

Anion Concentrator for RFIC-ER Systems

John Madden, Chris Pohl, Yan Liu, Kannan Srinivasan, and Sheetal Bhardwaj, Dionex Corporation, Sunnyvale, CA, USA

INTRODUCTION

In 2008, Dionex expanded RFIC by introducing a new family of systems; RFIC systems with Eluent Regeneration (RFIC-ER™). RFIC-ER systems use the electrolytic suppressor to regenerate the starting eluent after suppression. They provide benefits similar to RFIC-EG™ systems, offering simplicity, ease of use, and improved reproducibility. The two technologies differ in the additional advantages they offer for various user needs; while RFIC-EG systems provide isocratic and gradient method flexibility for a wide range of IC applications, RFIC-ER systems are designed specifically for a set of routine IC analyses, such as determination of anions or cations in drinking water. The major advantages of RFIC-ER are continuous operation, reduced waste disposal, and lower cost of ownership. However, RFIC-ER systems are restricted in the total amount of analyte that can be injected into the system before requiring that the eluent be replaced.

An RFIC-ER system can use the same 4L bottle of eluent for up to 28 days, or until a total of 20,000 µL of sample has been injected into the system, whichever comes first. If injection sizes are relatively small, (e.g., < 50 µL) the number of injections between eluent replacements can be relatively large—400 injections for the case of a 50 µL injection. Because most operators typically perform 100 injections per week or less, 4 weeks of nonstop operation is easily achievable under these conditions. However, for determination of low levels of analytes, larger injection sizes are required. 500 µL is typically required to determine bromate in drinking water at concentrations of 5 ppb or less. A direct injection of 500 µL of sample into an RFIC-ER system would exceed the maximum sample volume after only 40 injections; this translates to only a few days operation before an eluent change becomes necessary for many customers, which means many of the advantages of RFIC-ER are lost. By using a concentrator, the amount of sample loaded into the system can be significantly increased without increasing the amount of volume directly injected. Thus, a concentrator with a nominal void volume of 75 µL, can enable 266 injections regardless of the amount of sample loaded onto it. Here, the authors discuss a new concentrator (Anion Concentrator for Eluent Regeneration or AC-ER) which has been developed specifically for RFIC-ER systems and allows large sample volumes to be loaded into an RFIC-ER system with minimal disruption to the eluent change frequency.

Second, by combining the use of a concentrator with the technique of matrix elimination, it is also possible to overcome another limitation of RFIC-ER systems which is solvent compatibility. Here, authors discuss the use of the AC-ER for the analysis of common anions in ethanol matrices.

PRINCIPLES OF AC-ER

Figure 1 shows a schematic of a typical RFIC-ER system. In the case of an anion system, carbonate / bicarbonate eluent is pumped through the Anion Eluent Purification (AEP-ER1) column to remove any contaminant species before entering the analytical system. The ER1 column also retains any matrix counterions introduced with the sample. After separation, suppression and detection, the cell effluent is passed through the Anion Analyte Trap (AAT-ER2) column to remove the analyte co-ions. The suppressed eluent is then passed through the suppressor regenerant chambers where it is reunited with the eluent counterion to reform the eluent. The eluent is passed into the Anion Catalyzer Column (ACC-ER3) to recombine the hydrogen and oxygen generated in the suppressor regenerant chamber into water. A bubble sensor is used to ensure this recombination of electrolytic gasses is complete before the eluent is finally passed back into the eluent bottle for reuse.

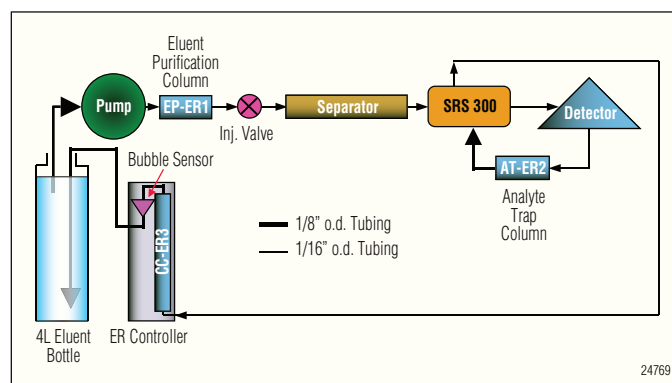


Figure 1. RFIC-ER system schematic.

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Upon injection, the AAT-ER2 column will remove all the analyte anions from the sample, while the AEP-ER1 column will remove the analyte cations. This means that for each injection a sample volume of pure water is added to the system, while the equivalent volume of eluent is removed. The net result is a small dilution of the eluent. With 4 L of eluent, 20,000 μL of sample injected into the system will dilute the eluent 0.5%. The linear solvent strength model shown below predicts that the log of the ratio of the retention factors is proportional to the log of the ratio of the eluent concentrations for divalent eluents such as carbonate and divalent analyte ions such as sulfate:

$$\log \left(\frac{k'_1}{k'_2} \right) \propto \log \left(\frac{[E_1]}{[E_2]} \right)$$

and to half the log of the eluent concentrations for monovalent analyte anions such as chloride and bromate:

$$\log \left(\frac{k'_1}{k'_2} \right) \propto \frac{1}{2} \log \left(\frac{[E_1]}{[E_2]} \right)$$

Thus, a decrease of 0.5% in eluent concentration translates into an increase of 0.5% retention factor for divalent anions and 0.25% for monovalent anions.

For the analysis of bromate, injection volumes of 500 μL are typically used to increase sensitivity to allow analysis of bromate at concentrations of 5 ppb or lower. For a traditional Ion Chromatograph, 500 μL can be directly injected, but such an injection in an RFIC-ER system would limit the total number of injections between eluent changes to 40. Such a small number of injections between eluent changes would mean the eluent is changed so frequently that many of the RFIC-ER advantages would be lost.

However, if a concentrator is used instead of direct injection, only the dead volume of the concentrator plus tubing and fittings is injected into system, regardless of the amount of sample actually loaded onto the concentrator. Thus, an Anion Concentrator optimized for use with ER systems (AC-ER) was developed. This concentrator has a dead volume of < 75 μL , including tubing. With an AC-ER installed, 266 injections can be performed on an RFIC-ER system before the eluent needs replacement, regardless of the volume of sample loaded. This translates into a 6-fold increase in the number of injections available between eluent changes for a 500 μL sample volume.

When a sample containing organic solvent is directly injected, the ER1 and ER2 columns will trap and remove any ionic impurities from the solvent, but the solvent matrix will enter the eluent bottle and alter the characteristics of the eluent. Electroactive solvents such as ethanol oxidize to acetate as they pass through the regenerate chambers of the suppressor. Initially the ER2 column will trap this acetate, but eventually the capacity of the ER2 column will be exceeded and acetate will accumulate in the eluent bottle. This will cause a gradual increase in the baseline, along with the appearance of an acetate dip in the chromatograms.

If, however, the solvent is first loaded onto a concentrator followed by a matrix elimination step, the ions within the solvent will be injected into the system and analyzed, but the solvent will be flushed to waste rather than entering the eluent. This enables the analysis of solvents such as ethanol on an RFIC-ER system without interferences from the matrix.

EXPERIMENTAL CONDITIONS

All ion chromatographic separations were performed using a Dionex ICS-1500 system equipped with an ER controller and Chromeleon[®] chromatography data system. A Dionex ASRS 300 (4 mm) electrolytic suppressor was used in AutoSuppression recycle mode. Deionized water with a specific resistance of 18.2 $\text{M}\Omega\text{-cm}$ was used to prepare all eluents and standards. Drinking water samples were collected from Sunnyvale, CA and filtered through a 0.45 μm filter. The operation of the AC-ER concentrator was evaluated using a Dionex AS23 (4 \times 250 mm) separation column with AG23 (4 \times 50 mm) guard column. The flow rate was 1.0 mL/min and the eluent used was 4.5 mM Na_2CO_3 with 0.8 mM NaHCO_3 prepared in a 4 L eluent bottle and used continuously for up to 28 days or 266 injections before replacement.

Chromeleon was configured to enable RFIC-ER Concentrator mode, with the volume set to 75 μL . This configures the eluent counter to increment 75 μL when an injection is made, regardless of the injection volume set in the sequence table.

RESULTS AND DISCUSSION

Experiments were conducted to evaluate the reproducibility, linearity, and MDL on solutions of bromate in deionized water matrices as well as Sunnyvale drinking water matrices. Additionally, a % Recovery experiment was conducted for bromate in the Sunnyvale drinking water matrix. Finally, a series of experiments were conducted to demonstrate the ability to analyze ethanol samples with an RFIC-ER system equipped with an AC-ER.

Reproducibility

A series of 9 injections were made of 5 ppb bromate in deionized water and 5 ppb bromate in Sunnyvale drinking water to determine reproducibility. (See Figures 2 and 3). The sample volume was set to 500 μL . The %RSD of the peak area for bromate was determined to be 5.12% for the deionized water matrix and 5.33% for the Sunnyvale drinking water matrix. (See Table 1).

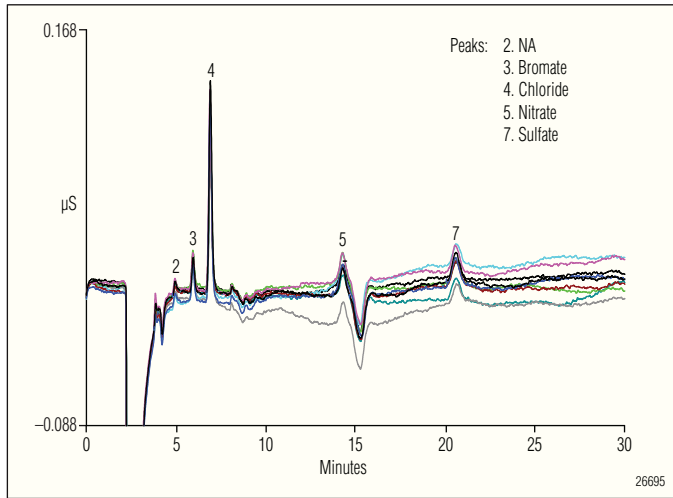


Figure 2. Overlay of 9 chromatograms of 5 ppb bromate in deionized water matrix; 500 μL of sample loaded on an AC-ER concentrator followed by analysis on a 4 mm IonPac[®] AS23 column under RFIC-ER operating conditions.

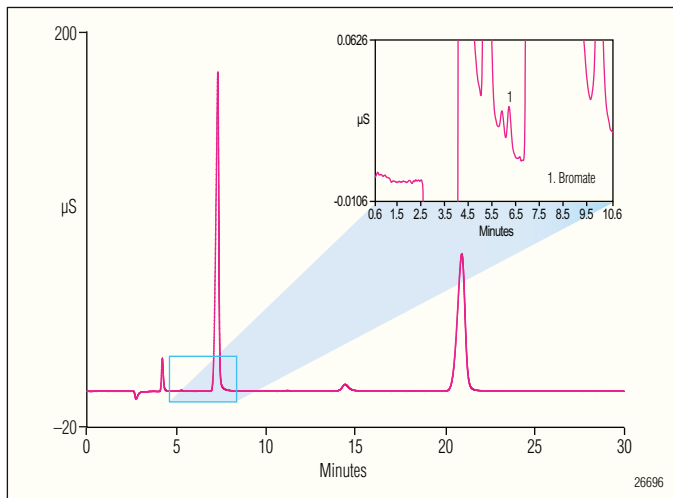


Figure 3. 5 ppb bromate in Sunnyvale drinking water matrix; 500 μL of sample loaded on an AC-ER concentrator followed by analysis on a 4 mm IonPac AS23 column under RFIC-ER conditions.

Table 1. Area Response for 5 ppb Bromate in Deionized Water and Sunnyvale Tap Water Matrices

	Area Response 5 ppb Bromate in D.I. Water	Area Response 5 ppb Bromate in Sunnyvale Tap Water
1	0.00409	0.00277
2	0.00398	0.00282
3	0.00416	0.00270
4	0.00421	0.00296
5	0.00400	0.00262
6	0.00421	0.00302
7	0.00435	0.00306
8	0.00466	0.00292
9	0.00402	0.00299
Average	0.00419	0.00287
St. Dev.	0.00021	0.00015
%RSD	5.12%	5.33%

Linearity

Linearity was determined for the deionized water matrix by injecting standards of bromate at levels of 0, 10, 20, 50 and 100 ppb in triplicate. For the Sunnyvale drinking water matrix the spikes were made at levels of 0, 5, 10 and 20 ppb and also analyzed in triplicate. In all cases 500 μL injections were made. The correlation coefficient for the deionized water matrix was 0.9993 and for the Sunnyvale drinking water matrix it was 0.9975.

MDL

A series of 7 injections were made of 5 ppb bromate in deionized water and 5 ppb bromate in Sunnyvale drinking water to determine the Minimum Detection Limit. The sample volume was set to 500 μL . The MDL for bromate in the deionized water matrix was determined to be 0.84 ppb, and for bromate in the Sunnyvale tap water matrix it was 0.72 ppb.

Table 2. Reported Concentration Values and Minimum Detection Limits for 5 ppb Bromate in Deionized Water and Sunnyvale Tap Water Matrices

	Area Response 5 ppb Bromate in D.I. Water
1	4.9682
2	5.0279
3	4.7771
4	5.0279
5	5.1951
6	5.5653
7	4.8010
St. Dev.	0.2679
MDL	0.8413

CONCLUSION

The results of our studies demonstrate that RFIC-ER systems when used with a low dead volume concentrator such as the AC-ER offer excellent performance in the determination of bromate in drinking water samples down to levels as low as 5 ppb. This makes RFIC-ER systems ideal for EPA Method 300.0 Part B, 300.1 Part B, or equivalent applications. Our results also indicate that RFIC-ER systems with the AC-ER concentrator provide excellent analysis of anions in solvents such as ethanol. RFIC-EG systems are still recommended for IC applications involving more complex samples or those requiring a wider choice of eluents and gradient separation capabilities.

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Dionex Corporation

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

North America

U.S./ Canada (847) 295-7500

South America

Brazil (55) 11 3731 5140

Europe

Austria (43) 1 616 51 25 Benelux (31) 20 683 9768; (32) 3 353 4294
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Asia Pacific

Australia (61) 2 9420 5233 China (852) 2428 3282 India (91) 22 2764 2735
Japan (81) 6 6885 1213 Korea (82) 2 2653 2580 Singapore (65) 6289 1190
Taiwan (886) 2 8751 6655

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