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Evaluating Ion Chromatography Suppression Options

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Introduction

In the years leading up to 1971, Hamish Small and the other ion chromatography (IC) pioneers at the Dow Chemical Company abandoned ion-exchange chromatography as a practical technique. They had found that the highly concentrated solutions needed to displace some analytes of interest created such a high level of noise that it masked the analyte signal.

Fortunately, 1971 saw the invention of a “stripper” (later termed a suppressor) to convert the highly-conducting molecules in the eluent to a low-conducting form against which the analyte signal could be clearly seen.

Since that time, suppressors have evolved and several types are now commercially available, and it can be difficult to compare the many options. In this white paper, we will look at the benefits and drawbacks of each.

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Non-suppressed

All IC systems can be run without suppression simply by bypassing whatever suppression devices are present. In order to lower background noise as much as possible, non-suppressed IC should utilize very low-capacity ion-exchange columns (such as the Thermo Scientific™ Dionex™ IonPac™ SCS 1 Silica Cation Separator Column) to ensure that only weak eluents are necessary (Figure 1). This requirement means that selectivity options are limited.

Chemically Regenerated Suppressors

Chemically regenerated suppressors, including packed bed, automatically-switching packed bed, and continuously regenerated suppressors, use chemical solutions to regenerate the suppressor.

Packed Bed Suppressor

The first suppressor type developed was the "packed-bed suppressor", and is the only suppressor type available from some vendors. This type of suppressor contains a large volume of high-capacity ion-exchange resin (cation-exchange resin for anion analysis, and anion-exchange resin for cation analysis), often packed into a column body.

The high capacity of packed bed suppressors extends their suppression ability, typically to eight hours, before they are exhausted. Once they are exhausted, they must be taken offline and regenerated for an extended period, typically overnight, before they can be used again. The drawbacks of the extended downtime for each regeneration meant that hydroxide eluents were not used in the early years of IC, despite their clear advantages.

Unfortunately, the large internal volume of these suppressors also led to peak dispersion and poor chromatographic performance.

Automatically-Switching Packed Bed Suppressor

One way to reduce the volume of packed bed suppressors is to take the suppressor offline and regenerate it after every analysis, but that is an inconvenient process. To avoid this, it is possible to attach multiple suppressor cartridges to a rotor and change cartridges after every run.

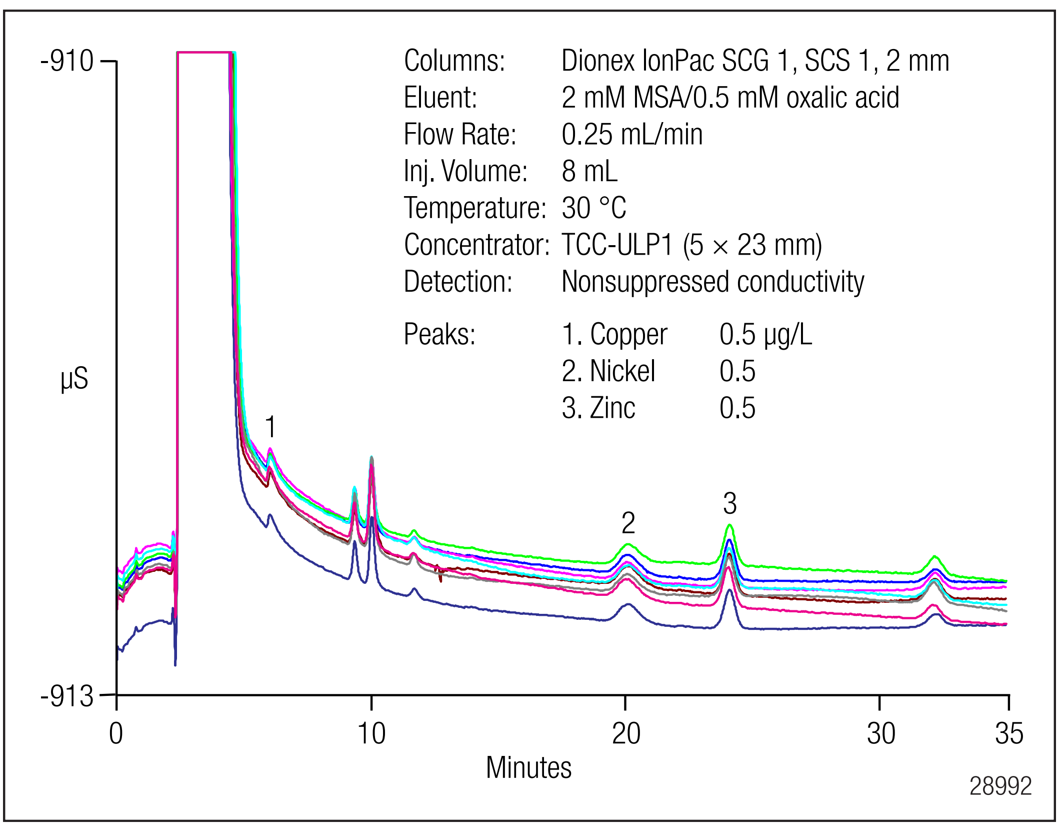


Figure 1. Non-suppressed conductivity detection of cations using a Dionex IonPac SCS 1 column separation.

Automating the switching, regenerating, and rinsing of the suppressor cartridges minimizes labor and downtime. However, to maintain chromatographic performance, the capacity of the suppressor cartridges has to be reduced significantly. As a result, these types of suppressors may run out of capacity during an analysis.

Additionally, automated switching makes it difficult to track which suppressor cartridge has been used for a given analysis, leading to validation issues. These include:

- When a cartridge becomes contaminated, it can be impossible to prove that certain injections were unaffected.
- Samples are likely to be run through a different cartridge than the standards used for calibration (Figure 2).

This approach is equivalent to running separate injections on different analytical columns during a sequence or calibration curve. It is impossible to verify true compliance and regulatory accuracy when switching packed bed suppressor columns between injections.

Continuously Regenerated Suppressor

Continuous regeneration addresses the issue of limited capacity in packed bed suppressors. When using continuous regeneration, regenerant solution is continuously passed through the suppressor via a parallel channel. This enables analyses of any duration without the prospect of running out of suppression capacity.

Regenerant solution must still be prepared. To mitigate the time taken for regenerant preparation, concentrated regenerant solutions can be purchased for dilution. The expense of an additional mechanism for moving the regenerant through the suppressor can be alleviated using techniques such as displacement chemical regeneration (DCR), where the conductivity cell effluent displaces the regenerant back through the suppressor.

Electrolytically Regenerated Suppressors

Electrolytically regenerated suppressors, including constant current and dynamically regenerated suppressors, use water and a potential applied across two electrodes to regenerate the suppressor, eliminating the need to prepare regenerant solution.

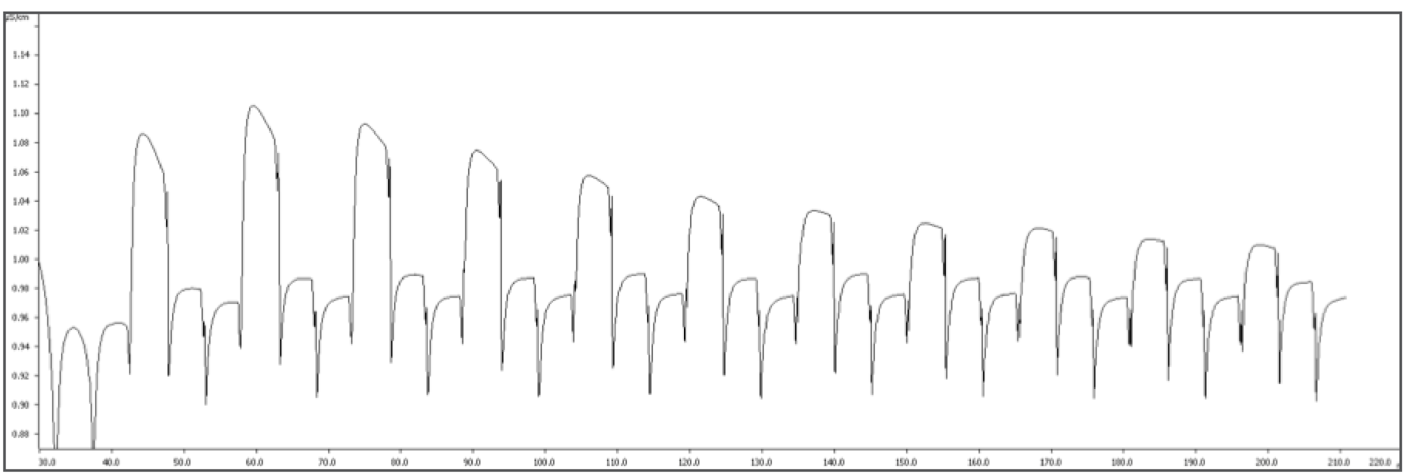


Figure 2. Example of baseline disruptions resulting from automatically switching packed bed suppressors. If standards are run on different suppressor cartridges from samples, spurious results may be obtained.

Constant Current Suppressor

The water required for regeneration can simply be the cell effluent (so-called “recycle” mode), or it can be delivered externally if the cell effluent is unsuitable for re-use (“external water” mode). Recycle mode removes the need for additional pumps or chemicals, and is therefore cost-effective, low-labor, and reagent-free. External water mode is used when the cell effluent is unsuitable, or unavailable, for re-use.

Early electrolytic suppressors generated 3–5 times the noise of the best performing chemical suppressors, so trace ion analysis was still best performed with chemical suppression. However, noise is considerably reduced in modern electrolytic suppressors, so they can be used successfully for trace-level work (Figure 3).

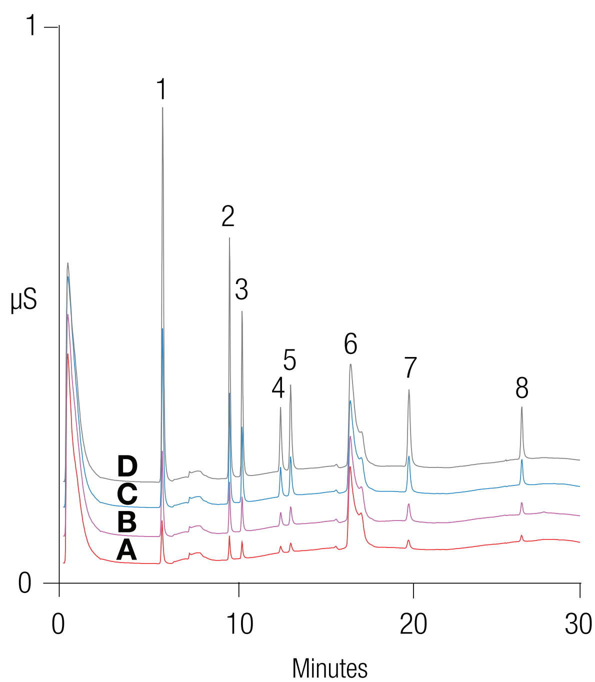
Until recently, all electrolytic suppressors operated by applying a fixed current across the electrodes. One drawback of this approach is that the operator must determine what current needs to be applied (usually by reference to the application material). More significantly, when running an eluent concentration gradient, the current applied needs to be high enough to regenerate the highest eluent concentration used. current applied needs to be high enough to regenerate the highest eluent concentration used. However, during the times when the eluent concentration is low, the excess current applied may increase noise and decrease the lifetime of the suppressor.

Finally, electrolytic suppressors are not suitable for eluents or samples containing high levels of organic solvents. These applications require a chemical suppressor.

Dynamically Regenerated Suppressor

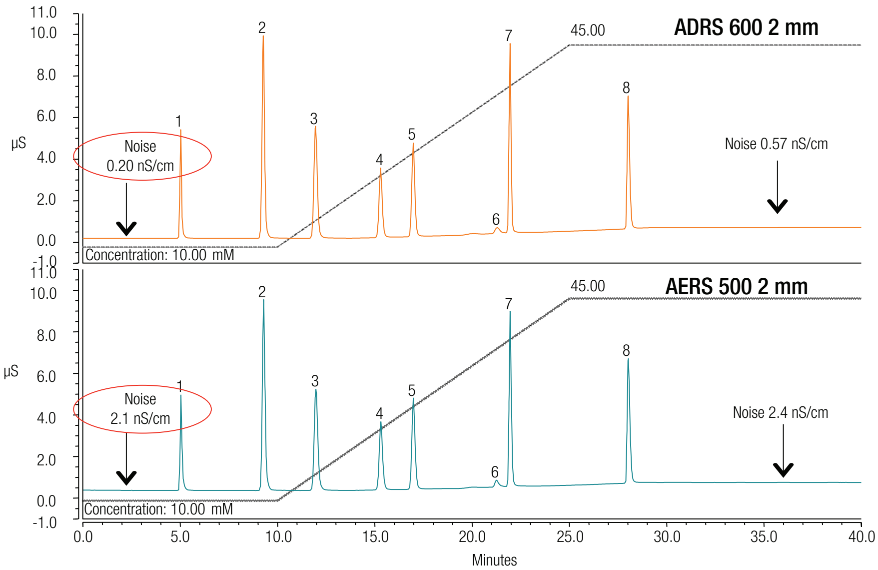
Dynamically regenerated electrolytic suppression overcomes some of the issues of constant current suppressors by maintaining a constant potential across the electrode throughout the analysis (Figure 4). As a result, only the current necessary to regenerate the suppressor is used. In this way, a dynamically regenerated suppressor:

- Minimizes training and set-up time
- Eliminates the potential for errors in the manual calculation of electrical currents
- Improves signal-to-noise ratio with concentration gradients by dynamically adapting to the changing eluent composition



Columns:	Dionex IonPac AG17-C, 4 × 50 mm Dionex IonPac AS17-C, 4 × 250 mm
KOH Eluent:	50 mM wash (4.5 min); 1 mM (-7 to 4 min), 1–12.5 mM (4–10 min); 12.5–20 mM (10–20 min); 20–35 mM (20–30 min)
Eluent Source:	Dionex EGC-500 KOH cartridge, with Dionex CR-ATC 600 trap column, Dionex high pressure degasser
Flow Rate:	1 mL/min
Inj. Volume:	Sample (10 mL), Standard (10–80 µL)
Column Temp.:	30 °C
Detection:	Suppressed conductivity, Dionex AERS 500 suppressor,
Sample Prep.:	Dionex CRD 300 inline degassing, Dionex AutoPrep, EWP, 30 mA
Concentrator:	Dionex UTAC-LP2, 4 mm
Sample Vol.:	Sample (10 mL), Standard (10–80 µL)
Samples:	A: 50 ng/L B: 100 ng/L C: 200 ng/L D: 400 ng/L
Peaks:	1. Fluoride 2. Chloride 3. Nitrite 4. Bromide 5. Nitrate 6. Carbonate 7. Sulfate 8. Phosphate

Figure 3. Calibration standards of 50 to 400 ppt on a system utilizing the Thermo Scientific™ Dionex™ AERS™ 500 Anion Electrolytically Regenerated Suppressor in recycled water mode.



Column: Thermo Scientific™ Dionex™ IonPac™ AS19-4µm 2 mm
Eluent (EG gradient): 10 mM from 0–10 min; 10 mM to 45 mM from 10–25 min; 45 mM from 25 min to 40 min
Flow rate: 0.25 mL/min
Inj. volume: 2.5 µL
Detection: Suppressed conductivity
ADRS 600 4.5 V
AERS 500 28 mA
Oven Temp: 30 °C

Peaks:
1. Fluoride
2. Chloride
3. Nitrite
4. Bromide
5. Nitrate
6. Carbonate
7. Sulfate
8. Phosphate

Figure 4. Comparison of baseline noise on a system running a potassium hydroxide gradient using constant current (Dionex AERS 500 Anion Electrolytically Regenerated Suppressor) and dynamically regenerated (Thermo Scientific™ Dionex™ ADRS 600 Anion Dynamically Regenerated Suppressor) suppressors.

Summary

Thermo Fisher Scientific offers the widest choice of suppression capabilities, ensuring that you can find the most suitable solution for your application.

Suppression Technique		Summary	# of vendors offering	
	Non-suppressed	Simple, but low sensitivity and selectivity	7+	ThermoFisher SCIENTIFIC
Chemically Regenerated	Packed-bed	High sensitivity, but large dead volume and downtime	3	
	Automatically switching packed-bed	Reduces downtime, but limited capacity and no traceability	3	
	Continuously regenerated	"Infinite" capacity, but still requires regenerant preparation	2	ThermoFisher SCIENTIFIC
Electrolytically Regenerated	Constant Current	Reagent and labor-free, not suitable for exotic applications	2*	ThermoFisher SCIENTIFIC
	Dynamically Regenerated	Always optimized, not solvent compatible	1	ThermoFisher SCIENTIFIC

*** Only Thermo Fisher Scientific offers *continuously regenerated* electrolytic suppression**

Find out more at **thermofisher.com/IC**

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