Electrolytic Devices for Automated Sample Preparation in Ion Chromatography

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INTRODUCTION

Many samples to be analyzed by ion chromatography (IC) require pretreatment before injection for a variety of reasons. Matrix elimination procedures may be necessary to remove contaminants that can interfere with an analysis or damage analytical columns. Neutralization of acid or base is often required before injection to prevent column overloading and other effects. The quality of trace analyses benefits from the purity of transfer/loading water. Electrolytic devices provide many approaches to solving inline sample preparation problems and offer advantages such as their continuously regenerated nature.

Manual sample pretreatment options can be expensive and time consuming. Manual procedures require skillful attention to detail by the operator and thus are susceptible to errors, and can be very difficult to monitor and verify.

Early innovations in the application of electrolytic devices to IC brought about a revolution with electrolytic suppression of the eluent prior to conductivity detection. Research in new membranes led to the development of cation analysis with electrolytic suppression. Subsequent developments in electrolytic devices produced Reagent-Free™ IC (RFIC™) systems with eluent generation (EG), which provides access to the most sensitive anion determinations and the most stable chromatography. In addition, EG provides electrolytic gradient elution, which is now a standard tool for IC. Gradient elution enables the analyst to selectively tune a separation to enhance the determination of target ions. Gradients also reduce analysis run time.

New approaches based on the use of electrolytic devices continue to emerge. The ability of modern IC systems such as the ICS-5000, ICS-3000, and ICS-2100 to integrate mounting and control of auxiliary valves and power supplies makes implementation of methods which use these electrolytic devices easy. An automated sample preparation approach managed by a PC-based data system provides precise control of sample preparation steps so that each sample is treated identically, and methods can be easily documented and transferred between instruments and laboratories. The concept of electrolytic sample preparation (ESP) was born from this combination of time- and labor-saving techniques.

ESP devices provide significant advantages. As they are continuously regenerated, they are less likely to change performance characteristics over time. In addition, system performance (sensitivity and reproducibility) is greatly enhanced using highly stable electrolytic devices. Device usage and performance can be monitored and tracked electronically. Methodology can be duplicated easily and transferred via computerized method files. A selection of electrolytic devices for automated sample pretreatment are reviewed here, including:

- Continuously Regenerated Trap Column (CR-TC): Lithium removal, hydroxide neutralization of borated water samples from nuclear power plants, using the CR-CTC II.
- AutoNeutralization™ cartridges: Neutralizes basic or acidic samples prior to injection.
- Electrolytic water purifier devices: Removes contaminating metals (e.g., in Bayer liquor). Purifies loading water for trace analysis.

CONTINUOUSLY REGENERATED TRAP COLUMN

Continuously Regenerated Trap Column (CR-TC) devices use the principles of electrolysis to remove ions from an eluent stream. Both anion removal (CR-ATC) and cation removal (CR-CTC II) devices are available.

Figure 1 shows a schematic of the CR-CTC II device, where a cation-exchange membrane separates the eluent stream from a channel of water used as a regenerant stream. A cathode resides on the regenerant stream side with an anode on the eluent stream side. Interfering cations are moved by electromotive forces through the cation-exchange membrane from the eluent stream into the regenerant stream. Because hydronium ion is generated in the eluent stream, samples containing hydroxide or other bases will be neutralized. The inverse situation applies to the case of the anion version of the CR-TC.

It should be noted that the void volume of these devices is less than 100 μL, so sample injections will typically show very little band broadening. Loading the sample onto a concentrator column after CR-TC treatment eliminates any residual band-broadening effects.
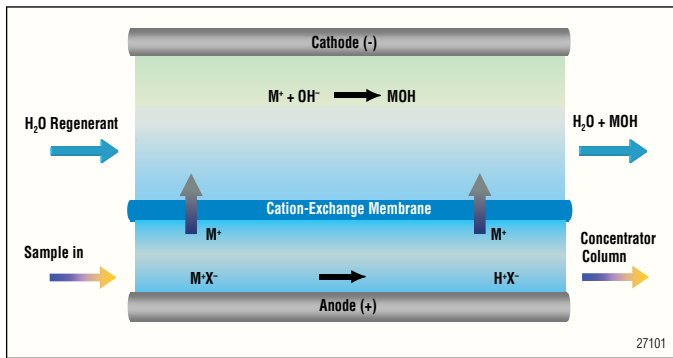
Figure1. CR-CTC schematic showing the removal of metals from a sample.

Application Example

Coolant water from pressurized water reactors typically contains lithium hydroxide. Trace analysis for anions in these water samples depends on the use of a concentrator column to effectively increase the concentration of target anions to a level which can be easily determined. Hydroxide acts as an eluent for early eluting (weakly retained) anions of interest, particularly fluoride and chloride. These analytes are poorly retained on a concentrator column. In the chromatogram shown in Figure 2, the untreated sample shows poor recovery of fluoride and chloride as they are pushed off the column by hydroxide in the sample. Pretreatment with a CR-CTC II neutralizes hydroxide and borate, providing good recovery of fluoride and chloride. Figure 3 shows a plumbing schematic of the system used for this application. Similar applications developed for trace analysis use an electrolytic water purifier for sample loading, thus eliminating the need for the loading pump and trap column.
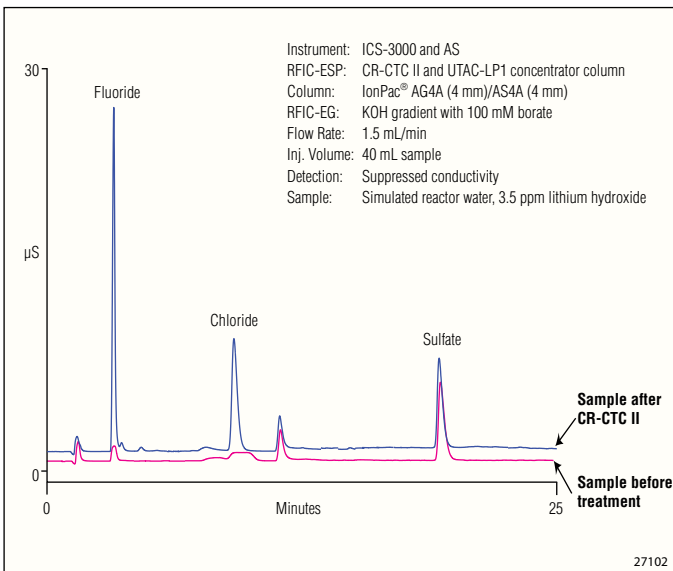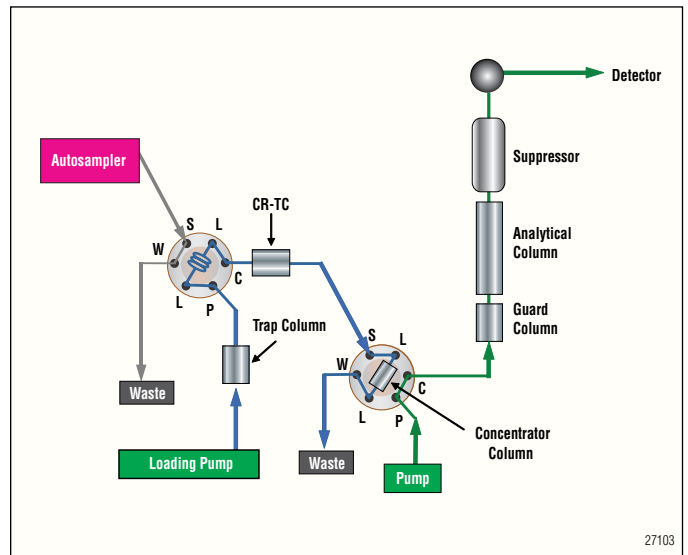

Figure 3. Plumbing schematic showing the used of CR-TC for automated sample pretreatment.

The addition of an electrolytic water purifier to the system permits the application to be performed using a single pump. This allows the analysis to be run on a system such as the ICS-2100 ion chromatograph, a moderate-cost instrument. Figure 4 illustrates this configuration.
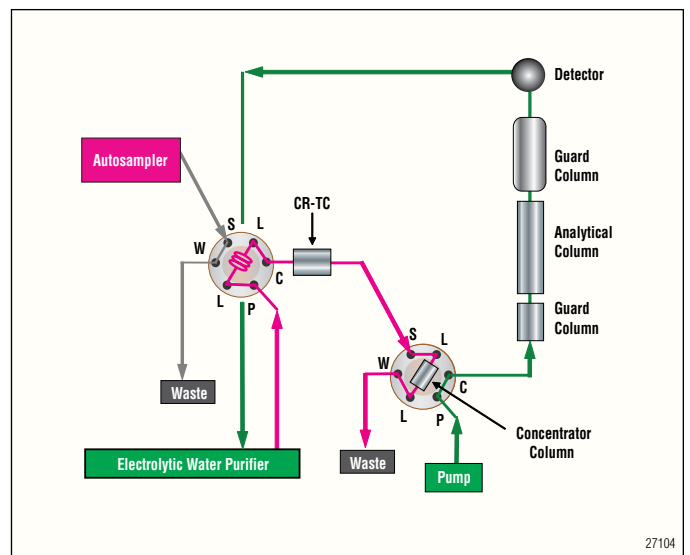

Instrument: ICS-3000 and AS
RFIC-ESP: CR-CTC II and UTAC-LP1 concentrator column
Column: IonPac® AG4A (4 mm)/AS4A (4 mm)
RFIC-EG: KOH gradient with 100 mM borate
Flow Rate: 1.5 mL/min
Inj. Volume: 40 mL sample
Detection: Suppressed conductivity
Sample: Simulated reactor water, 3.5 ppm lithium hydroxide

Figure 2. Borated water sample before and after treatment with CR-CTC II.

Figure 4. Use of electrolytic water purifier for sample loading.

AUTONEUTRALIZATION DEVICES

The determination of anions in concentrated bases and the determination of cations in concentrated acids have many important applications in industrial, health and safety, and environmental fields. Calcium, for example, can be an environmental contaminant as well as being a useful part of some industrial processes. Concentrations of potassium and sodium must be controlled in foods and pharmaceuticals for human and animal consumption. Many industrial processes are sensitive to contaminants.

IC with suppressed conductivity detection is a highly useful technique for measuring ionic species, particularly at low concentration levels. Direct injection of concentrated acids or bases will overload the column with the acid cations or base anions. This causes poor chromatography that makes accurate ion quantification difficult if not impossible.

Samples can, of course, be neutralized manually but this process exposes the operator to additional manipulations of highly corrosive and toxic materials. AutoNeutralization cartridges are very high-capacity electrolytic ion-exchange devices that perform neutralization without manual intervention. In the case of base neutralization, the device generates hydronium ions and uses an electrical potential and concentration gradient to drive them into the sample through ion-exchange membranes. Similarly for cation samples in acid, hydroxide ions are generated and transferred into the sample stream where they neutralize excess acid.
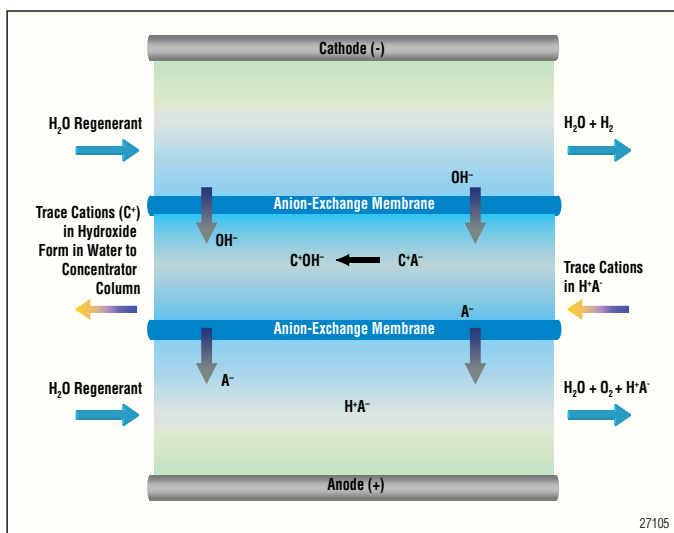

Figure 5. AutoNeutralization cartridge schematic showing neutralization of concentrated acid for trace cation analysis.

Using a concept called Park and Neutralize, a sample can be trapped in the AutoNeutralization device for as long as necessary to fully neutralize the sample matrix. The sample can then be transferred to a concentrator column, and from there on to the final analytical separation column. Figure 5 shows a schematic of an AutoNeutralization cartridge used to neutralize an acid sample before the analysis of cations in the sample. Figure 6 shows the plumbing schematic used for this application.
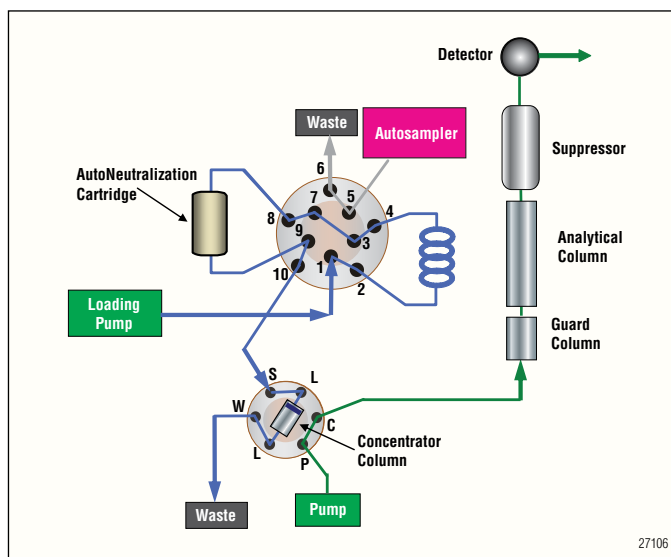

Figure 6. Plumbing schematic for the AutoNeutralization device.

Application Example

Hydrofluoric acid is dangerous to handle; minimizing sample manipulation is necessary for safety in the laboratory. The AutoNeutralization device can be used effectively to automatically prepare the sample for analysis. Figure 7 shows the results of a cation analysis after neutralization with the Autoneutralization device. Without this neutralization, the high concentration of hydronium ions in the sample would make resolution of the early eluting analytes impossible.
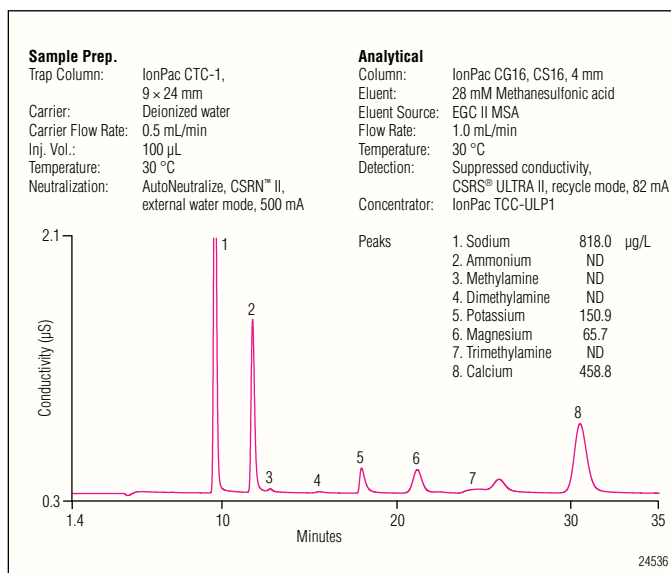

Figure 7. Trace-level determination of cations and amines in hydrofluoric acid.

ELECTROLYTIC WATER PURIFIER

Electrolytic water purifiers (EWP) can produce low-flow-rate streams of water of exceptional purity. These water streams can be used for displacement water for loading samples onto concentrator columns, either directly or via another sample preparation device such as the CR-TC example cited above.
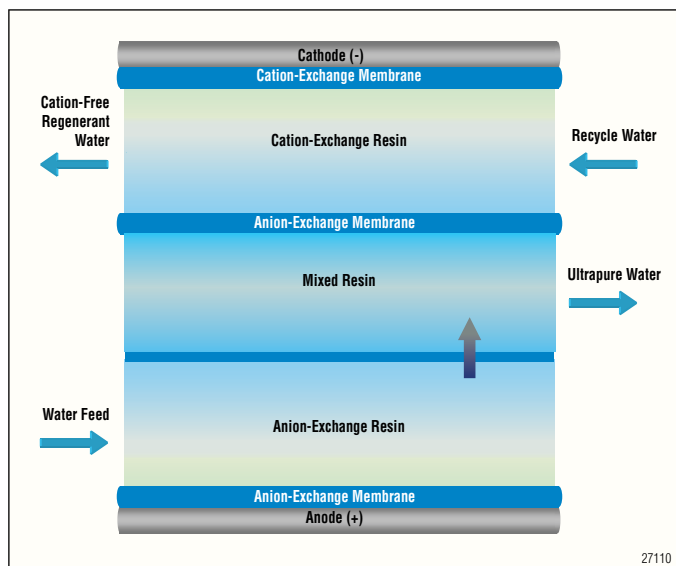

Figure 8. Example of the design of an electrolytic water purifier to be used in anion analysis.

The use of an EWP eliminates the need for a loading pump. Loading pumps are sources of contamination and reduce the ability of a system to perform trace level analyses. The closed loop nature of a system with an EWP is inherently much lower in potential contaminants.

EWP units are devices packed with various ion-exchange resins. Electrolytic water purifier units can be powered by an external low-voltage power supply or, most conveniently, by a built-in power supply such as that provided by an ICS-2100 instrument.

Application Example

Process water used in semiconductor fabrication requires strict monitoring and identification of impurities. The chromatogram below demonstrates limits of detection for the process water used in semiconductor fabrication. Achieving this level of sensitivity depends upon extremely high purity of the blank water used.

An additional feature of this application is the use of a small loop/large loop scheme for calibration. Standards can be used at a concentration level 1000× higher than that of the sample. This eliminates the difficulty of preparing standards at the ng/L level.
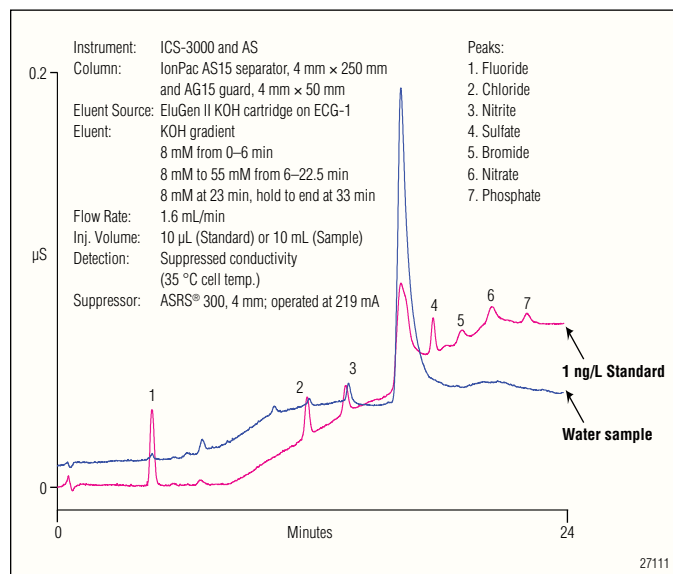

Figure 9. Overlay chromatograms of trace-levels of anions in standards and process water used in semiconductor fabrication.

Figure 9 shows low-level analysis of anions in a purified water sample, overlaid with standards at concentration levels of 1 ng/L. Analytical results of this quality are obtainable under carefully controlled conditions; otherwise, sample contamination from the environment can be difficut to avoid. For example: nitrate and nitrite contamination are readily observable in samples that have been exposed to typical laboratory air.

Figure 10 illustrates the plumbing schematic used for this application. As just described, the electrolytic water purifier (EWP) processes recycled water from the eluent stream after the suppressor. This inline processing reduces contamination from the external environment (bottles, the air, etc.) Integration of the power supply for the EWP and the secondary valve into the IC, as well as control of the entire system from the chromatography data system makes setup and operation relatively easy. Method transfer from system to system is also simplified.
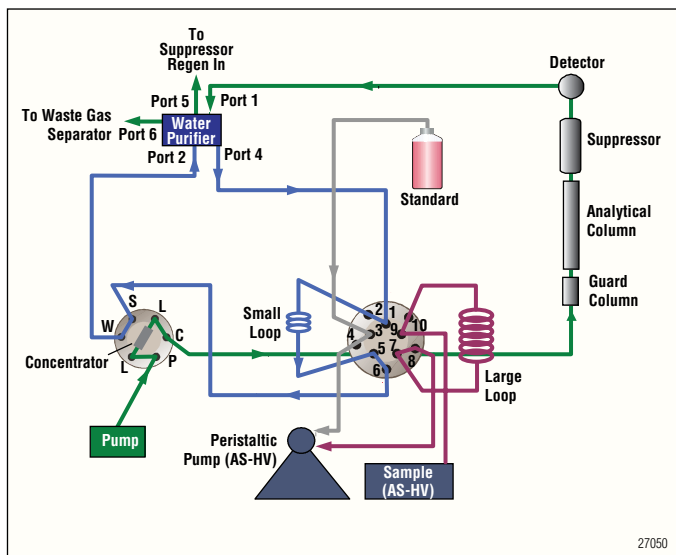
Figure 10. Schematic flow diagram of a trace analysis system using an electrolytic water purifier for sample loading.

CONCLUSION

Several approaches to ESP techiques are represented here. These techniques, along with the high-performance ion chromatography afforded by innovations such as EG technology, simplify the approach to sample pretreatment and high-sensitivity analysis.

Electrolytic automated sample pretreatment techniques enable easy method transfer and simplified validation, as all sample preparation and analysis steps are controlled, monitored, and recorded by a PC-based chromatography data system. Errors incurred due to manual sample handling are eliminated along with the need for costly sample reprocessing.

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