

# Novel Electrodeionization Devices: Applications in Inorganic Analysis

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## ABSTRACT

Electrodeionization (EDI) is a well established technique for the production of ultrapure water (UPW). In this paper the authors discuss novel electrodeionization devices which have been developed primarily for use in chemical analysis. These EDI devices can be incorporated directly into the analytical instruments for on-line production of UPW, or can be used off-line for automated sample dilution or sample preparation. Applications of these EDI devices in trace analysis of inorganic ions will be shown.

## INTRODUCTION

Electrodeionization (EDI) is a well established technique for the production of ultrapure water (UPW). Conventional EDI uses mixed bed depletion chambers for the removal of contaminant ions. Recent advances in EDI cell chemistries have resulted in the improved removal of weakly ionized contaminants and improved resistance to fouling from calcium and magnesium [1]. To date, all commercial EDI systems have been developed for process and laboratory level UPW production.

UPW is the most commonly used reagent in inorganic analysis. Techniques such as ion chromatography, atomic spectroscopy and inorganic mass spectrometry rely on UPW in order to achieve low detection limits. In most instances, water is taken from a bench top laboratory water purifier and used to make reagents or transferred to a container for sample processing. This non-point-of-use process can result in contamination of the water from container leaching, bacterial growth or absorption of contaminants from the air. In addition, the quality of the UPW produced from bench top water purifiers varies over time as the mixed polishing beds become expended. This variation in water quality results in inconsistent chemical blanks, which compromise detection limits.

EDI offers the advantage of being a dynamic process and as a result can produce a consistent UPW product. We have used this advantage of EDI to develop point-of-use EDI devices, which are designed for integration into the analytical instrument and analysis process. In this paper we will demonstrate the use of these EDI devices in trace analysis using ion chromatography (IC).

## EXPERIMENTAL

The Trovion CIRA electrolytic purifiers (Trovion Pte. Ltd., Singapore) were used as point-of-use EDI devices for IC analysis. [Figure 1](#) shows a schematic of a CIRA purifier used for the analysis of anions by IC. [Figure 2](#) shows a CIRA purifier used for the analysis of cations by IC. The CIRA devices were used with a Dionex RFIC<sup>®</sup> (Reagent Free Ion Chromatography) ICS-1500 ion chromatograph (Dionex Corp, Sunnyvale, CA). For anion analysis by IC, a Dionex AS 17 separator (2 mm) column was used with an ASRS300 suppressor. Potassium hydroxide eluent was generated using the RFIC<sup>®</sup> electrolytic eluent generator. For cation analysis, a Dionex CS12A separator column (2 mm) was used with a CSRS300 suppressor. Methane sulfonic acid was generated using the RFIC electrolytic eluent generator. The Dionex RFIC<sup>®</sup> electrolytic eluent generation system uses a deionized water feed to electrochemically produce eluents. A Trovion CIRA 10X electrolytic purifier was used to deionize the water inline with the electrolytic eluent generation system.

The CIRA 11A electrolytic purifier is a layered EDI device with two discreet depletion chambers as shown in [Figure 1](#). The CIRA purifiers are designed to operate in a flow rate range of 0.1 to 10 mL · min<sup>-1</sup> and their compact size makes them ideal for integrating into analytical instrumentation. CIRA can be configured so that water flows through one or both depletion chambers in parallel or serial fashion. For the experiments performed below, the suppressed anion eluent (water containing trace anions) exiting the conductivity cell of the IC was passed through the anion-mixed bed depletion chamber. The product water is deionized and the anion level in the product water is below 0.1 ng · kg<sup>-1</sup>. This UPW is then used to process the next

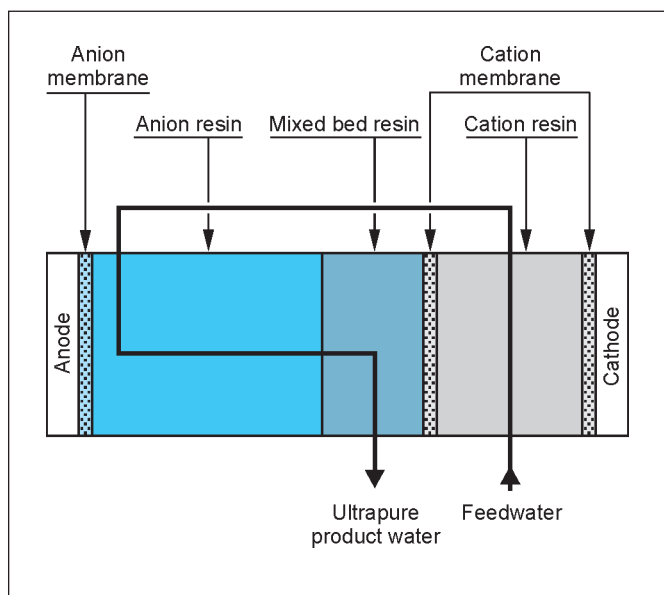


Figure 1:  
Schematic of a CIRA 11A electrolytic purifier.

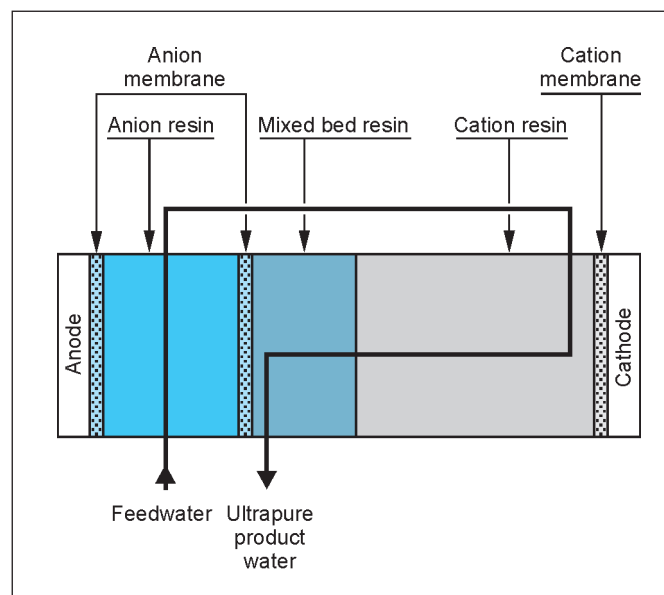


Figure 2:  
Schematic of a CIRA 11C electrolytic purifier.

sample or standard. The UPW from the CIRA 11A is used to rinse the large volume sample loop, which prevents sample carry-over and lowers the blank. The cation depletion chamber of the CIRA 11A can be used to remove cations from the sample or from the suppressor waste stream. Table 1 shows some of the properties of the CIRA 11A and 11C.

For cations analysis, the suppressed eluent (water containing trace cations) is passed through the cation-mixed bed depletion chamber. The product water is deionized and the cation level in the product water is below  $0.1 \text{ ng} \cdot \text{kg}^{-1}$ . The UPW from the CIRA 11C is used to rinse the large volume sample, which prevents sample carry-over and reduces the blank. The anion depletion chamber of the CIRA 11C can be used to remove anions from the sample or the suppressor waste stream.

This approach of purifying the waste stream and using the purified waste stream for calibration and sample processing is referred to as IonPrep. The diagram in Figure 3 shows this basic configuration of the IC system for ultra trace analysis with IonPrep and the CIRA purifier [2]. With the addition of a large volume autosampler, this configuration allows for fully automated calibration and analysis at part-per-trillion (ppt or  $\text{ng} \cdot \text{kg}^{-1}$ ) levels. Note that in the configuration shown in Figure 3, only one analytical pump is required. Sample and standards are drawn into the sample loops using a peristaltic pump.

This configuration allows for fully automated operation, and the CIRA purifier results in extremely low and consistent chemical blanks. Figure 4 shows a Dionex RFIC ICS-1500 ion chromatograph configured with the Trovion IonPrep system with CIRA for ultra trace analysis.

Property	11A	11C
Layered chamber	Anion-mixed bed	Cation-mixed bed
Void volume (layered chamber)	800 $\mu\text{L}$	800 $\mu\text{L}$
Homogeneous chamber	Cation	Anion
Void volume (homogeneous chamber)	200 $\mu\text{L}$	200 $\mu\text{L}$
Typical voltage	25 V @ 30 mA	25 V @ 30 mA
Flow rate	0.1 to 10 $\text{mL} \cdot \text{min}^{-1}$	0.1 to 10 $\text{mL} \cdot \text{min}^{-1}$

Table 1:  
Properties of CIRA electrolytic purifiers.

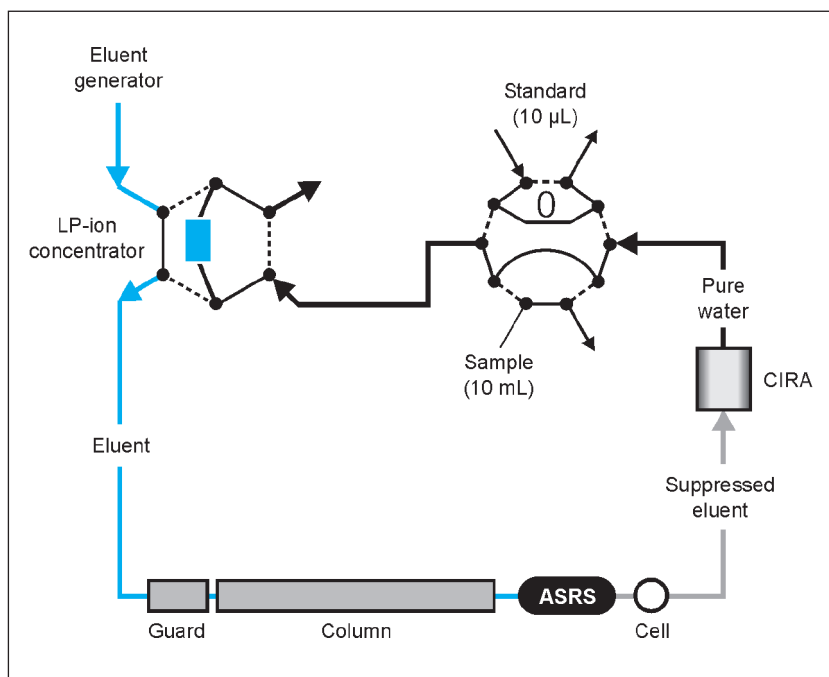


Figure 3:  
IC schematic using CIRA electrolytic purifier.  
ASRS ASRS suppressor

Figure 4:  
IC system with IonPrep for trace ion analysis.

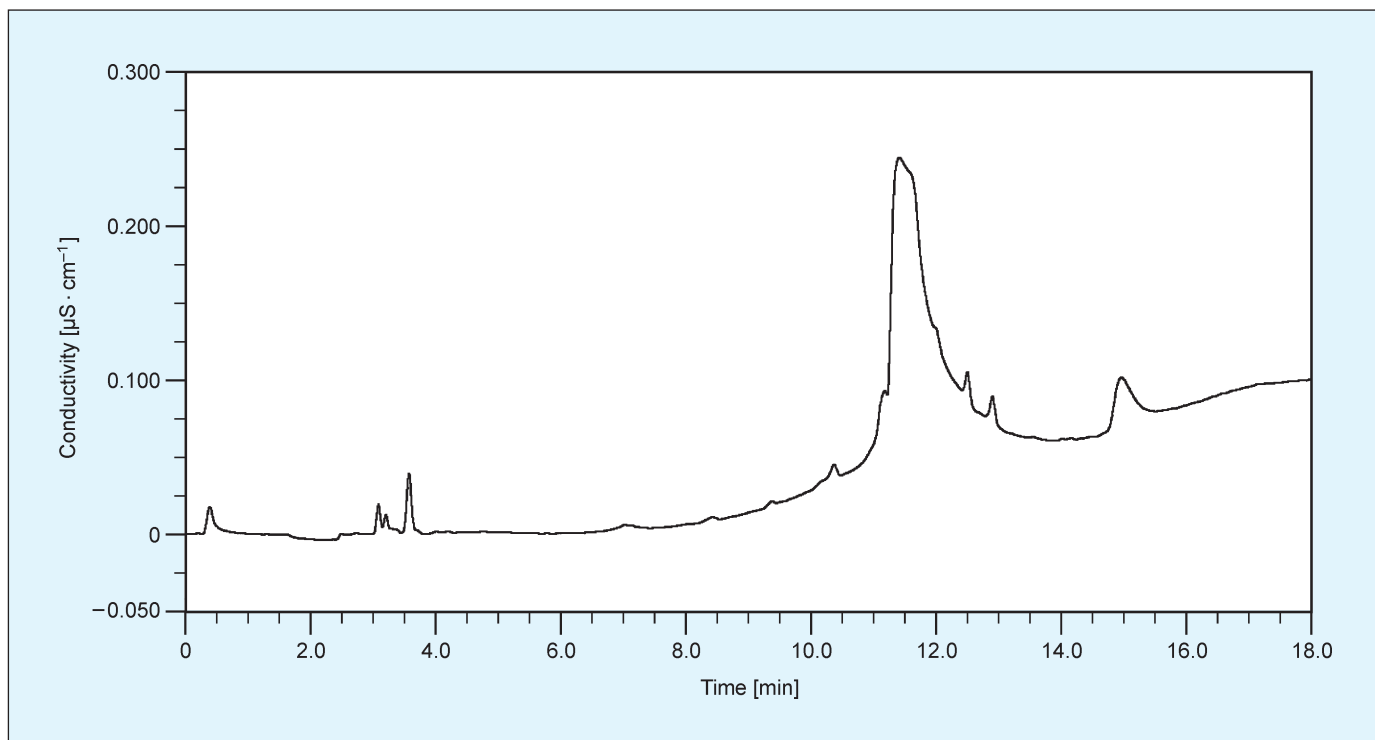


Figure 5:  
IC anion blank with IonPrep.

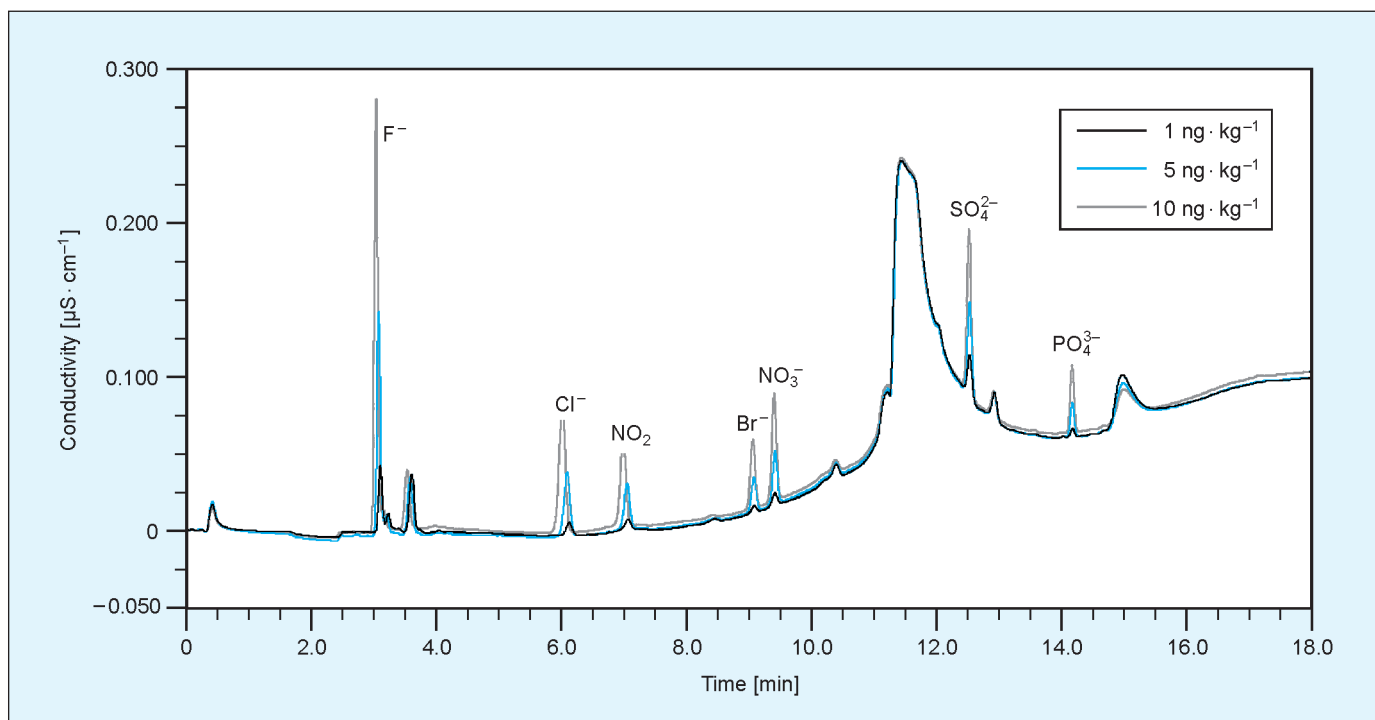


Figure 6:  
IC anion calibration at the  $\text{ng} \cdot \text{kg}^{-1}$  level using IonPrep.

## RESULTS

Figure 5 shows a typical system blank that results when using a 20 mL sample loop. The trace anions (sub  $\text{ng} \cdot \text{kg}^{-1}$ ) shown in this chromatogram result from concentrating 20 mL of the conductivity cell waste which was purified by passing through the anion-mixed bed depletion chamber of the CIRA 11A. The peak at 11.8 min is carbonate, which is not analyzed in this system.

Figure 6 shows an overlay of a calibration run at the 1, 5 and 10  $\text{ng} \cdot \text{kg}^{-1}$  levels for the common anions. The calibration is performed automatically by using a single part-per-billion anion standard, loading the small loop (10  $\mu\text{L}$ ) and then diluting with the CIRA water in the 20 mL loop. This results in a 2 000 fold dilution of the  $\text{ng} \cdot \text{kg}^{-1}$  standard, which allows for calibration at the  $\text{ng} \cdot \text{kg}^{-1}$  level. This novel approach is feasible as a result of the point-of-use UPW produced from CIRA [3]. The UPW from CIRA is used for dilution of the standard and rinsing of the system between samples. As a result, detection limits in the low to sub  $\text{ng} \cdot \text{kg}^{-1}$  level can be achieved routinely for monitoring ionic contamination in UPW.

## CONCLUSION

Point-of-use electrolytic water purifiers, based on EDI technology, have been developed for integration into analytical instrumentation. Using the electrolytic purifiers with ion chromatography, we have demonstrated the ability to measure common ions at the low part-per-trillion level. The point-of-use electrolytic purifiers will find use in other inorganic analytical applications including automated sample pretreatment and reagent purification and preparation.

## REFERENCES

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- [3] *US Patent Application*, **2006**. US2006-0231403.

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