 1. Diagram of eluent suppression for anion chromatography.

Key Words

Ion Chromatography (IC), Dionex CERS 500 Cation Electrolytically Regenerated Suppressor, Dionex AMMS Anion MicroMembrane Suppressor, Salt-Converter Mode, Dionex IonPac SCS 1 Silica Cation Separator Column, Nonsuppressed Conductivity

Introduction

Conductivity detection is separated into two applications: suppressed and nonsuppressed. For the latter, indirect conductivity detection is a term also used in scientific literature, because background conductance resulting from the eluent electrolyte is very high (typically between 600 and 800 μS/cm). Historically we also find the term single column ion chromatography (IC), because a nonsuppressed IC system requires only a separator column without the suppression device.

Detection methods can be categorized as direct and indirect. Conductivity detection, part of the direct detection category, is a bulk-property detection method—it only measures conductivity irrelevant of the source, which could be eluent or analyte, anion or cation. Thus, conductivity detection in IC is analogous to refractive index (RI) detection in classical high-performance liquid chromatography (HPLC). By combining it with a suppressor system, we convert the conductivity detector into an analyte-specific one.

Indirect detection methods should be avoided whenever possible because they are characterized by a limited working range, low sensitivity and specificity, and a strong dependence on temperature. In an analogy with HPLC, no one would consider using a RI detector for detecting phenol. We need to apply the same reasoning to IC. Today, indirect detection methods are only employed if there is no alternative, or if different compound classes are to be analyzed in the same run without regard for sensitivity, for example, analysis of wine for sugars, alcohols, and major organic acids.

General Requirements for a Liquid Chromatography Detection System

- High sensitivity and specificity
- Low sensitivity for the mobile phase and nonanalyte sample components
- Robustness
- High reproducibility

Indirect (Nonsuppressed) Conductivity Detection

In 1979, Prof. Jim Fritz, Iowa State University, Ames, IA, USA, introduced the concept of indirect (nonsuppressed) conductivity detection. He used salts of organic acids, such as potassium dihydrogenphthalate, as an eluent for separating anions because the resulting background conductance was lower than that of inorganic salts. For many years, analytical chemists discussed the occurrence of positive and negative system peaks in the chromatogram interfering with analyte peaks. Even then it was difficult to understand why this method was proposed, because system peaks do not occur when using a suppressor system.

Fritz also used organic acids, such as dipicolinic (pyridine-2,6-dicarboxylic) acid, for indirect conductivity detection of cations, and the resulting problems are similar. In this case the system peak is the peak for all anions, which appears in the column void volume. Depending on size, it can interfere with early eluting analyte cations. Even with organic acid eluents, background conductance is approximately 600 µS/cm, so that low-conducting analyte cations appear as negative signals in the chromatogram. When reversing the polarity of the detector, the resulting chromatograms can be acquired with a conventional chromatography data system. Depending on the anion concentration, the system peak in the void volume is either positive or negative.

The low cation-exchange capacity of the separator to be used, a prerequisite to working with low-eluent concentrations needed to limit the background conductance, is a huge disadvantage. As a result, column overloading effects are often observed in this form of cation analysis, even at relatively low analyte concentrations.

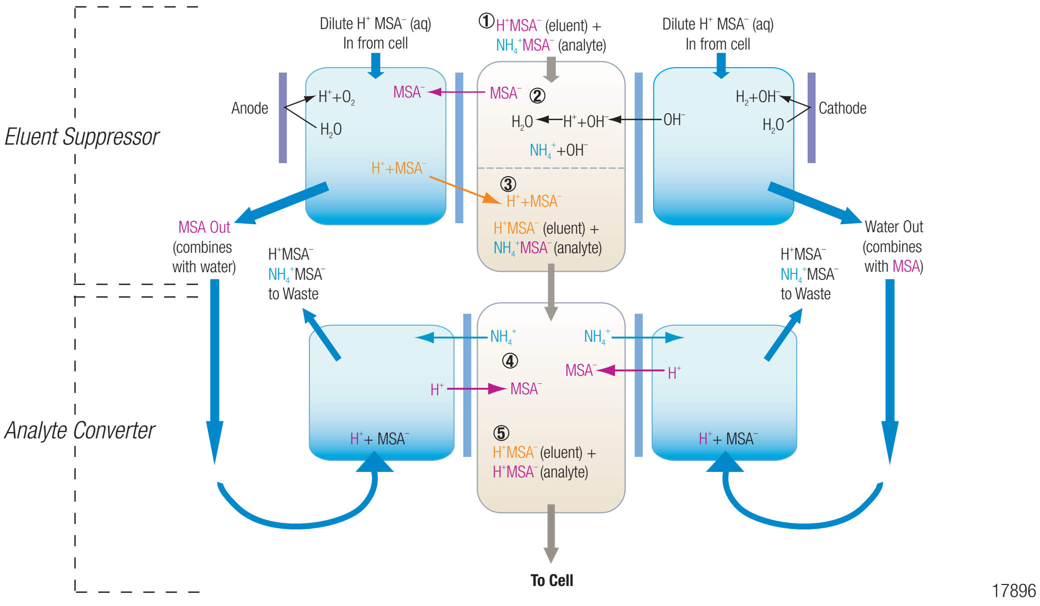

Figure 2. Thermo Scientific™ Dionex™ SC-CSRS™ 300 Salt Converter Cation Self-Regenerating Suppressor operational schematic.

Necessity of Suppressor Systems

Today, analytical chemists worldwide agree that suppressor systems are necessary for sensitive and specific anion-exchange chromatography; however, the discussion continues as to whether suppressor systems for cation analysis are necessary. Unfortunately, this discussion often has been emotional rather than scientific, with marketing aspects emphasized.

The most common arguments against suppressed conductivity detection for cation analysis include the nonlinear calibration behavior for weakly dissociated amines and cations, such as ammonium, which is scientifically accurate. Even though this problem can be solved by employing a quadratic calibration curve, suppressed conductivity for amines and ammonium is less sensitive due to the equilibrium between ammonia and the dissociated ammonium as the suppression product. Moreover, analytical chemists prefer linear calibration behavior, which requires fewer calibration levels.

Undoubtedly, suppressors and their operation are not free, especially when using chemical suppression with tetrabutylammonium hydroxide (TBAOH) as the regenerant. Of course, there are those who claim that nonsuppressed conductivity detection is more sensitive than suppressed conductivity, which only proves that the difference between response factor and sensitivity is not always understood. Lastly, there are those who claim that nonsuppressed conductivity detection enables the simultaneous analysis of transition metals and alkali-/alkaline-earth metals, which might only be feasible in special cases.

The problem of nonlinear calibration behavior for weakly dissociated cations can be solved in a very elegant way by combining a Thermo Scientific™ Dionex™ CERS™ 500 Cation Electrolytically Regenerated Suppressor with a Thermo Scientific™ Dionex™ AMMS™ Anion MicroMembrane™ Suppressor (salt-converter mode). In this form of suppression, all cations are first converted into mesylates, while in the second suppressor all cations are replaced by hydronium ions to form MSA. Because MSA is a strong organic acid and thus completely dissociated, we not only observe higher sensitivity for all cations but also linear calibration curves.

Nonsuppressed Conductivity Detection Put to the Test

Many are unaware that Hamish Small, the inventor of modern IC, involved himself in the discussion about suppression in cation analysis. In his book, *Ion Chromatography*, published in 1989, he uses a computer simulation to compare the relative sensitivity of both applications of conductivity detection for the separation of sodium and potassium. For a nonbiased comparison, he kept parameters such as the stationary phase volume, capacity of the separator column, injection volume, and selectivity coefficients for Na^+ and K^+ constant. The result of this computer simulation clearly proved that the response factors for cations are higher in nonsuppressed conductivity detection, but sensitivity is lower due to the significantly higher noise level caused by the high background conductance.

A suppressor system for cation analysis is not always required. Analyte determinations at high concentrations can also be performed with nonsuppressed conductivity detection to avoid large dilutions or very small injection volumes. Stakeholders of nonsuppressed conductivity detection often tout the advantages of polymer-coated silica columns for the isocratic separation of of mono- and divalent cations together with hydrophilic amines, such as alkanolamines. For example, mono-, di-, and triethanolamine are used individually or in combination in a number of chemical processes, including the conditioning of feed water in the power-generating industry. Not all IC users know that Thermo Fisher Scientific™ also offers such a stationary phase column, the Thermo Scientific™ Dionex™ IonPac™ SCS 1 Silica Cation Separator column.

Polymer-Coated Silica Column Solution

Because all polymer-coated silica columns exhibit a poor uniformity of the polymer coating, resulting in insufficient lot-to-lot reproducibility, the Dionex IonPac SCS 1 column is not extensively promoted. However, with 3 mM MSA as the eluent, this analysis can be performed on the Dionex IonPac SCS 1 column. Based on a column length of 250 mm, the relatively long analysis time of more than 30 min (compared to generally under 10 min for a suppressed system) is a general disadvantage in this method.

Like other polymer-coated silica columns, the Dionex IonPac SCS 1 column has a very low cation-exchange capacity to utilize low eluent concentrations while keeping the background conductivity below 1 mS/cm. Instead of MSA, organic dicarboxylic acids with their complex properties can also be used as eluent if different selectivities are required. When performing this analysis on the Dionex IonPac CS19 column with suppressed conductivity detection under isocratic conditions, analysis time can be cut in half! Therefore, even low analyte concentrations can be detected due to excellent baseline stability.

Another disadvantage of polymer-coated silica columns based on poly(butadiene/maleic acid) is the relatively poor compatibility with acidified samples. With an acid content in the sample of only 20 mM, most of the carboxyl groups on the stationary phase surface are protonated, which makes the separation of divalent cations almost impossible. Polymeric cation exchangers tolerate approximately five times more acid in the sample because the carboxyl groups in the monomer used for the functionalization have a lower pK value.

Analyzing Several Classes of Cationic Compounds Using Nonsuppressed Conductivity

In principle, the ability to simultaneously analyze alkali- and alkaline-earth metals, ammonium, amines, and transition metals with nonsuppressed conductivity detection is possible using the Dionex IonPac SCS 1 column for analysis, although again with a long analysis time. Even though zinc, cobalt, and manganese can be separated from other inorganic cations under the respective chromatographic conditions, it is still an exception as other transition metals, if present, interfere with the determination of standard cations.

Detractors will state that transition metals precipitate in the suppressor system. This is inaccurate, because only very small amounts of analytes are injected onto the column, so the solubility product is not exceeded. Yes, in the suppressor system transition metals convert to their respective hydroxides which, with very few exceptions, are not dissociated and thus not detected.

As previously discussed, the use of suppressor systems is mandatory for employing high-capacity columns or gradient elution techniques. Low cation-exchange capacity of separator columns required for nonsuppressed conductivity detection leads to column overloading with analyte concentrations in the mg/L range. To avoid column overloading effects and to deal with large concentration ratios between cations, especially between sodium and ammonium, a high-capacity cation exchanger is required which, in turn, requires a higher eluent concentration. Using the Dionex IonPac CS16 column as an example, the eluent concentration under standard conditions is 30 mM MSA. This eluent concentration is not compatible with nonsuppressed conductivity detection; background conductivity would be in the upper mS/cm range. When employing a concentration gradient in combination with conductivity detection, we have a very similar situation. Although the standard application in cation analysis—the separation of alkali- and alkaline-earth metals—does not require a gradient elution technique, isocratic approaches are not suitable for strongly retained cations, screening analyses, or for complex samples containing various amines. Therefore, with only a nonsuppressed cation system, the applications are limited.

An excellent example for a useful application of a gradient elution technique in cation analysis is the separation of biogenic amines together with standard inorganic cations. Biogenic amines are much more strongly retained than alkaline-earth metals, which would lead to long analysis times and severe band broadening under isocratic conditions. When employing a concentration gradient, late-eluting peaks will be focused and thus detected almost as sensitively as early eluting ones. Today, modern cation exchangers (Dionex IonPac CS17, CS18 and CS19 columns) allow such separations to be carried out with purely aqueous mobile phases that can be produced by a Reagent-Free™ IC (RFIC™) system.

Conclusion

Cation suppressors are not mandatory for all applications, although the large number of advantages definitely justifies the investment. The real problem with cation suppression in the past, namely the lower sensitivity and nonlinear calibration behavior for weakly dissociated cations, has long been solved. Hopefully, this information helps differentiate between fact and fiction regarding suppression in cation chromatography, dispelling often emotional, rather than fact-based arguments.

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