

Recent developments in ion chromatography instrumentation replace the art of the reagent bottle with the science of electrochemistry.

Until recently, ion chromatography (IC) labs could log in samples using bar codes and automated tracking systems, then read out the results directly to a digital computer file, but the system in between required the skills of a trained technician to prepare eluent and regenerant solutions. The technician had to handle large quantities of acidic or basic solutions, and solution contamination or small variations in preparation technique would bias the results of the analysis. One after another, over the past five years, the manually prepared solutions necessary for IC have been replaced with solutions generated by modules within the instrument itself, to the point where new IC instruments can plausibly be called "reagent-free".

Generate, Trap, Suppress

Manual solution preparation has been replaced at three stages of the IC process: eluent generation, contaminant trapping, and eluent conductivity suppression. Coupling eluent generation with continuously regenerated trap columns and electrolytic suppression thus creates the system that the Dionex Corp. (Sunnyvale, CA) markets as a Reagent-Free IC system. This development has been particularly useful in opening up new applications in the analysis of anions using hydroxide eluent solutions.

Laboratories in the environmental, food, and pharmaceutical sectors frequently use aqueous hydroxide solutions as eluents for anion analysis using IC. Hydroxide eluents have certain distinct advantages over the carbonate-bicarbonate eluents used for anion analysis, including a broader linear response range for analyte conductivity

and higher sensitivity. They also allow eluent gradients, an effective means of eluting highly retained ionic analytes, thereby expanding the peak capacity for

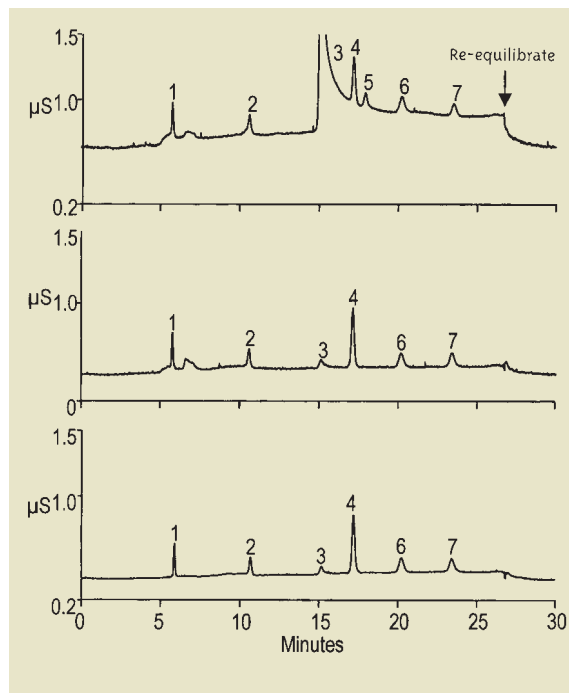


FIGURE 1: Anion trapping significantly affects the quality of the resulting chromatograms (conductivity in microsiemens is plotted vs. retention time). Top, no anion trap; middle, conventional anion trap column; bottom, continuously regenerated anion trap column. (Courtesy of Dionex Corp.)

a given separation. Despite these advantages, hydroxide eluents were not widely adopted because preparing them was problematic. Because hydroxide solutions are excellent carbon dioxide traps, carbonate ion contamination in the eluent is common. Carbonate is a stronger eluent than hydroxide. Therefore, inconsistent eluent preparation leads to variable amounts of carbonate in the eluent, producing retention time differences between eluent preparations.

This problem was solved with the introduction of eluent generation technology (1). Although the eluent generator delivers all the benefits of hydroxide eluents, the automation of eluent preparation has driven its rapid adoption for routine IC and has changed the way ion analysis is accomplished in a wide variety of laboratories. The analyst simply fills an eluent bottle with high-quality deionized water that then

moves into the potassium hydroxide generation chamber where the water is electrolyzed at a platinum cathode to form hydroxide ions. (Potassium ions are supplied from a replaceable cartridge.) For every hydroxide ion generated, a potassium cation migrates across the cation-exchange membrane, separating the potassium electrolyte reservoir and the potassium hydroxide generation chamber to produce the potassium hydroxide eluent. Charge balance is achieved by the production of hydronium ions produced by the electrolysis of water at the platinum electrode in the potassium electrolyte reservoir. The potassium hydroxide eluent then passes through a continuously regenerated anion trap column (CR-ATC, see below) and then through a degasser to remove the hydrogen gas formed at the cathodes of the eluent generator and CR-ATC and on to the anion-exchange column. The current applied for electrolysis and the flow rate determine the concentration of the potassium hydroxide. By installing an alter-

nate cartridge in the eluent generator, methane sulfonic acid eluents can be generated for cation IC.

Because IC analysis, especially gradient IC, relies so heavily on ultrapure eluent solutions, a trap column was a common feature between the pump and the sample injection valve. Typical trap columns contain high-capacity, low-efficiency ion-exchange resins that remove trace contaminants. This year, however, Dionex introduced the CR-ATC, a high-pressure, continuously regen-

erated trap column that operates indefinitely, using electrolytically assisted regeneration instead of off-line chemical regeneration. The continuous removal of contaminants, including carbonate ions, from the eluent solution eliminates a major source of variability in the procedure, and it improves sensitivity, resolution, and reproducibility of results. Figure 1 shows how trapping source water contaminant ions between the eluent generator and the sample injection port influences the resulting chromatogram. A standard solution containing fluoride (1), chloride (2), carbonate (3), sulfate (4), nitrate (6), and phosphate (7) ions was run using no anion trap (top), a conventional anion trap (middle), and the continuously regenerated anion trap column (bottom). (Peak 5 was not identified.)

After the analyte solution exits the chromatographic column, it passes through a suppressor unit that neutralizes the hydroxide ions in the eluent solution, flattening the chromatogram baseline and enhancing the signal from the analytes (see box, "The Dow of Ion Chromatography"). The intro-

duction of a self-regenerating suppressor module simplified IC because it made obsolete the preparation of acidic or basic regenerant solutions (2). Instead, the self-regenerating suppressor electrolyzes the cell effluent to generate the ions needed to reduce the conductivity of the eluent. This simplification eliminates the need for suppressor regeneration solutions (which can be expensive for cation IC), making IC viable for a wider range of applications.

Reagent-Free Benefits

Eliminating manual solution preparation produces several positive consequences for IC analysis. First and foremost, it simplifies IC, and thus reduces errors. The operator needs only to fill the eluent bottle with water, eliminating the need for training in eluent preparation. With preparation errors a thing of the past, repeat analyses decrease, saving both time and money.

Lab safety is also improved because the analyst is no longer exposed to the concentrated acids and bases used to make IC eluents. Pump maintenance is reduced because the pump is only required to deliv-

The Dow of Ion Chromatography

In 1975, Hamish Small, Timothy Stevens, and William Bauman of the Dow Chemical Co. (Midland, MI) published the paper that signaled the birth of ion chromatography (IC). They described the chromatographic determination of inorganic anions using an anion-exchange separation column followed by a second "stripper column" to reduce the conductivity of the eluent, prior to conductivity detection (1). The stripper column soon came to be known as the eluent suppressor, and the detection method was referred to as chemically suppressed conductivity. IC allowed analysts to simultaneously determine inorganic anions such as fluoride, chloride, nitrate, phosphate, and sulfate. IC also freed scientists from numerous tedious, expensive, and often inaccurate wet chemical assays, and therefore, it was rapidly adopted by laboratories around the world.

Over the years, improvements in ion exchange columns and chemical suppression extended the application of IC far beyond simple inorganic anions and cations. One major improvement was the introduction of the micromembrane suppressor (2). This suppressor enabled the use of high-capacity, ion-exchange columns and gradient elution, and therefore expanded the use of IC to additional sample types and analytes. For example, mono-, di-, and trivalent organic acids could be determined after an anion-exchange separation using a sodium hydroxide gradient. Self-regenerating suppressors have replaced micromembrane suppressors for most applications.

References

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er deionized water, and no eluent proportioning is necessary. Eluent composition, whether gradient or isocratic, is controlled by the current applied to the eluent generation device. The chromatographer no longer has to rely on the health of the proportioning valve or multiple pumps to form a gradient. Tight control of current, which is technically easy to accomplish,

produces a high fidelity of eluent composition and gradient formation, yielding very reproducible retention times.

Yan Liu and colleagues at Dionex Corp. found a major improvement in retention time reproducibility when using an eluent generator for hydroxide gradient separation of early-eluting, trace-level inorganic anions and organic acids in high-purity water (3). Reproducible retention times increase confidence in peak identification and reduce the need for repeat analyses and manual data analysis.

Because the entire IC system, including the eluent generator, can be computer-controlled, the lab manager can establish the programs and injection sequences that the operator can run, but not modify, thus ensuring a high fidelity of operation. The operator simply fills the eluent bottle with water, loads the autosampler, and loads and starts the injection sequence.

Method Development

Eluent generation also provides many benefits for method development labs and for labs required to analyze a variety of sample types. By varying the current, eluent generation makes gradient chromatography as easy as isocratic chromatography. A methods development chemist can quickly test a wide range of separation conditions and can design gradient methods to be transferred to other labs without concern about differences in eluent preparation between analysts or proportioning differences between pumps. Therefore, the chemist receives all the benefits of gradient chromatography with greater facility than traditional (manual eluent preparation) isocratic chromatography.

Eluent generation has also enabled chromatographers to receive all the benefits of hydroxide eluents for anion analysis. The use of hydroxide eluents yields improved linear analyte response compared to carbonate eluents and, therefore, greater confidence in quantifying unknown samples. Hydroxide eluents also yield the highest sensitivity for anion analysis and, likewise, provide greater confidence in identifying and quantifying low anion concentrations. The high purity of the eluents produced by eluent generation benefits the determination of trace-level ions in high-ionic-strength samples.

Future Directions

What does the future hold for IC? Eluent generation has already simplified IC,

increased the level of analysis automation, and spurred the development of new ion-exchange columns to address specific samples and analytes. The analytical chemistry community is only at the beginning of these trends, and IC will become more automated, more application specific, and even easier to run.

References

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