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Electrolytic Water Purification for Reagent-Free Ion Chromatography

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Introduction

Reagent Free Ion Chromatography (RFIC) requires deionized water to electrolytically produce eluents for ion exchange-based separations. For anions separations, electrolytic eluent generators can produce base (KOH or carbonate/bicarbonate) or acid (methanesulfonic acid). The continuously regenerated electrolytical 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.

RFIC system uses a one to four liter eluent container that is filled with deionized water as the eluent source. Dionex recommends ASTM/Type I water which has a resistance of > 18.0 MΩ/cm (or a conductivity of 0.055 µS/cm). Bench top water purification systems ("water polishers") are designed to produce deionized water with resistivity $\geq$ 18.0 MΩ/cm. In reality, the quality and consistency of the deionized water varies depending on the feed water and the condition of the purification cartridges used for deionization.

This poster describes a point of use, electrolytic water purification 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. This electrolytic water purification system eliminates issues associated with deionized water quality for RFIC system and improves analytical performance, reduces water usage and thus, minimizes waste disposal.

Experimental

Instrument

Trovion ***i***WP Electrolytic Water Purification system consisting of:
Reagent Pump Controller
CIRA EP

Dionex ICS 2000 with a
EGC II KOH eluent generator and
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 4mm (anion self- regenerating suppressor, SRS)
Detection: Suppressed Conductivity

Chromatographic Method

1. IonPac AS20 - 0.25 mL/min, 15 mM KOH
2. 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 a conductance of 0.0550 µS/cm @ 25°C. The best conductivity/resistivity meters are not useful for measuring ionic contamination below 1 ppb. This in only true for fully ionized contaminants such as common inorganic salts (NaCl, Na_2SO_4). This sensitivity does not apply to weakly ionized contaminates 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]

The resistivity meters on bench top water polishers are relatively crude indicators of ionic purity. Table 1 below shows chloride measurements in water from four different bench top water polishers. In all case, the water was collected with the resistivity display of 18.2 MΩ-cm. Since most bench top water polishers use static ion exchange beds for deionization, the quality of the product water varies as the resins of the deionization cartridges becomes “contaminated” with the ions being removed. Carbonate is generally the highest concentration contaminant in the feed water for bench top polishers, thus the anion capacity is consumed by carbonate/bicarbonate. Recycling water in a bench top water polisher causes additional consumption of the anion capacity since 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].

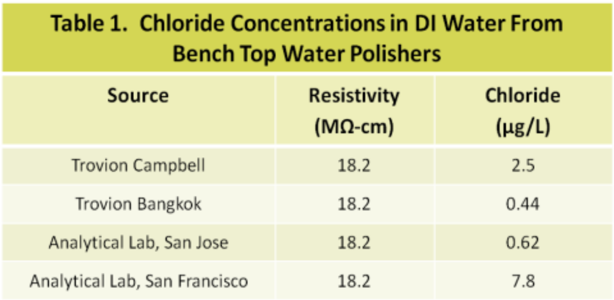


Table 1. Chloride Concentrations in DI Water From Bench Top Water Polishers

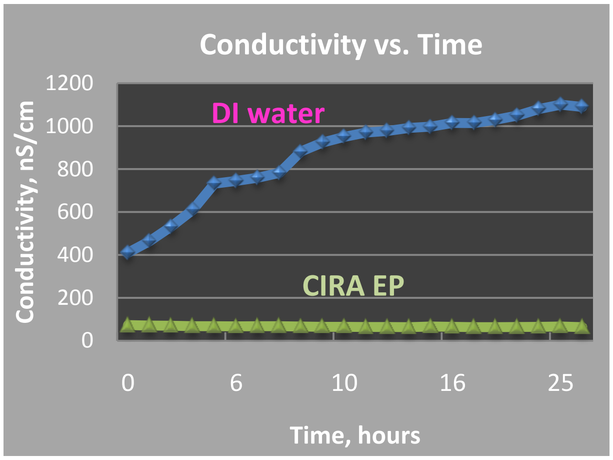
Source	Resistivity (MΩ-cm)	Chloride (µg/L)
Trovion Campbell	18.2	2.5
Trovion Bangkok	18.2	0.44
Analytical Lab, San Jose	18.2	0.62
Analytical Lab, San Francisco	18.2	7.8

Water collected into a 2 L eluent container from a bench top water polisher was placed on a Dionex IC as was pumped at 1.0 mL/min directly to a conductivity cell, by passing all eluent generator components, valve and separator column. The eluent container was agitated periodically. Data was collected at one hour intervals for 24 hours. The results are shown in Figure 1. The conductivity continually rises as a result of the absorption of carbon dioxide from the air. The carbon dioxide forms carbonic acid as shown in equation 1

$$CO_2 + H_20 \rightarrow H_2CO_3 \rightarrow H^+ + HCO_3^- \quad \text{(Eq.1)}$$

In anion RFIC, carbonate in the water used for eluent generation analyte will as be observed in a gradient run as higher background conductivity, as a carbonate peak and will also cause a baseline shift in the gradient.

Figure 1. Conductivity for DI Water



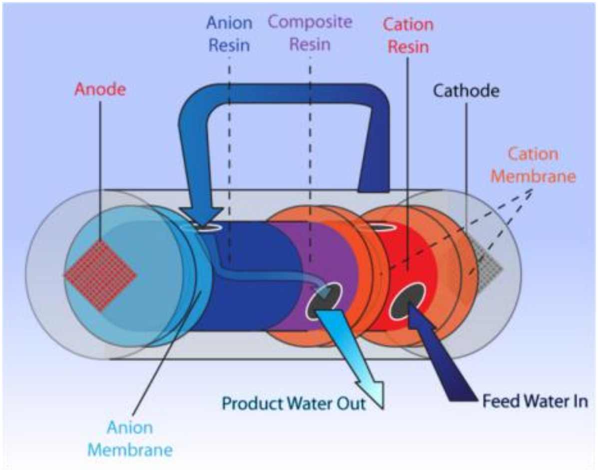
The Trovion ***i***WP solves the problems of trace ionic contaminants and carbonate in DI water using a novel electrolytic water purifier at the inlet to the RFIC pumping system. This ensures production, in real time, of ionically pure water for electrolytic eluent generation and suppression. The Trovion ***i***WP, shown in Figure 2, consists of the Reagent Pump Controller (RPC) and the CIRA EP electrolytic water purifier. The RPC contains a variable speed, heavy duty, dual channel peristaltic pump, constant current power supply (for the

Figure 2. Trovion *i*WP

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.

The CIRA EP is an analytical scale electrolytic water purifier which uses continuous, electrolytic regeneration to ensure highly efficient ion removal and 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, distilled, Type I, II or III waters.

Figure 3. CIRA EP Flow Schematic



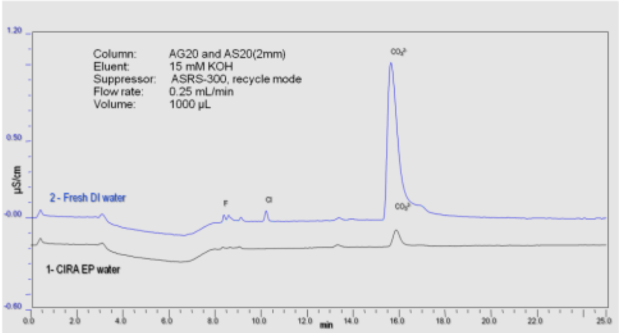
Water from the eluent bottle is drawn to the peristaltic pump and pumped to the feed water inlet of the CIRA EP. The feed water passes through the two ion depletion chambers, producing the ionically pure water. The purified water then flows to four outlet ports; two ports for IC pumps and two ports for suppressors, as shown 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.

Figure 4. CIRA EP Rear Panel

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.

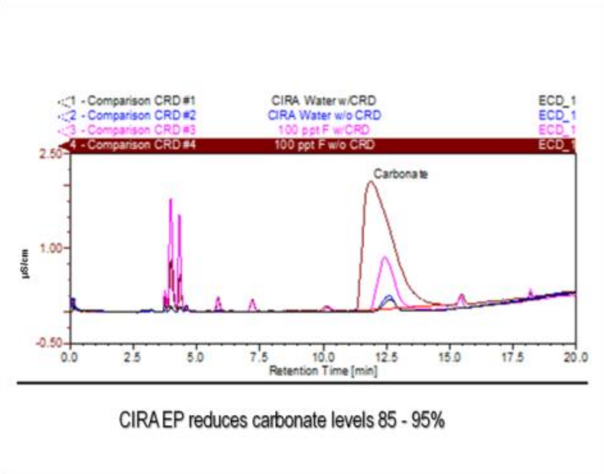
Figure 5 shows a comparison of polisher DI water and CIRA EP water analyzed as a sample in an isocratic RFIC anion run. In addition to the large reduction in the carbonate peak for the CIRA EP water, other anionic contaminants such as fluoride and chloride are also at lower concentrations in the CIRA 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. Product water from the CIRA EP passed through a second conductivity cell and the results are shown in the lower trace. Note that the conductivity value is close to theoretically "pure" water over the 24 hour period

Figure 5. Anion IC of DI Water and CIRA EP Water



(55 nS/cm). Figure 6 compares RFIC anion data for CIRA EP water vs. a 100 ppt standard prepared in DI water. The two water sources were run as samples using the AutoPrep[3,4] technique for ultra-trace analysis with a 10 mL sample loop. Reduction in carbonate was compared with and without a CRD-200. The CIRA EP reduces carbonate 85-95%. (see Table 2). Figure 7 shows a schematic of an RFIC system using the Trovion *i*WP. The system is shown operating the SRS in the vacuum induced aerosol regeneration mode (VIAR, patent pending). This is an external water mode for the SRS that uses a low flow rate (0.5-0.8 mL/min) combined with applying 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 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 hours.

Figure 6. CIRA EP is Effective for Decarbonation



CIRA EP reduces carbonate levels 85 - 95%

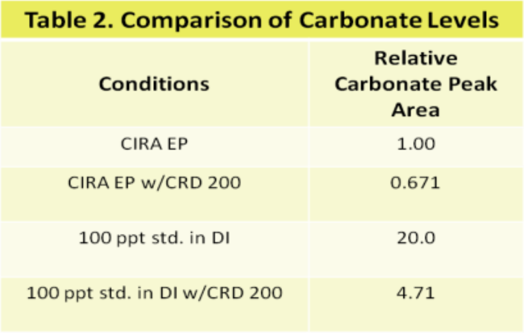


Table 2. Comparison of Carbonate Levels

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

Figure 7. *i*WP with RFIC (VIAR mode)

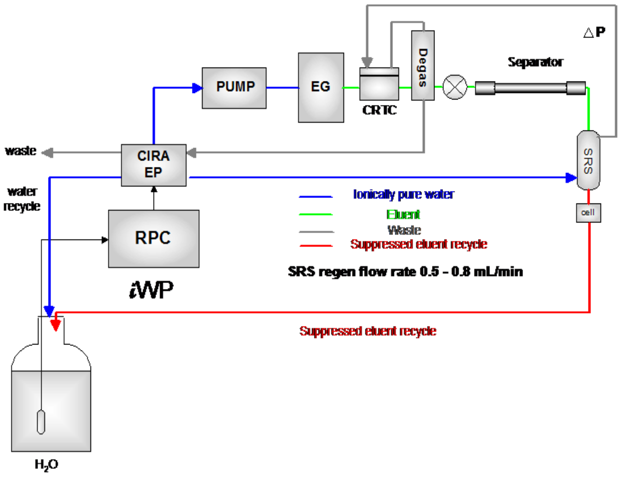
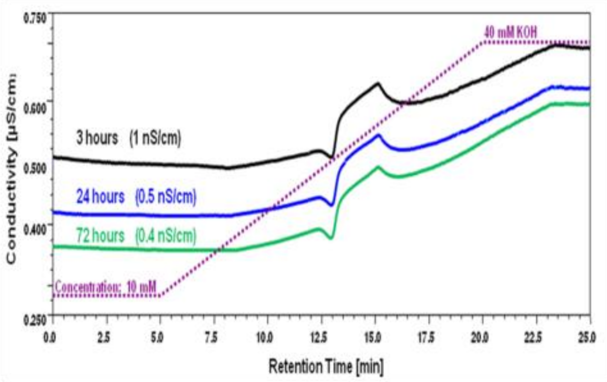
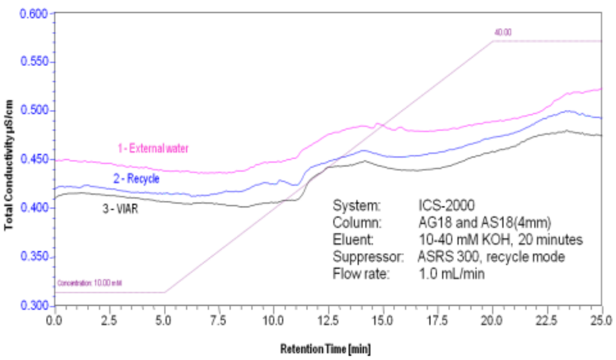


Figure 8. CIRA EP Water Reduces Background Conductivity and Noise (noise in parenthesis)



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. In Figure 9, a comparison of the three SRS

Figure 9. VIAR Provides Low Noise with Low Water Consumption



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 (with suppressed eluent recycle). The advantages of the VIAR mode with suppressed eluent recycle include

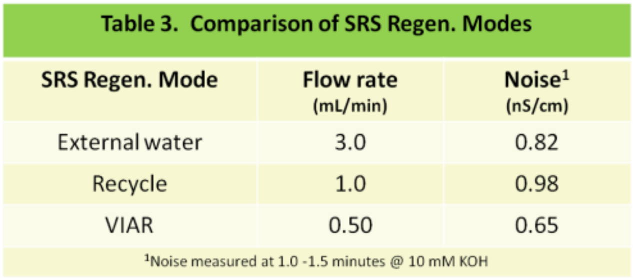


Table 3. Comparison of SRS Regen. Modes

SRS Regen. Mode	Flow rate (mL/min)	Noise[1] (nS/cm)
External water	3.0	0.82
Recycle	1.0	0.98
VIAR	0.50	0.65

[1]Noise measured at 1.0 -1.5 minutes @ 10 mM KOH

- reduced external water consumption and waste by > 85%
- noise equal to or lower than conventional external water
- provides higher KOH concentration to CRD 200 to improve carbonate removal efficiency
- simple to implement using the RPC

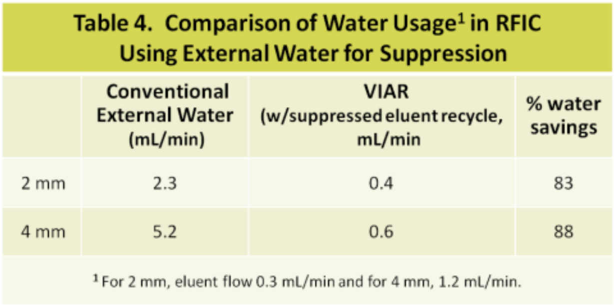


Table 4. Comparison of Water Usage[1] in RFIC Using External Water for Suppression

	Conventional External Water (mL/min)	VIAR (w/suppressed eluent recycle, mL/min	% water savings
2 mm	2.3	0.4	83
4 mm	5.2	0.6	88

[1] For 2 mm, eluent flow 0.3 mL/min and for 4 mm, 1.2 mL/min.

Summary

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

- Production of "ionically" pure water in real time for RFIC eluent generation and suppression at analytical flow rates
- Uses electrolytic technology consistent with Dionex RFIC (EG, CR-TC,SRS,ESP)
- Consistent water quality as result of continuous electrochemical regeneration (no cartridges to replace or dispose)
- Highly efficient decarbonation results in lower background, less drift and smaller carbonate peak
- Improves CRATC 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)
- Feed water can be RO, Type I, II or III Dual channel ready
- Simple to maintain
- Small foot print
- Dual channel ready

References

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