Electrolytic Water Purification for Reagent-Free Ion Chromatography

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INTRODUCTION

Reagent-Free™ Ion Chromatography (RFIC™) systems require deionized water to electrolytically produce eluents for ion-exchange-based separations. For anion separations, electrolytic eluent generators can produce base (KOH or carbonate/bicarbonate) and for cation separations, they can produce acid (methanesulfonic acid). The continuously regenerated electrolytic suppressors also require deionized water for regeneration (either external water or recycled water from the conductivity cell waste). Ionic contaminants in the deionized water will affect purity, concentration, and accuracy of the electrolytically generated eluents. These contaminants may manifest themselves in the separation as additional peaks, increased background conductivity, and large baseline shifts in gradient separations. Ionic contaminants in the electrolytically generated eluents compromise separations, reproducibility, and detection limits.

The RFIC system uses a 1–4 L eluent container filled with deionized water as the eluent source. Dionex recommends ASTM/Type I water which has a resistance > 18.0 MΩ-cm (or a conductivity of 0.055 µS/cm). Benchtop water purification systems (or water polishers) are designed to produce deionized water with resistivity > 18.0 MΩ-cm. However, the quality and consistency of the deionized water varies on the feedwater and the condition of the purification cartridges used for deionization.

This work describes a point-of-use, electrolytic water purification (EWP) system designed specifically for RFIC. The Trovion *i*WP system produces ionically pure water at analytical flow rates just prior to use by the RFIC system. Point-of-use deionization eliminates problems with storing deionized water in eluent containers. The system can also be used to provide external water for electrolytic suppressors. The EWP *i*WP system eliminates issues associated with deionized water quality in RFIC systems and improves analytical performance, reduces water usage, and thus minimizes waste disposal.

EXPERIMENTAL

Instrument

Trovion *i*WP system consisting of:

- Reagent Pump Controller
- CIRA EP

Dionex ICS-2000 system consisting of:

- EGC II KOH eluent generator
- Continuously Regenerated Anion-Trap Column (CR-ATC)

Chromatography Conditions

Columns: IonPac® AS18 or AS20, as specified

Flow rate: As specified

Suppressors: ASRS® 300, 2 and 4 mm

Detection: Suppressed conductivity

Chromatographic Method

IonPac AS20: 0.25 mL/min, 15 mM KOH

Ion Pac AS18: 1.0 mL/min, KOH gradient, as specified

RESULTS AND DISCUSSION

Deionized water has a theoretical resistivity of 18.2 MΩ-cm or 0.0550 µS/cm at 25 °C. The best conductivity/resistivity meters are not useful in measuring ionic contamination below 1 ppb. This is true for fully ionized contaminants such as common inorganic salts (NaCl, Na_2SO_4). This sensitivity does not apply to weakly ionized contaminants such as carbonate, silicate, and borate. The following describes the current capabilities of these meters:

> ***"With the current detection sensitivity of conductivity meters, no effect is seen on the conductivity value as long as the ionic contamination remains below 1 µg/L NaCl equivalent overall."*** [1]

Resistivity meters on benchtop water polishers are relatively crude indicators of ionic purity. Table 1 shows chloride measurements in water from four different benchtop water polishers. In all the cases, water was collected with the resistivity display at 18.2 MΩ-cm. Since most benchtop water polishers use static ion-exchange beds for deionization, the quality of the product water varies as the resins of the deionization cartridges become contaminated with the ions being removed. Carbonate is the highest concentration of contaminants in the feedwater for benchtop polishers, thus the anion capacity is consumed by carbonate/bicarbonate. Recycling water in a benchtop water polisher causes additional consumption of the anion capacity because the recycled water absorbs carbon dioxide from the air. As the anion capacity is consumed by carbonate/bicarbonate, the removal efficiency for other anions decreases.[2]

Table 1. Chloride Concentrations in DI Water From Benchtop Water Polishers

Source	Resistivity (MΩ-cm)	Chloride (µg/L)
Trovion, Campbell	18.2	2.5
Trovion, Bangkok	18.2	0.44
Analytical Lab, San Jose	18.2	0.62
Analytical Lab, San Francisco	18.2	7.8

In the study presented here, water was collected into a 2 L eluent container from a benchtop water polisher, placed on the Dionex IC, and pumped at 1.0 mL/min directly to a conductivity cell bypassing all eluent generator components, valve, and separator column. The eluent container was agitated periodically. Data was collected at 1 h intervals for 24 h. The results are seen in Figure 1. Due to the absorption of carbon dioxide from the air, the conductivity continually increases. The carbon dioxide forms carbonic acid as seen in equation 1:

Equation 1: $$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

In anion RFIC, carbonate in the water used for eluent generation may be observed in a gradient run as higher background conductivity, a baseline shift in the gradient, or as a carbonate peak.

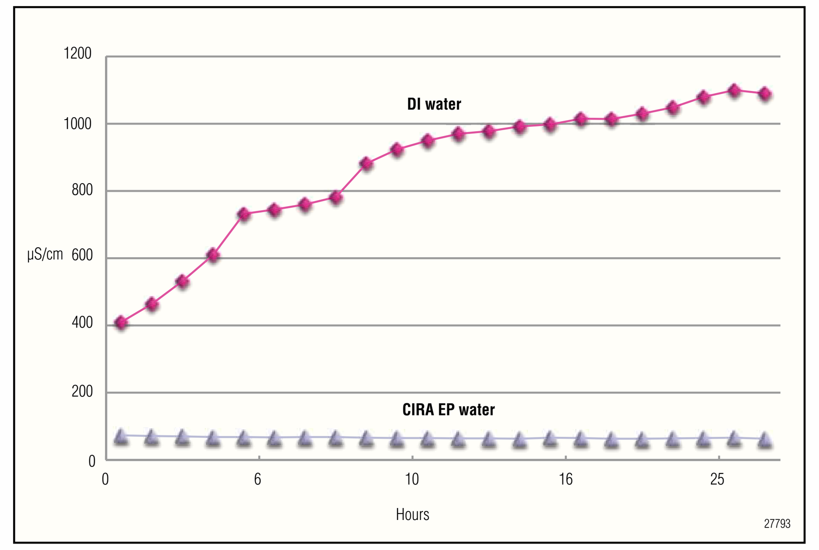
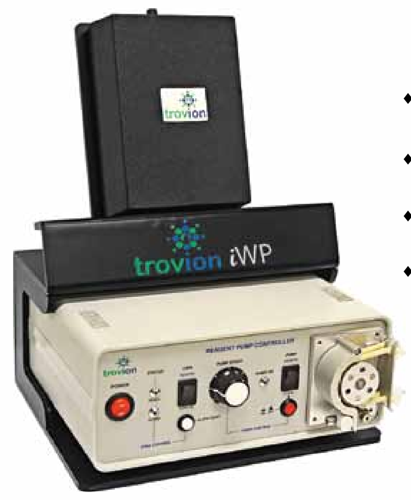


Figure 1. Conductivity for DI water.

The Trovion *i*WP solves the problems of trace ionic contaminants and carbonate in DI water using a novel EWP at the inlet to the RFIC pumping system. This ensures production–in real time–of ionically pure water for electrolytic eluent generation and suppression. The Trovion *i*WP system (Figure 2) consists of a Reagent Pump Controller (RPC) and the CIRA EP electrolytic water purifier. The RPC consists of a variable speed, heavy-duty, dual-channel peristaltic pump, constant current power supply (for the CIRA EP), and relay/TTL input control by the IC system. This unit is compact and does not require a separate water reservoir as it uses the eluent bottle of the RFIC system.



- Point-of-use water-electrolytic water purification system designed specifically for RFIC
- Uses patent pending CIRA electrolytic ion removal and regeneration (EIR2) technology
- Improves IC background conductivity by removal of carbonate and trace ions from RFIC eluent water
- Reduces SRS external water usage by using vacuum induced aerosol regeneration (VIAR)

Figure 2 . Trovion iWP.

The CIRA EP is an analytical-scale electrolytic water purifier that uses continuous electrolytic regeneration to ensure highly efficient ion removal and to maintain the ion exchange material in the fully regenerated form, thereby optimizing the ion removal capacity. By using homogenous cation and anion resin beds, the removal of weakly ionized contaminants, such as carbonate and silicate, is greatly improved compared to conventional deionization using mixed resin beds. Power consumption of the CIRA EP is below 1 W. Figure 3 shows the internal components of the CIRA EP. The small volume of ion-exchange material used in the CIRA EP (2 mL) does not contribute significantly to the total organic carbon content (TOC) of the product water. This eliminates the need for a UV lamp for photo-oxidization of organics. The CIRA EP can purify RO and Type I, II, or III waters.

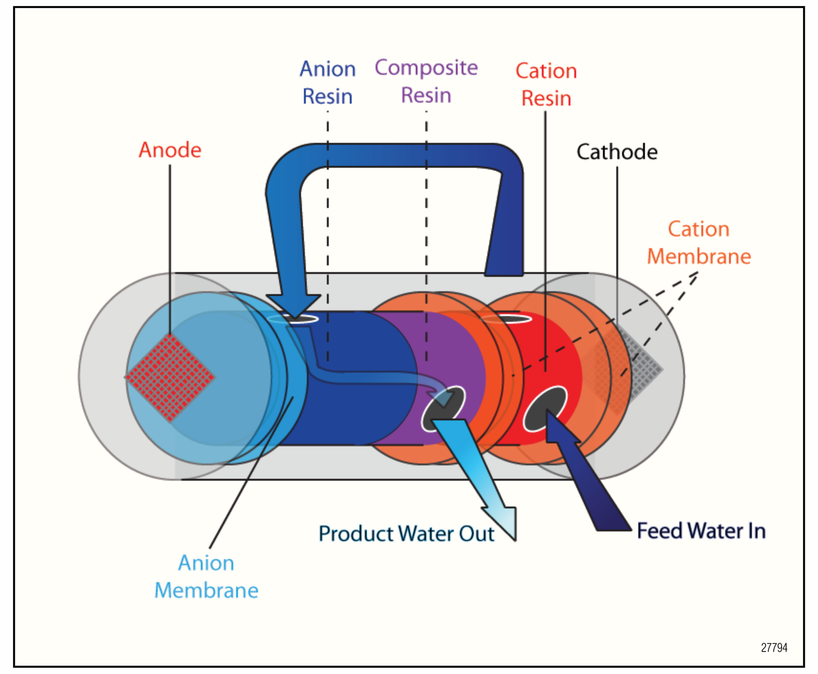


Figure 3. CIRA EP flow schematic.

Water from the eluent bottle is drawn from the peristaltic pump and pumped to the feedwater inlet of the CIRA EP. The feedwater is passed through the two ion depletion chambers, producing the ionically pure water. The purified water then flows to four outlet ports; two ports for IC pumps and two ports for suppressors, as seen in Figure 4. The port marked **Return** sends excess purified water back to the eluent container. If only one IC system is being used, the other outlet ports are plugged. Unlike static mixed bed deionization, the CIRA EP is continuously regenerated, so water can be recycled without comprising device lifetime or water quality.

- **Feed Water** – RO, distilled or DI water from eluent bottle
- **Return** – Excess purified water to eluent bottle
- **Rinse In** – Regenerant from SRS waste
- **Rinse Out** – Waste
- **Eluent 1** – Ionically pure water to IC pump 1
- **Supp.1** – Ionically pure water to IC suppressor 1
- **Eluent 2** – Ionically pure water to IC pump 2
- **Supp. 2** – Ionically pure water to IC suppressor 2

Figure 4. CIRA EP.

The ion-exchange removal of trace ionic contamination is more effective in water than in an acid or base eluent. By removing trace ionic contamination (including carbonate) in the deionized water before the RFIC pump, the ion removal capacity of the CR-ATC can be maximized, resulting in pure acid or base eluents.

Figure 5 shows a comparison of polisher DI water and CIRA EP water analyzed as a sample in an isocratic RFIC anion run. In addition to the large reduction in the carbonate peak for the CIRA EP water, other anionic contaminants such as fluoride and chloride are also at lower concentrations in the CIRA EP water compared to the polisher DI water. In Figure 1, the lower trace was generated by passing the DI water from the first conductivity cell to the CIRA EP feed inlet. The product water from CIRA EP passed through a second conductivity cell and the results are shown in the lower trace. Note that the conductivity value was close to theoretically pure water over the 24 h period.

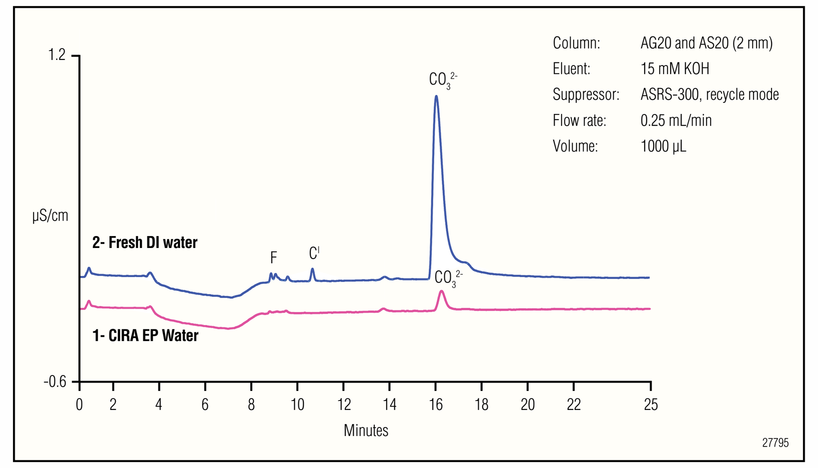


Figure 5. Anion purity comparison of CIRA EP water and benchtop polisher water.

Figure 6 compares RFIC anion data for CIRA EP water vs a 100 ppt standard prepared in DI water run as samples from a benchtop water polisher. This data was obtained using the AutoPrep[3,4] technique for ultratrace analysis with a 10 mL sample loop. Reduction in carbonate was compared with and without a CRD 200. The CIRA EP water has 85–95% lower carbonate than the DI water (see Table 2).

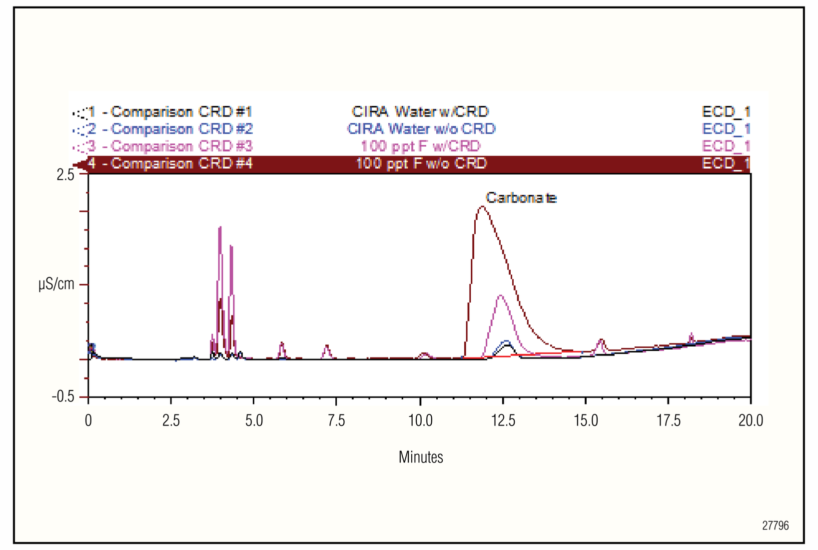


Figure 6. CIRA EP is effective for decarbonation. Chromatogram overlay of four different sample injections to AutoPrep. Condition: 10 mL large loop.

Figure 7 shows a schematic of an RFIC system using the Trovion *i*WP. The system is shown operating in the SRS® in the Vacuum Induced Aerosol Regeneration mode (VIAR, patent pending). This is a type of external water mode for the SRS and uses a low-flow rate (0.5–0.8 mL/min) combined with a vacuum at the SRS regenerant outlet. The vacuum is created using the second channel of the RPC peristaltic pump. The suppressed eluent (water containing trace anions or cations) from the conductivity cell can be recycled to the eluent container, thereby further reducing water usage and waste generation. The system can also be operated in the SRS recycle mode.

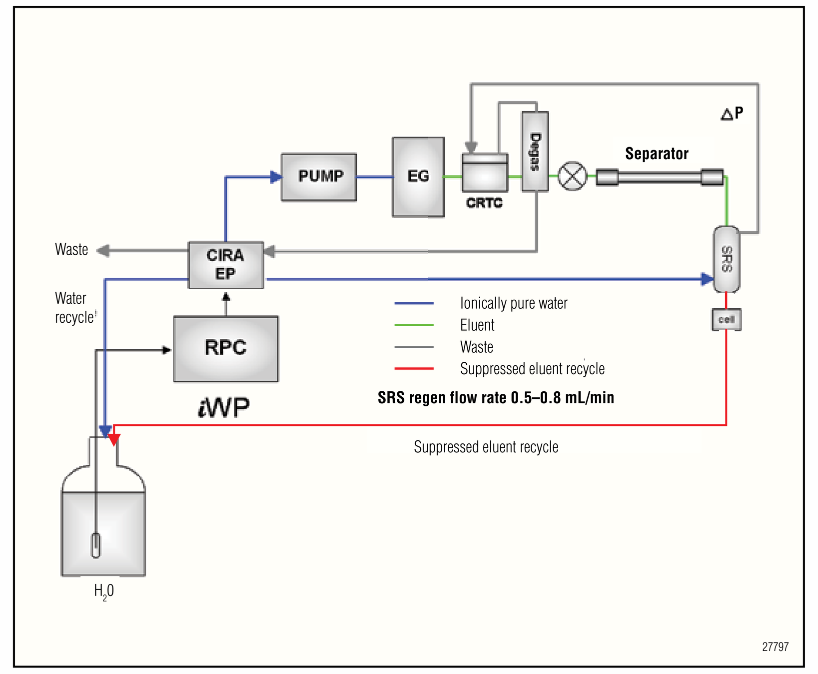


Figure 7. iWP with RFIC (VIAR mode).

Figure 8 compares anion RFIC data using the Trovion *i*WP system to purify the water for electrolytic eluent generation and suppression. The data are gradient blanks collected at 3, 24, and 72 h. Note that the background conductivity, carbonate peak, and gradient baseline shift decreases as the CIRA EP water is used. Carbonate present in the RFIC system (primarily in the CR-ATC) decreases as the low carbonate CIRA EP water is used in the system. The noise decreases as the background conductivity and carbonate levels decrease.

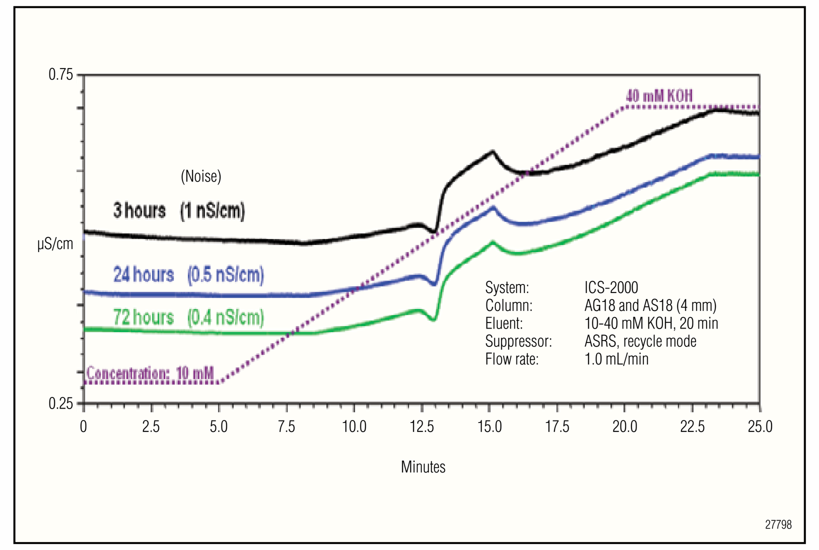


Figure 8. CIRA EP water reduces background conductivity and noise.

In Figure 9, a comparison of the three SRS regeneration modes, recycle, external water, and VIAR is shown. The lowest noise is obtained in the VIAR mode as shown in Table 3. Table 4 shows a comparison of water usage in conventional external water and the VIAR mode. When combined with suppressed eluent recycle mode, the advantages of the VIAR include:

- Reduced external water consumption and waste by > 85%
- Noise equal to or lower than conventional external water
- Higher KOH concentration to the CRD 200 improves carbonate removal efficiency
- Simple to implement using the RPC

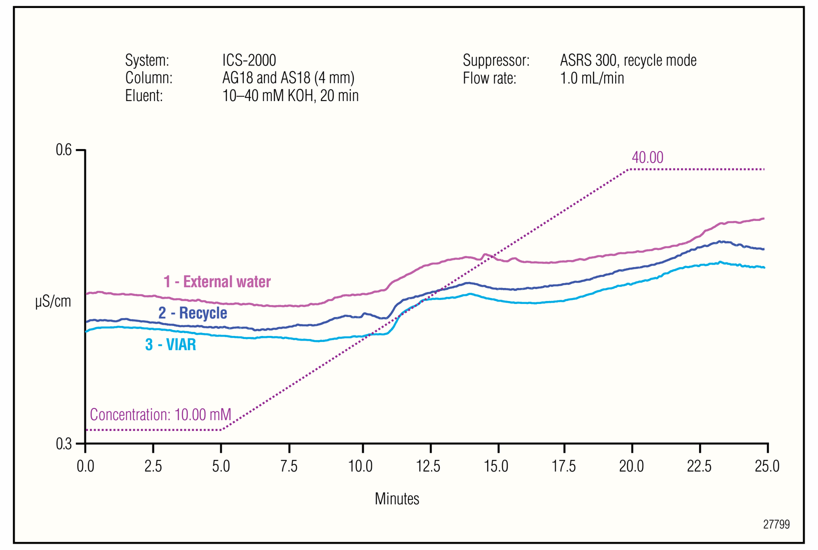


Figure 9. VIAR provides low noise with low water consumption.

Table 2. Comparison of Carbonate Levels

Conditions	Relative Carbonate Peak Area
CIRA EP	1.00
CIRA EP w/CRD 200	0.671
100 ppt std. in DI water	20.0
100 ppt std. in DI w/CRD 200	4.71

Table 3. Comparison of SRS Regen. Modes

SRS Regen. Mode	Flow rate (mL/min)	Noise[a] (nS/cm)
External water	3.0	0.82
Recycle	1.0	0.98
VIAR	0.5	0.65

[a] Noise measured at 1.0–1.5 min at 10 mM KOH.

Table 4. Comparison of Water Usage[b] in RFIC Using External Water for Suppression

	Conventional External Water (mL/min)	*i*WP External Water VIAR Mode (mL/min)	% Water Savings
2 mm	2.3	0.4	83
4 mm	5.2	0.6	88

[b] For 2 mm, eluent flow 0.3mL/min and for 4 mm, 1.2 mL/min with suppressed eluent recycle mode.

SUMMARY

The Trovion *i*WP electrolytic water purification system solves the problems of water quality when used with the Dionex RFIC system. The advantages of this system include:

- Production of ionically pure water in real time for RFIC eluent generation and suppression at analytical flow rates
- Use of electrolytic technology that is consistent with the Dionex RFIC systems (EG, CR-TC, SRS, ESP)
- Consistent water quality as a result of continuous electrochemical regeneration (no cartridges to replace or dispose)
- Highly efficient decarbonation resulting in lower background, less drift, and smaller carbonate peak
- Improved CR-ATC performance by reducing carbonate load
- Greatly reduced water consumption and waste generation with improved SRS performance (VIAR mode with suppressed eluent recycle)
- Low TOC without UV (no lamp to replace)
- Feedwater can be RO, Type I, II, or III
- Dual-channel ready
- Simple to maintain
- Small footprint

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