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Achieving Low Baseline Noise for Anion Determinations by Suppressed Conductivity Using Carbonate Eluents

INTRODUCTION

Chromatographic sensitivity can be defined as the signal divided by the noise (sensitivity = S/N).¹ To achieve the highest sensitivity, baseline noise must be minimized while maintaining analyte signal. Chromatographic baseline noise can be divided into short-term noise (high frequency) and long-term noise (low frequency). Short-term noise usually arises from detector electronics and properties unique to the method of detection (e.g., stray light in UV detection). Long-term noise usually originates with the pump, properties of detection method, the eluent, the column, and the effect of temperature on each of these items. For additional information on chromatographic noise see references 1 and 2.

Although most ion determinations are well above the baseline noise level, there are determinations that demand high sensitivity. For example, bromate must be determined in drinking water at single-digit ppb levels³ and perchlorate must be determined at similarly low levels.⁴ This technical note describes parameters for achieving low baseline noise (1 ± 0.2 nS) when determining anions by suppressed conductivity using an IonPac® AS14 column with its recommended eluent on a DX-500 chromatography system.

EXPERIMENTAL

DX-500 Ion Chromatography system consisting of:

- GP50 Gradient Pump with a GM3 mixer (P/N 42126) installed between the pump and the injection valve
- CD20 Conductivity Detector
- DS3 Conductivity Cell
- LC30 Chromatography Oven
- AS50 Autosampler

The equipment was controlled and the data analyzed using PeakNet® chromatography software.

REAGENTS AND STANDARDS

Deionized water (DI H₂O), 18 MΩ-cm resistance or better
AS14 Eluent Concentrate (Dionex Corporation,
P/N 53560)

Anion Standard: [ppb] (F⁻: 100; Cl⁻: 200; NO₂⁻: 300; Br⁻: 500; NO₃⁻: 500; HPO₄²⁻: 800; SO₄²⁻: 600)

CHROMATOGRAPHY CONDITIONS

Columns: IonPac AS14, 4 × 250 mm (P/N 46124)
IonPac AG14, 4 × 50 mm (P/N 46134)

Eluent: 3.5 mM Na₂CO₃/1.0 mM NaHCO₃

Flow Rate: 1.2 mL/min

Inj. Volume: 25 µL

Detection: Suppressed conductivity,
ASRS® ULTRA
(4 mm) in external water mode at
4–10 mL/min, 100 mA

Conductivity
Cell Settings:
Temperature: 35 °C
Thermal Compensation: 1.7

Data Collection
Rate: 5 Hz

Savitzky-Golay
Filter Settings: 25 points (5.0 s), 10 iterations

Expected System
Backpressure: 1500–2000 psi

Expected
Background
Conductivity: 17.6 µS

Eluent Preparation

Dilute 10 mL of AS14 Eluent Concentrate to 1 L with deionized water. Mix and install under helium head pressure (35–55 kPa, 5–8 psi).

Measurement of Noise

Noise was measured using the Optimize module in the PeakNet chromatography software. Select a 1-min section of the chromatogram and under Auto Threshold, click on the measure button, and record the peak-to-peak noise value. In this document all noise values are an average of at least eight alternating one-minute segments of the chromatogram (e.g., 1–2 min, 3–4 min, 5–6 min, etc.).

Parameters for Low Suppressed Conductivity Baseline Noise

General System Conditions

After the system has been set up as described in the Experimental Section, the background conductivity should be about 17.6 μS . If the background is greater than 22 μS , there is a problem with the setup. High backgrounds can be a result of incorrect eluent preparation (too strong), old eluent, or incomplete suppression. After ensuring that there is adequate external water flow (4–10 mL/min), set the ASRS power setting to 500 mA. If this action reduces background, the suppressor is not working efficiently at 100 mA and should be regenerated using the procedure described in the QuickStart Document (Document #031368-01) that is packaged with the suppressor. If the suppressor is not functioning, the background will be many times higher than the expected background, regardless of the power setting. New suppressors should be prepared and installed as described in the QuickStart Document. This preparation includes the installation of one backpressure coil. Remember that the suppressor power should be off when there is no eluent flowing through it. A suppressor that is on with no eluent flowing through it can be permanently damaged. It is also important that the suppressor power is on when eluent is flowing through it. If eluent flows through the suppressor with the power off, its membrane will be converted from the acid to the sodium form. This will lead to high backgrounds the next time that power is supplied to the suppressor and will require that the suppressor be regenerated with acid as described in the QuickStart Document.

In general, higher backgrounds lead to higher baseline noise. For this reason, one should expect higher baseline noise values for eluents with higher ionic strengths than the eluent used here (e.g., the 9 mM sodium carbonate eluent used with the IonPac AS9-HC).³ Because suppressed sodium hydroxide eluents have very

low backgrounds (1–4 μS), analysts requiring the most sensitive ion determinations choose, when possible, a column that can separate their analytes with a sodium hydroxide eluent.⁵

The Pump

To achieve the lowest noise possible, a high-quality chromatography pump that delivers precise, pulseless flow is required. This pump must be primed. A pump that is not primed has small bubbles trapped in the pump heads. Though unnoticed when determining analytes at mg/L concentrations, this problem is readily identified when doing low-level determinations. Figure 1A shows a typical noise trace of an unprimed pump. In this example, the noise is only 1.13 nS, but it is often higher (2–5 nS). After priming the pump as described in the GP50 Operator's Manual, the noise was reduced to 0.811 nS, as shown in Figure 1B.

To minimize the contribution of the pump to the total baseline noise, a GM3 mixer should be installed between the pump and the injection valve. Figure 2 shows the effect of the GM3 on baseline noise. In this example, there is no suppressor and water is flowing through the conductivity cell at 1.0 mL/min. The chromatogram in Figure 2A was collected without a GM3 and the noise was 2.43 nS. After installation of the GM3 (Figure 2B), the noise was reduced to 0.268 nS.

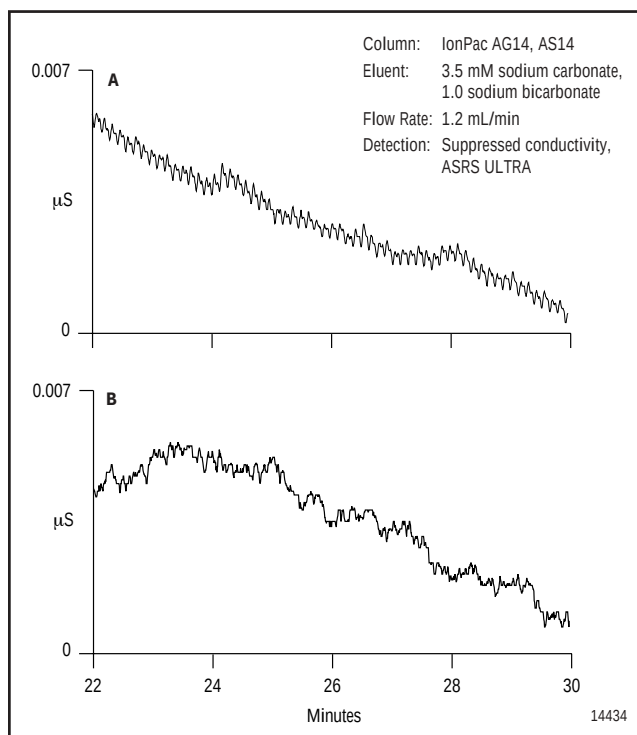


Figure 1. Conductivity noise: unprimed (A) vs a primed (B) pump.

Detection

In addition to the parameters detailed in the first section, the following conditions should be established to ensure the lowest possible baseline noise. The DS3 should be set at 35 °C with a temperature compensation of 1.7 °C. If the DS3 cell is in a chromatographic oven that is controlling column temperature, the cell should be set at least 2 °C above the oven temperature. If the cell is set at the oven temperature, the conductivity measurement will be subject to noise created by oven temperature regulation.

Although most anion determinations can be run using the ASRS recycle mode, the lowest baseline noise is achieved by using the ASRS in the external water mode. Figure 3 Panel A shows an example of the baseline noise when the ASRS is operated in recycle mode and Panel B shows the same ASRS operated in external water mode. The noise in the recycle mode was 3.23 nS and was decreased to 0.890 nS in the external water mode.

Smoothing Algorithms

After data collection, the smoothing algorithms available in PeakNet can be used to increase S/N.⁶ Figures 4 and 5 show the effect of using the Savitzky-Golay algorithm on a determination of seven anions at sub-ppm levels. Ten iterations of a 25-point (5 Hz) Savitzky-Golay algorithm were applied to the chromatogram. At a collection rate of 5, applying the algorithm to 25 points is equal to 5 s of data. If data had been collected at 1 Hz, we would apply the algorithm to five points. Application of smoothing algorithms to too many points will distort the chromatogram. Figure 4 shows the effect of the 25 point Savitzky-Golay algorithm when it is applied to the seven-anion chromatogram. The unfiltered data (Panel A) has noise of 0.854 nS. Application of the smoothing algorithm (Panel B) decreases baseline noise to 0.655 nS. Figure 5 shows that the application of the smoothing has little effect on the peak areas and

Analyte	Amount (ppb)	Peak Height (×10 ⁷)	Peak Height after Smoothing (×10 ⁷)	S/N	S/N after Smoothing	Peak Area (×10 ⁸)	Peak Area after Smoothing (×10 ⁸)
Fluoride	100	2.018	1.807	236	276	1.318	1.278
Chloride	200	1.319	1.269	154	194	1.197	1.194
Nitrite	300	1.787	1.750	209	267	1.892	1.895
Bromide	500	1.431	1.418	168	216	1.982	1.981
Nitrate	500	1.505	1.497	176	229	2.587	2.583
Phosphate	800	0.7397	0.7385	86.6	113	1.887	1.884
Sulfate	600	1.617	1.616	189	247	4.542	4.534

* Noise before and after smoothing are 0.854 and 0.655 nS

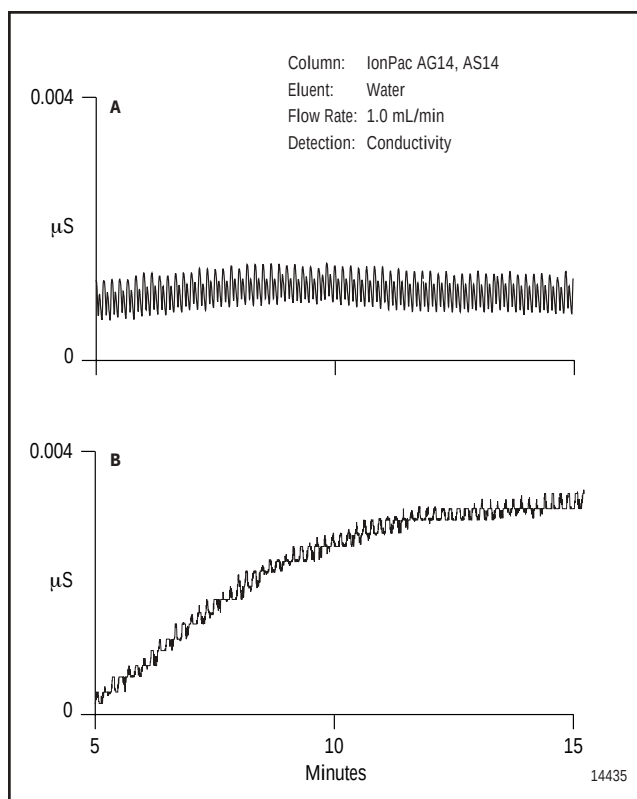


Figure 2. Conductivity noise: without a GM3 mixer (A) and with a GM3 mixer (B).

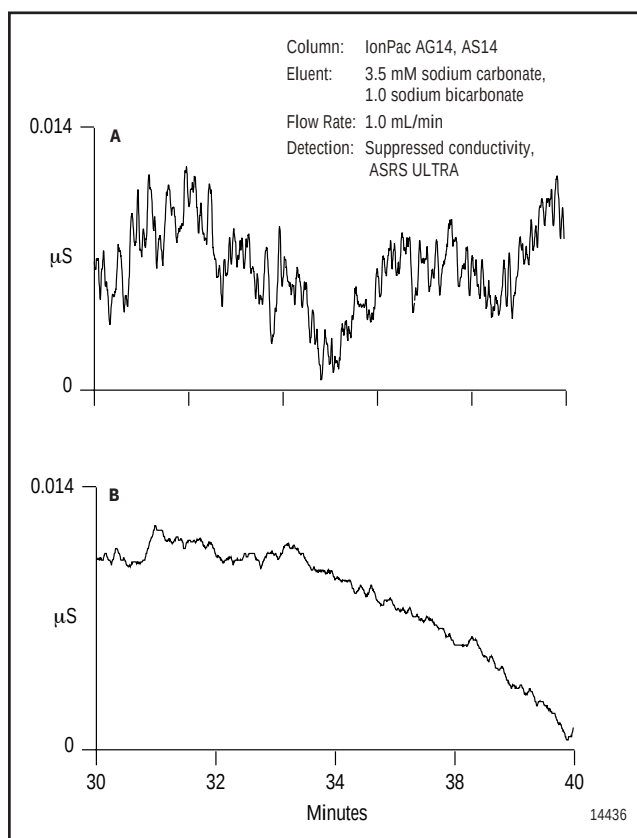


Figure 3. Conductivity noise: recycle (A) vs. external water (B) mode.

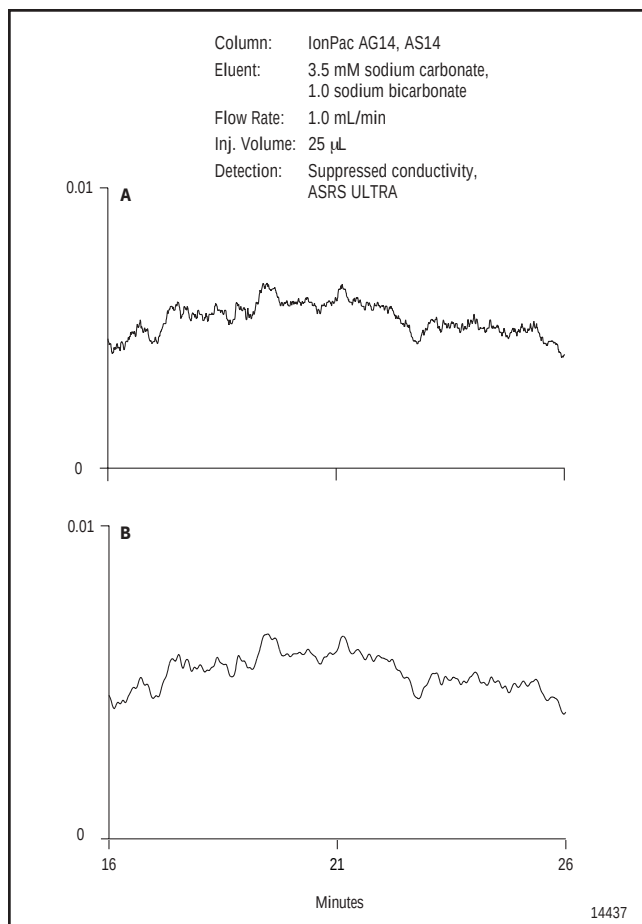


Figure 4. Conductivity noise: without (A) and with smoothing (B); smoothing, 10 iterations of a 25-point (5 Hz) Savitsky-Golay.

peak heights of the seven anions. The changes in peak heights, peak area, and S/N due to smoothing are reported in Table 1. The height of the early eluting fluoride peak is most affected by smoothing (a 10% loss in peak height), yet there is still a 17% improvement in S/N. For all other peaks there is less peak height loss and greater gains in S/N.

CONCLUSION

This technical note outlines the parameters necessary to achieve low baseline noise for ion chromatography with suppressed conductivity detection. Though this technical note focuses on carbonate eluents, the techniques discussed should also lower baseline noise in other eluents, including hydroxide.

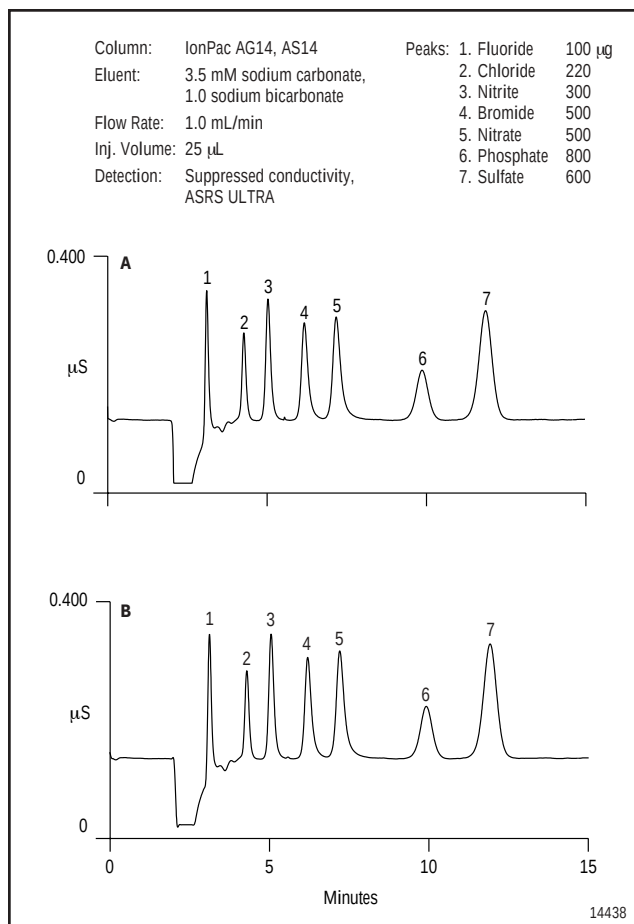


Figure 5. Anion chromatogram before and after smoothing; smoothing, 10 iterations of a 25-point (5 Hz) Savitsky-Golay.

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