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A new suppressor design for low noise performance with carbonate eluents for Ion Chromatography

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ABSTRACT

Carbonate and bicarbonate based eluents have been applied for ion analysis from the inception of ion chromatography. The product of suppression with carbonate and/or bicarbonate eluent is carbonic acid which is weakly dissociated and tends to outgas. While the act of suppression enhanced the signal for fully dissociated ions and lowered the background to a weakly dissociated level, the overall noise performance, however, varied depending on the suppression mechanism. Chemical suppression with a membrane suppressor yielded low noise performance with carbonate and/or bicarbonate eluents. Electrolytic suppression, on the other hand, resulted in a relatively higher noise with carbonate based eluents when compared to chemical suppression. In this work, we investigated the root cause of noise with electrolytic suppressors and carbonate based eluents. Further, a new electrolytic suppressor design based on a three-electrode design is discussed in this paper and provided low noise performance with carbonate and/or bicarbonate eluents.

1. Introduction

Ion Chromatography (IC) with conductivity detection is the preferred method for analyzing ions [1–4]. In Ion Chromatography, an ion exchange based retention and elution of the analyte is pursued with eluents such as sodium hydroxide or sodium carbonate that contribute significantly to the background conductivity. A suppressor device is used to suppress the eluent to a weakly dissociated form prior to detection of analytes of interest using a conductivity detector. The suppressor exchanges the counterions to the eluent with hydronium or hydroxide ions and converts the eluent to a weakly ionized form. For example, when pursuing anion analysis with sodium carbonate eluent, the sodium ions which are the counterions to the carbonate eluent ion is exchanged with hydronium ions thus converting the conductive sodium carbonate eluent to a weakly dissociated carbonic acid form. The suppressor supplies the hydronium ion in the above example.

When pursuing anion analysis, the suppressor contained cation exchange functionalities to suppress the eluent counterions and sample counterions which are cations. Similarly, when pursuing cation analysis, the suppressor contained anion exchange functionalities to suppress the eluent counterions and sample counterions which are anions. Also, note that the analytes are not retained by the ion exchange functionalities thereby allowing good quantitation of the analytes.

Before the advent of Reagent-Free Ion Chromatography (RFIC^{TM}) technology with automated eluent preparation, one of the common eluents for suppressed ion chromatography was carbonate based, since the carbonate eluent could be prepared easily in the laboratory with relatively inexpensive high purity salts and with less interference from the ambient environment. The carbonate-based eluents are converted to carbonic acid in the suppressor. Carbonic acid is a weakly dissociated species with a pKa1 of 6.35 and pKa2 of 10.32. The residual conductivity of carbonic acid ranged between 10 µS/cm and 30 µS/cm and the background value after suppression was dependent on the concentration of the carbonate and bicarbonate ions present in the eluent.

The original suppressors were ion exchange resin based packed bed suppressors where the conversion of the eluent to a weakly dissociated form occurred via ion exchange on the surface of the ion exchange resin. The packed bed suppressor however required an offline regeneration step to convert the ion exchange resin back to a useful regenerated form [1]. This regeneration step was accomplished offline when the ion exchange capacity was depleted. More recently there are suppressor devices that use multiple packed beds to accomplish a pseudo-continuous mode of operation [5,6]. While one packed bed is being used for suppression, another bed is regenerated offline with appropriate regenerant. Additional rinses with deionized water to displace the regenerant and prepare the third bed for suppression was pursued offline. These operations required dispensing means for the regenerant, a switching valve and a supply of regenerant and deionized water [7]. Continuously regenerated suppressors based on ion exchange membrane and ion exchange screens were developed to facilitate

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continuous operation without any downtime. The first commercially introduced suppressor devices were chemically regenerated and allowed for continuous operation of the ion chromatograph without any downtime [8–10]. The continuously regenerated membrane based suppressor device comprised of two ion exchange membranes defining a central eluent channel and two outside regenerant channels which were fitted with ion exchange materials. The continuously regenerated devices also required a supply of regenerant and dispensing means for the regenerants. The devices, however, did not require any additional rinses and operated continuously with the supply of regenerant. A key challenge with the technique as noted in the early papers was the need to choose the regenerant concentration and type to minimize chemical leakage across the ion exchange membranes and into the eluent channel [13]. Nevertheless, the technique worked well and minimal leakage was observed as evident from the reported backgrounds of carbonate eluents in the chemical mode of operation. The background performance of the chemical suppressors was comparable to the electrolytic suppressors for carbonate based eluents when the sulfuric acid regenerant concentration was minimized to less than three times the eluent concentration and the regenerant was supplied at a flow rate that was twice the eluent flow rate [14].

Electrolytic suppressors were developed subsequently which did not require a regenerant acid for operation and operated with an external stream of deionized water [11,12]. The design was similar to the chemical suppressor and two platinum electrodes were fitted into the outside regenerant channels and were used for the water-splitting reactions. By using a voltage well above the water splitting voltage, the device split water and generated hydronium and hydroxide ions at the platinum anode and the platinum cathode respectively. A recycle mode of operation was developed that used the suppressed eluent after detection as a source of deionized water for the electrolysis reaction and provided a facile means of supplying regenerant for the electrolysis reactions. Due to the simplicity of operation, the recycle mode of operation was the preferred mode of operation with aqueous eluents [15].

When suppressing cation containing eluents for anion analysis using an electrolytic suppressor, the cation or counterion to the eluent ion is exchanged with hydronium ions present on the surface of the ion exchange membrane or screens thereby affecting suppression. Concomitantly hydronium ions generated from the electrolysis of water are electrically driven due to the applied voltage from the anode to the cathode thereby regenerating the ion exchange functionalities within the suppressor. Consequently, a continuously regenerated surface is readily available for suppression. The flow of the suppressed eluent into the regenerant channel serves two purposes, a) Continuously supplies a self-sustained source of water required for the electrolysis reactions b) Continuously removes electrolysis gases and byproducts including eluent and sample counterions to waste. The anion analytes are converted to the acid form by exchanging the analyte counterions with hydronium ions. It can be seen from the above description that if the regeneration step was incomplete the conversion of the analyte to the acid form would also be incomplete and the peak response would be lower than when suppression is complete.

It is well accepted in IC that as the background increases the noise increases and therefore a higher noise with carbonate based eluents was the norm as opposed to hydroxide based eluents which were converted to pure water by the suppressor and typically showed a background signal of < 1 µS/cm. The typical noise observed with hydroxide eluents were in the < 1 nS/cm range whereas the noise with carbonate based eluents with an electrolytic suppressor were in the 3–5 nS/cm range. The typical noise observed with carbonate based eluents with a chemical suppressor was in the < 1 nS/cm range. Thus, based on the above noise values for carbonate based eluents, the expected S/N ratio is typically 3–5× lower for the electrolytic suppressor versus the chemical suppressor since the signal for an analyte after suppression remained consistent between the two suppressor types [21,22]. Of course in some instances these differences in S/N could be offset by injecting more sample volume. Nevertheless, it is important to understand the root cause of these differences in noise performance.

To achieve low noise with carbonate based eluents it is customary to employ a carbonate removal device (CRD) [20]. The CRD is a gas permeable membrane placed between the suppressor and the detector. The carbonic acid background is carbon dioxide in equilibrium with water. The CRD removes the carbon dioxide gas from the suppressed eluent and by removing the carbon dioxide gas from the carbonic acid background, a water-like low background is feasible. The CRD, however, requires a base regenerant stream for removing the carbon dioxide efficiently as carbonate or a vacuum setup to aid the removal of the dissolved carbon dioxide. The use of a CRD results in a background signal close to 1 µS/cm and the noise is similar to that of suppressed hydroxide eluents thereby achieving consistent S/N ratios. The above results seem to support that higher background signal was the root cause of the observed high noise. It should, however, be noted that electrolytic suppressor device such as the Atlas Electrolytic Suppressor (AES) showed low noise with carbonate eluents typically in the 1–2 nS/cm range even when the suppressed background signal was high from the carbonic acid. The AES had a monolith based ion exchange material in the eluent channel [16]. Similarly a membrane-based chemical suppressor called the Micromembrane suppressor (MMS) or a Chemically regenerated suppressor (CRS) showed low noise performance in the 1 nS/cm range despite the suppressed carbonic acid background signal was higher relative to water. The suppressor had a screen based ion exchange material for the MMS and ion exchange resin-based material for the CRS in the eluent channel. These observations suggested that the physical ion exchange form in the eluent channel was not the contributing factor to the noise. The expected noise values with the various suppressor types and CRD are summarized in Table 1. In this paper, we explore the root cause of the noise with electrolytic membrane suppressors using carbonate based eluents.

2. Materials and methods

2.1. Equipment

All chromatography was performed on a Thermo Fisher Scientific

Table 1
Summary of observed noise for various suppressor types and with a CRD installed.

Suppressor setup	Eluent channel ion exchange material	Eluent type	Typical observed noise	Typical observed noise with CRD
Electrolytic - AERS 500	Resin based	Hydroxide	≤ 1 nS/cm	≤ 0.5 nS/cm
Electrolytic - AERS 500	Resin based	Carbonate and/bicarbonate	3–5 nS/cm	1–2 nS/cm
Electrolytic-ASRS 300 (Previous Generation product)	Screen based	Carbonate and/bicarbonate	3–5 nS/cm	1–2 nS/cm
Electrolytic – AMMS 300 (Previous Generation product)	Screen based	Carbonate and/bicarbonate	≤ 1 nS/cm	≤ 0.3 nS/cm
Chemical - ACRS 500	Resin based	Carbonate and/bicarbonate	≤ 1 nS/cm	≤ 0.3 nS/cm
Electrolytic – AES	Resin based	Carbonate and/bicarbonate	1–2 nS/cm	NA