

Ion Chromatography Systems with Eluent Regeneration and Their Applications to Groundwater and Drinking Water Analysis

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INTRODUCTION

The advent of Reagent-Free™ Ion Chromatography (RFIC™) has fundamentally changed the routine IC operation by making it an easy to use, powerful, and reliable analytical technique. RFIC systems combine the use of three electrolytic technologies: 1) Electrolytic Eluent Generation produces acid, base, or salt eluents for IC separations, 2) Self-Regenerating Electrolytic Suppression produces the regenerant ions necessary for eluent suppression and allows continuous operation with less maintenance, and 3) Continuously Regenerated Trap Columns (CR-TC) remove trace level contaminants. RFIC systems with eluent generation (RFIC-EG™) make it possible to perform a wide range of ion chromatographic separations using only deionized water as the carrier. For many applications, RFIC-EG systems provide high performance with increased sensitivity and the flexibility to perform isocratic and gradient separations using acid, base, or salt eluents.

To expand RFIC capabilities, RFIC systems with Eluent Regeneration (RFIC-ER™) systems have been developed recently. These 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 the 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. In this paper, we will discuss the operation principles of RFIC-ER systems and demonstrate the applications of RFIC-ER systems in determination of common cations and anions in groundwater and drinking water samples.

OPERATION PRINCIPLES OF RFIC-ER SYSTEMS

Figure 1 shows the basic components of an RFIC-ER system and illustrates its operation. Eluent from the reservoir is pumped through the analytical column, SRS® 300 suppressor, and detector, separating and detecting the analytes. Suppressed eluent from the detector is routed through an IonPac® analyte trap column (ER2) that removes the analyte ions, allowing the eluent to be regenerated for reuse. The suppressed eluent then passes through the suppressor regenerant

chambers, supplying water for the electrolytic suppression of the eluent and reclaiming the eluent ions and oxygen and hydrogen generated by the electrolysis. The suppressor effluent is then passed through an IonPac Catalyzer column (ER3) which recombines the hydrogen and oxygen. This not only eliminates the buildup of gases, allowing continuous operation, but also stoichiometrically converts the hydrogen and oxygen gases back into water. Converting the gases back into water prevents the increase in eluent concentration that would occur over time due to the consumption of water by the electrolysis. The eluent is then returned to the eluent reservoir. Before its use in chromatographic separations, the regenerated eluent is further purified by an IonPac Eluent Purification Column (ER1), which traps any contaminant species that may be introduced by the samples and/or liberated from the system operation, retains the matrix counterions introduced with the sample, and ensures the purity of the regenerated eluent.

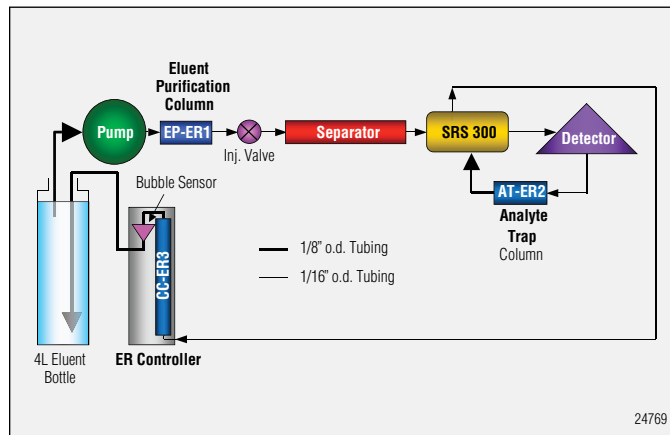


Figure 1. RFIC-ER system schematic.

RFIC-ER systems are compatible with carbonate/bicarbonate and methanesulfonic acid (MSA) eluents. After the initial eluent is prepared, the systems can operate continuously for up to four weeks without user intervention. Heavy workloads or samples with high-strength matrices may necessitate more frequent replacement or regeneration of analyte trap columns and eluent. Dionex Chromeleon® software system wellness features monitor usage of these components, alerting the operator when maintenance is required.

EXPERIMENTAL CONDITIONS

All ion chromatographic separations were performed using Dionex ICS-1000 or ICS-1500 or ICS-2000 or ICS-3000 systems equipped with ER controllers and Chromeleon chromatography data system. Dionex SRS-300 electrolytic suppressors were used in the Auto-Suppression recycle mode. Deionized water with a specific resistance of 18.2 M Ω -cm was used to prepare all eluents or standards. Drinking water samples were collected from Fremont, CA, San Jose, CA, and Sunnyvale, CA. Groundwater samples were collected from a well in Morgan Hill, CA. The operation of RFIC-ER systems was evaluated using several Dionex anion and cation-exchange separation columns. Table 1 summarizes the detailed chromatographic conditions for various anion and cation columns that are compatible with RFIC-ER systems. Appropriate eluents were prepared in 4 liter eluent bottles and used continuously for up to 28 days before replacement.

| Table 1. Typical RFIC-ER System Operating Conditions | | | | | |
|--|--------------------|---|--|-----------------|--|
| Separation Column | Flow Rate (mL/min) | Eluent | Volume of Eluent Used over 28 Days (L) | | Volume of Eluent Saved Per Year Using RFIC-ER System (L) |
| | | | RFIC-ER | Conventional IC | |
| AS4A | 2.0 | 1.8 mM Na ₂ CO ₃ / 1.7 mM NaHCO ₃ | 4.0 | 80.6 | 998 |
| AS9-HC | 1.0 | 9.0 mM NaCO ₃ | 4.0 | 40.3 | 472 |
| AS14 | 1.2 | 3.5 mM Na ₂ CO ₃ / 1.0 mM NaHCO ₃ | 4.0 | 48.4 | 577 |
| AS14A | 1.0 | 8.0 mM Na ₂ CO ₃ / 1.0 mM NaHCO ₃ | 4.0 | 40.3 | 472 |
| AS22 | 1.2 | 4.5 mM Na ₂ CO ₃ / 1.4 mM NaHCO ₃ | 4.0 | 48.4 | 577 |
| AS23 | 1.0 | 4.5 mM Na ₂ CO ₃ / 0.8 mM NaHCO ₃ | 4.0 | 40.3 | 472 |
| CS12A | 1.0 | 20 mM MSA | 4.0 | 40.3 | 472 |
| CS16 | 1.0 | 30 mM MSA | 4.0 | 40.3 | 472 |

RESULTS AND DISCUSSION

RFIC-ER systems are designed for routine determination of anions or cations in samples matrices of low to moderate ionic strength such as drinking water, groundwater and surface water samples. RFIC-ER systems comply with US EPA Methods 300.0 Part A and 300.1 Part A or equivalent methods for monitoring water purity. Using RFIC-ER systems, isocratic separations of anions can be performed using carbonate/bicarbonate eluents. For example, Figure 2 shows the separation of common anions on a 4 mm IonPac AS23 column under RFIC-ER operating conditions. For 20 consecutive runs, the retention time RSD ranged from 0.02% for phosphate to 0.06% for sulfate; the peak area RSD ranged from 0.08% for nitrite to 0.4% for sulfate. Isocratic separations of cations can be performed using MSA eluents. Figure 3 shows the separation of common cations on a 4 mm IonPac CS12A column under RFIC-ER operating conditions. For 20 consecutive runs, the retention time RSD ranged from 0.04% for magnesium to 0.05% for lithium; the peak area RSD ranged from 0.09% for calcium to 0.18% for ammonium. These results indicate that RFIC-ER systems offer excellent reproducibility in determination of target anions and cations.

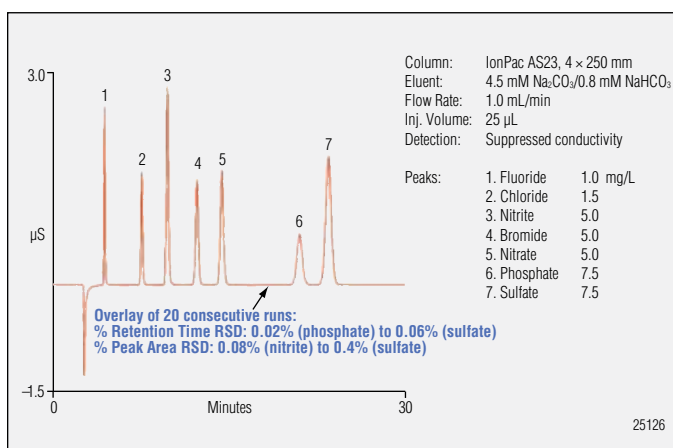


Figure 2. Separation of seven common anions on a 4 mm IonPac AS23 column under RFIC-ER operating conditions.

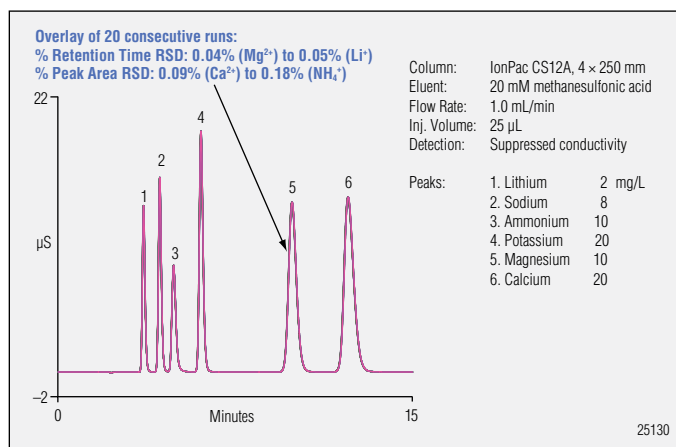


Figure 3. Separation of six common cations on a 4 mm IonPac CS12A column under RFIC-ER operating conditions.

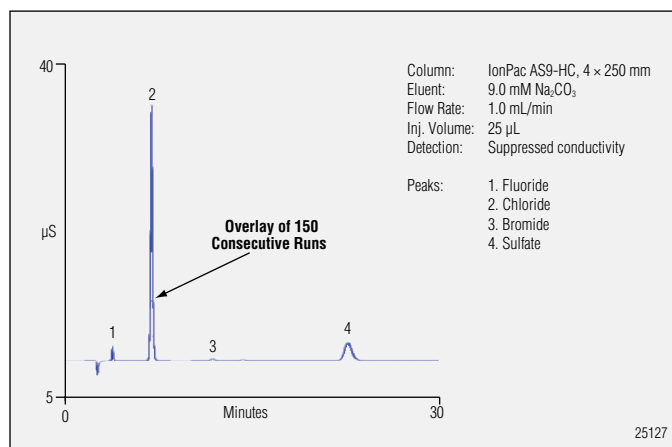


Figure 4. Determination of common anions in a Sunnyvale drinking water sample using a 4 mm IonPac AS9-HC column under RFIC-ER operating conditions.

RFIC-ER systems were used to determine common anions and cations in drinking water and groundwater samples. Figure 4 shows the determination of common anions in drinking water samples using a 4-mm IonPac AS9-HC column. Bromide was added to the drinking water sample as a marker ion at 1.0 mg/L level. For 150 consecutive injections, the retention time RSD was 0.1% for fluoride and bromide, 0.08% for chloride, and 0.09% for sulfate; the peak area RSD was from 0.2% for fluoride and sulfate, 0.03% for chloride and 0.9% for bromide.

Figure 5 shows the determination of common cations in drinking water samples using a 4 mm IonPac CS12A column. Potassium was added to the sample as a marker ion at 1.0 mg/L level. For 300 consecutive injections, the percent retention time RSD was 0.09% for sodium and potassium, 0.1% for magnesium and calcium; the percent peak area RSD was 0.2% for sodium and 0.4% for potassium, magnesium and calcium. These results demonstrate that the RFIC-ER system offers excellent reproducibility in determination of target anions and cations in drinking water samples. Figure 6 shows the determination of common anions in a groundwater sample using a 4 mm IonPac AS23 column. This sample contained a relatively high concentration of nitrate (69 mg/L) possibly due to the fact that it was collected from a well located near agricultural land.

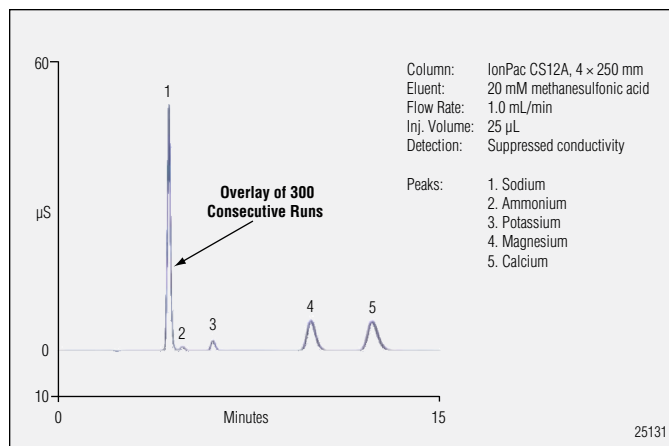


Figure 5. Determination of common cations in a Sunnyvale drinking water sample using a 4 mm IonPac CS12A column operated under RFIC-ER operating conditions.

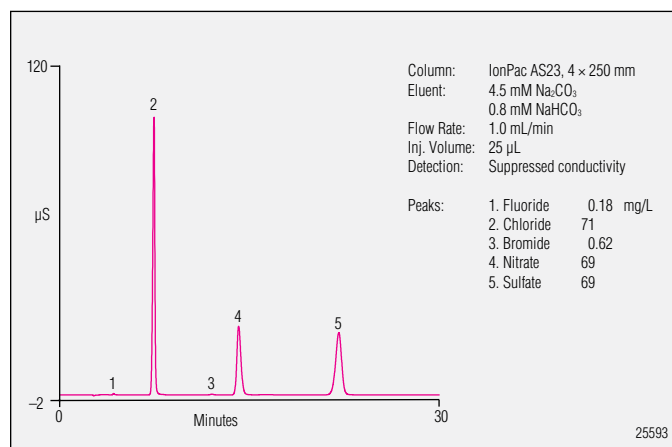


Figure 6. Determination of common anions in a groundwater sample using a 4 mm IonPac AS23 column under RFIC-ER operating conditions.

RFIC-ER systems are designed to operate continuously. The benefit of such systems is that they are always on, and always ready for analysis. The system can remain equilibrated and calibrated without operator intervention. In one study, a 4 mm IonPac AS22 column was used for the isocratic separation of anions in Sunnyvale drinking water samples. After calibration with six different concentrations of a seven anion standard (fluoride, chloride, nitrite, bromide, nitrate, phosphate and sulfate), one standard was tested daily as a calibration check standard. Analyte peak area changes remained within 4.2% for 28 days, as shown in Figure 7. The highest variances occurred in the biologically active nitrate and phosphate. Peak area variance of chloride, which is less prone to biological consumption, remained within 2%. This demonstrates that the system can remain stable enough for continuous use over four weeks without recalibration.

Table 2 shows results obtained from another study in which a drinking water sample was analyzed repeatedly over a period of 15 days. The system was calibrated once at the beginning of this study. Using the determination of chloride as an example, the results demonstrate again that the RFIC-ER system was able to provide highly consistent results over an extended period. RFIC-ER systems have also been evaluated for long term performance. Figure 8 shows representative chromatograms obtained over the course of 2000 injections of a drinking water sample. The results demonstrate that the RFIC-ER system provided highly reproducible separation of common anions in drinking water samples over an extended period.

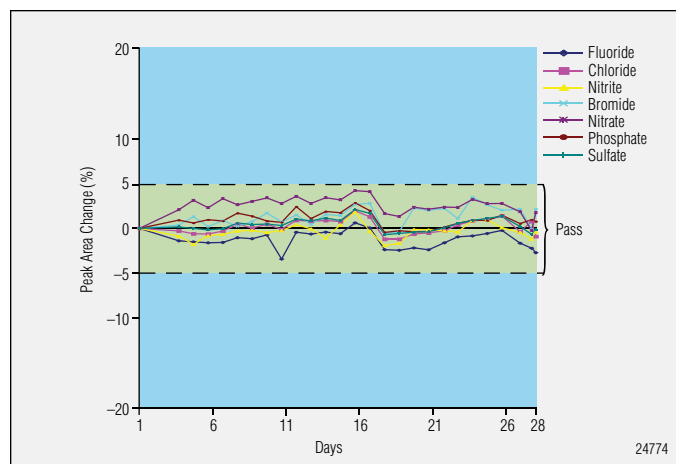


Figure 7. RFIC-ER calibration performance.

| Date | Average Chloride Retention Time (min) (n=20) | RSD (n = 20) | Average Chloride Concentration (mg/L) (n = 20) | RSD (n = 20) | Average Chloride Peak Plate Number (n=20) | RSD (n = 20) |
|------------|--|--------------|--|--------------|---|--------------|
| 12-09-2007 | 7.193 | 0.06% | 100.97 | 0.07% | 10905 | 0.45% |
| 12-13-2007 | 7.200 | 0.08% | 98.34 | 0.16% | 10807 | 0.62% |
| 12-20-2007 | 7.210 | 0.05% | 99.89 | 0.06% | 10850 | 0.23% |
| 12-23-2007 | 7.215 | 0.05% | 99.55 | 0.13% | 10841 | 0.43% |

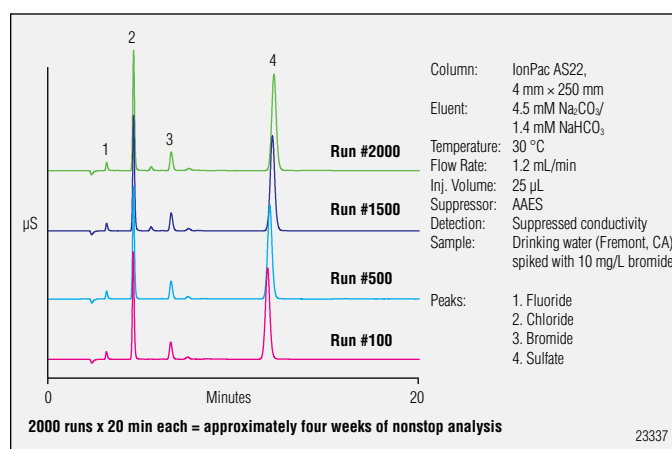


Figure 8. Long-term performance of the RFIC-ER system for the determination of common anions in a drinking water sample.

4 Ion Chromatography Systems with Eluent Regeneration and Their Applications to Groundwater and Drinking Water Analysis

CONCLUSIONS

The results of our studies demonstrate that RFIC-ER systems offer excellent performance in the determination of common anion and cations in drinking water and groundwater samples. Our results also indicate that RFIC-ER systems can remain fully equilibrated and calibrated for long periods. RFIC-ER systems provide key advantages of RFIC systems including ease-of-use and improved reproducibility. RFIC-ER systems can operate continuously for up to four weeks without user intervention, other than loading samples after the initial 4 liter volume of eluent is prepared. RFIC-ER systems offers additional benefits of nonstop operation, minimal

waste generation, increased productivity, and lower cost of ownership. RFIC-ER systems target the applications for determination of common anions and cations in drinking water, surface water, and groundwater. RFIC-ER systems are ideal for EPA Method 300.0 Part A, 300.1 Part A or equivalent applications. RFIC-ER systems are not suitable for high-ionic strength matrices such as untreated wastewaters, and are not compatible with gradient separations or detection methods that alter the eluent composition. 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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