# Weak Cation-Exchange Resin Based Concentrator and Trap Column for Ion Chromatography

K. Srinivasan, S. Bhardwaj, R. Lin, C. Pohl, Dionex Corporation, Sunnyvale, CA, USA


## ABSTRACT

Concentrator columns are typically used in ion chromatography (IC) to focus trace ions of interest before analysis. Typically, latex-based anion exchangers are used for concentrating anions. The latex-based anion exchangers are prepared by agglomerating an anion-exchange latex phase on a cation-exchange resin substrate with sulfonic acid functional groups. The cation-exchange phase, however, suffers from the disadvantage of a low bleed of leachates comprised primarily of sulfonated oligomers and sulfate. In some cases, when pursuing trace-level analysis, the presence of the sulfate blanks leads to poor quantification of sulfate. The low bleed of oligomeric sulfates from the concentrator column can affect the life time and performance of down-stream consumables such as the column and the suppressor. Typically, the problems with low bleed have been addressed by cleaning the concentrator column for several weeks prior to installation on a trace analysis system. This approach, however, is cumbersome. An alternate approach would be to design a phase that would not have a sulfate blank issue. This poster will discuss the design of a carboxylic-acid-based weak cation-exchange resin phase for the concentrator column application.

Application of the carboxylate-phase-based latex-agglomerated concentrator column for analysis of trace anions will be shown here. Another application for the above phase would be in polishing sample cations prior to anion analysis. A carboxylate-based cation polisher column and a continuously-regenerated trap column device will be used for polishing cations from samples.




## INTRODUCTION

Trace-level anion analysis is presently performed by large loop injection or by preconcentration using a concentrator column. Preconcentration is the preferred means for analysis at low µg/L or ng/L concentrations.

### Concentrator columns:

- Styrene DVB-based stationary phase that is sulfonated, then agglomerated with a latex phase with anion-exchange groups
  - Sulfonation is typically accomplished by reacting the phase with sulfuric acid or chlorosulfonic acid at high temperatures.
- Possible issues observed during trace level analysis:
  - Sulfonated oligomers and sulfate leaches out of the stationary phase at trace levels.
  - May impact quantitation of sulfate, particularly when pursuing trace analysis.
  - May impact the background:
    - » Requires offline cleanup or equilibration of the concentrator column.
    - » Requires a blank correction.
  - May contaminate downstream consumable products such as columns, suppressors, etc.
    - » Requires a cleanup of consumables.

## ULTRA TRACE ANION CONCENTRATOR (UTAC)

**A weak cation-exchange phase that has carboxylate functional groups:**

- Styrene DVB-based phase grafted with acrylic acid monomer to create a grafted carboxylate polymer layer, then agglomerated with an aminated latex phase
  - No leachates that interfere with analysis
  - No sulfonated oligomers or sulfate
  - Excellent quantitation of sulfate
  - No need for long concentrator column equilibration steps

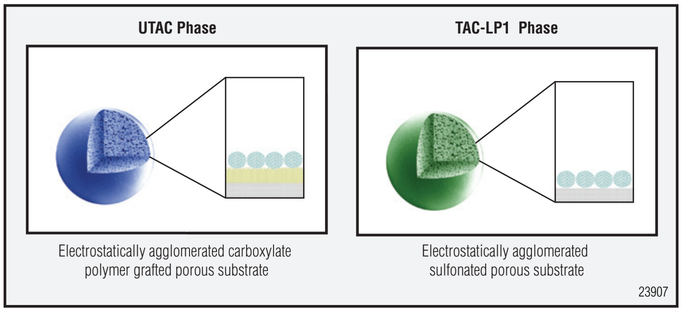


*Figure 1. The above schematic shows the UTAC phase with latex attached to a polymeric layer grafted on top of the Styrene DVB phase. A TAC-LP1 phase is shown for comparison purposes and has the latex attached to the sulfonated groups (not shown) on top of the Styrene DVB phase.*

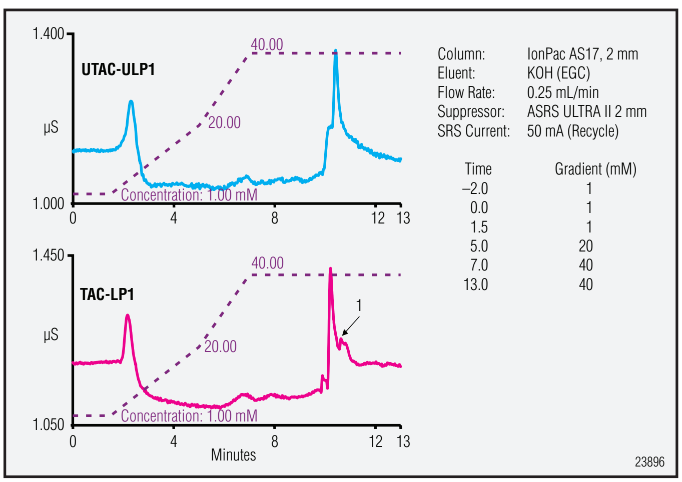


*Figure 2. The above figure compares the performance of an IonPac UTAC-ULP1 (5 × 23 mm) and IonPac TAC-LP1 (4 × 35 mm) concentrator columns under gradient conditions without an injection. A peak corresponding to sulfate (1) was detected using the TAC-LP1 concentrator whereas the UTAC-ULP1 concentrator did not show any such peak.*

Table 1 shows reproducibility of retention time and response (n=20 runs). See Figure 4 for experimental conditions. A DXP pump was used for sample delivery and showed a response RSD of less than 2%. The response, when plotted against the volume concentrated, showed an excellent fit to a quadratic curve using the UTAC concentrator column (Table 2). See Figure 4 for experimental conditions. The correlation coefficients are depicted in the table for the volume range of 0.5 mL to 12 mL. The sample was a 1000-fold dilution of a seven-anion standard from Dionex.

**Table 1. Retention Time and Peak Area Reproducibility (n = 20)**

| Peak | Retention Time RSD | Area RSD* |
|---|---|---|
| Fluoride | 0.36 % | 1.26% |
| Chloride | 0.27% | 1.15% |
| Nitrite | 0.25% | 1.72% |
| Bromide | 0.14% | 1.28% |
| Nitrate | 0.13% | 1.26% |
| Phosphate | 0.08% | 1.38% |
| Sulfate | 0.11% | 1.27% |

**Table 2. Response versus Volume Concentrated (0.5 mL to 12 mL)**

| Analyte | *$R^2$ |
|---|---|
| Fluoride | 0.999 |
| Chloride | 0.998 |
| Nitrite | 0.999 |
| Bromide | 0.999 |
| Nitrate | 0.999 |
| Phosphate | 0.999 |
| Sulfate | 0.999 |

*Quadratic fit

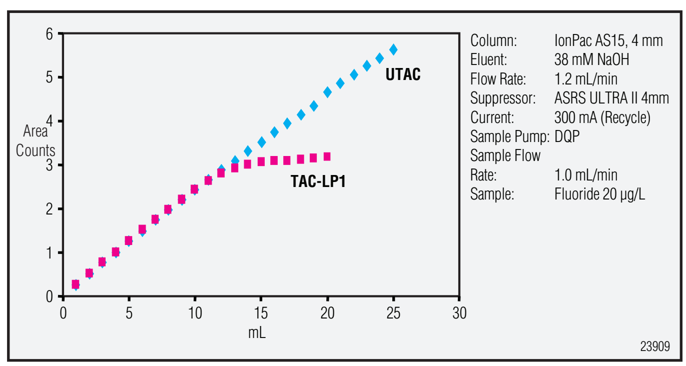


*Figure 4. Fluoride recovery was monitored for a wide range of sample volume using both an UTAC concentrator and TAC-LP1 concentrator column and AS15 chemistry. The above results indicated excellent performance of the UTAC concentrator column.*

## CATION POLISHING APPLICATIONS

- Sample polishing is typically required for samples containing high levels of divalent and metal ions.
  - Presence of divalents and metals at high concentration impact peak shape and recovery of various ions such as fluoride, sulfate and phosphate.
- When pursuing anion analysis:
  - Polishing cations from the sample stream improves recovery.
- With conventional sulfonated phases:
  - Issues with sulfonated oligomers and blanks.
- Carboxylate phases:
  - Overcome the limitation of sulfate-based leachates.

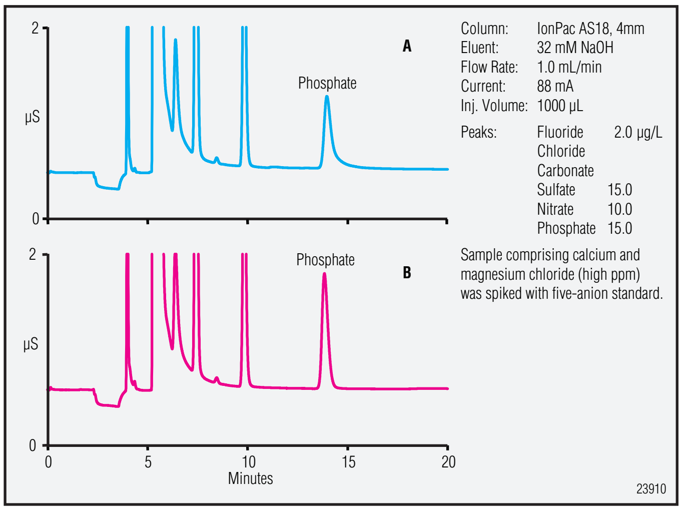


*Figure 5. Comparison of anion analysis when the system was exposed to high levels of calcium and magnesium. Chromatogram A shows the analysis of a five-anion standard with added calcium and magnesium. Poor peak shape for phosphate can be inferred from above. When the sample stream was polished using a CP1 (6 × 16 mm) polisher column the recovery of phosphate improved and excellent peak shape was achieved as shown in chromatogram B.*

## ANION ANALYSIS IN BORATED WATERS IN THE NUCLEAR POWER INDUSTRY

- Trace anions in borated waters with low concentration of cations
  - Large volume preconcentration followed by analysis
- Trace anions in borated waters with mg/L levels of lithium
  - Offline polishing of the samples to remove lithium
  - Packed bed column is used
    - » Needs monitoring for residual capacity
    - » Needs replacements when capacity is depleted or offline regeneration
    - » Added processing steps and labor

## CONTINUOUSLY-REGENERATED CATION TRAP COLUMN II (CR-CTC II) AS A SAMPLE PREP TOOL

- Continuously electrolytically-regenerated trap column
- No down time
- No offline regeneration steps
- Labor savings
- Reliable
- Issues
  - Sulfonated substrate resin tends to leach at low levels
    - » Sulfate peak detected without injection
    - » Hence not suitable for sample polishing
    - » Requires long equilibration or cleanup to reduce sulfate levels
- Solution
  - Design a carboxylate-phase substrate resin
  - No issue with sulfate-based leachates
  - Ideally suited for sample polishing applications
    - » No sulfate detected without injection
    - » No cleanup needed

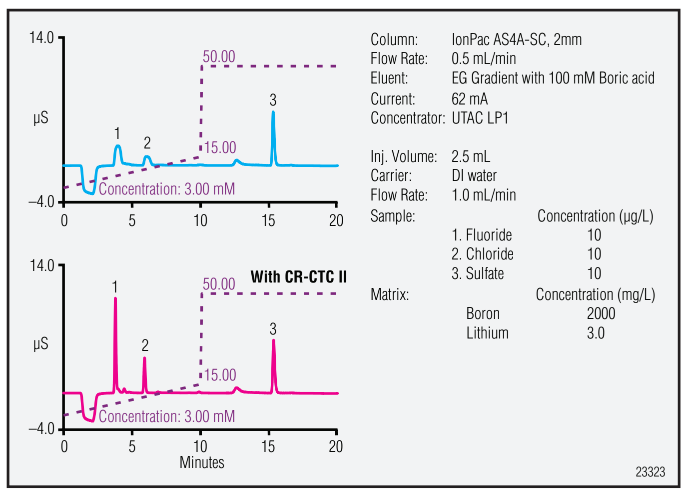


*Figure 6. Analysis of a simulated borated water sample consisting of trace anions and lithium. The polishing step ensures excellent recovery of peak shapes and response for all ions. In the above example a CR-CTC II polisher was used in-line for polishing the sample.*

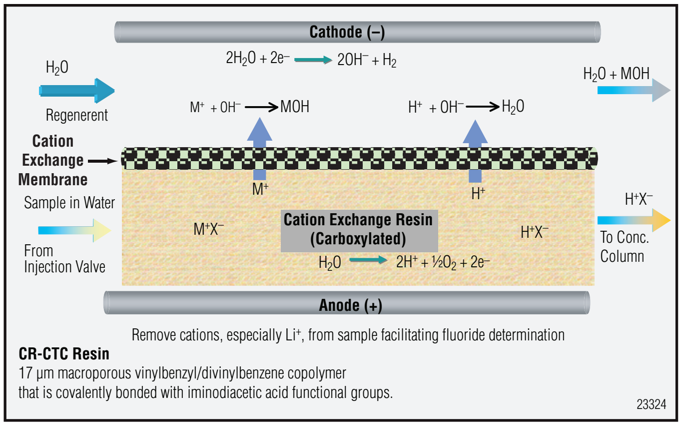


*Figure 7. Operation schematic of a CR-CTC II. The cations from the sample stream are driven towards the cathode and exit the device as a base, whereas as the anions in the sample are converted to the acid form and exit the device in the acid form for further analysis.*

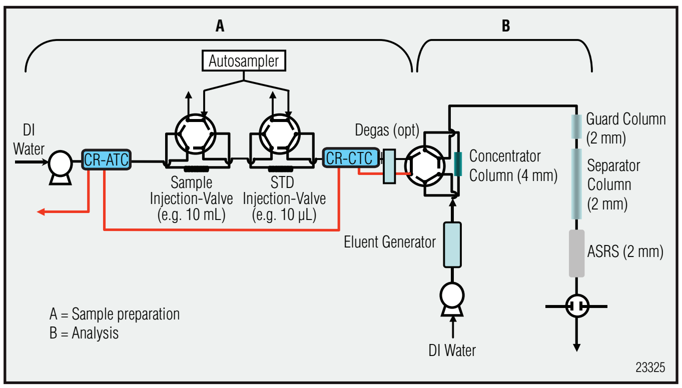


*Figure 8. Instrumentation setup for both sample prep or polishing (A) and analysis (B). It is also possible to polish the sample stream by directly diverting the sample into the CR-CTC II.*

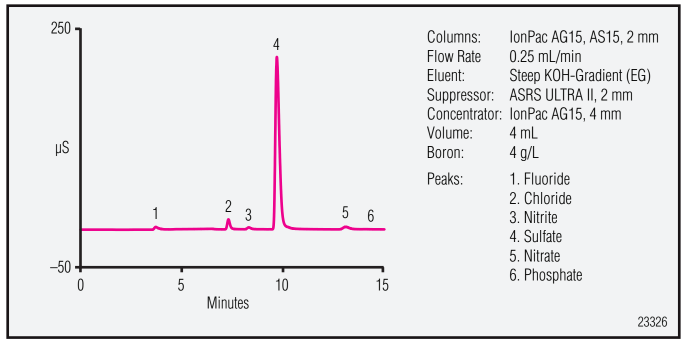


*Figure 9. Analysis of a simulated borated water sample is shown above.*

# CONCLUSIONS

- A carboxylate-based resin was found acceptable for preconcentration and for sample polishing applications.
  - Sulfate peaks originating from leachates were eliminated, leading to excellent quantitation of sulfate.
- With continuously-regenerated cation trap columns (CR-CTC II), continuous polishing is possible
  - Required no cleanup.
    - » Labor and time savings
  - Leachates containing sulfate were eliminated.
  - Complete automation of the polishing step became possible.



**Dionex Corporation**
1228 Titan Way
P.O. Box 3603
Sunnyvale, CA
94088-3603
(408) 737-0700

**North America**
U.S. (847) 295-7500
Canada (905) 844-9650

**South America**
Brazil (55) 11 3731 5140

**Europe**
Austria (43) 1 616 51 25 Benelux (31) 20 683 9768 (32) 3 353 4294
Denmark (45) 36 36 90 90 France (33) 1 39 30 01 10 Germany (49) 6126 991 0
Ireland (353) 1 885 1700 Italy (39) 02 51 62 1267 Switzerland (41) 62 205 9966
United Kingdom (44) 1276 691722

**Asia Pacific**
Australia (61) 2 9420 5233 China (852) 2428 3282 India (91) 22 28475235
Japan (81) 6 6885 1213 Korea (82) 2 2653 2580 Singapore (65) 6289 1190

**www.dionex.com**



LPN 1924-01 03/07