Electro-elution ion chromatography: controlling sample retention by electrochemically generating or modifying the mobile phase[1,2]

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Abstract

A new ion chromatographic technique called electro-elution ion chromatography is described. An electrochemical process is used to generate or moderate the mobile phase composition inside the column. The technique offers several advantages over traditional ion chromatography. For example, only water is required as the mobile phase for anion and cation analysis. This reduces cost and chemical waste. Since the concentration of the electrolysis products is directly proportional to the amount of current applied, traditional gradient separation can be accomplished by time-based programming of the current or voltage applied across the column. This eliminates the need for a gradient pump. This technique is self-suppressing, eliminating the need for a suppressor system.   © 1997 Elsevier Science B.V.

Keywords: Electro-elution ion chromatography; Mobile phase composition; Inorganic anions; Inorganic cations

1. Introduction

Since its introduction in 1903, chromatography has added several branches to the separation science. Liquid chromatography (LC) itself has branched out to various forms and is one of the most successful chromatographic techniques used. In liquid chromatography, including ion chromatography (IC), sample elution from the analytical column is controlled by many factors. One such factor is the mobile phase composition. Mobile phase is prepared off-line by mixing solvents or chemicals and pumping it through the column using a high pressure pump. In certain applications, a gradient pump delivers a mobile phase composition that changes during the analysis.

Discovery of a new type of chromatographic technique is described in this paper. This technique is called 'electro-elution chromatography' (this device and technique are patent pending). Electrochemistry is the main principle behind this technique. Sample elution is still controlled by the mobile phase composition, however, the mobile phase composition is generated inside the column via an electrochemical process.

Application of an electrical field to the chromatographic stationary phase to manipulate the retention of sample analytes has been previously reported [1–4]. Conductive stationary phases such as porous and nonporous glassy carbon particles were used. In

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[1] Note: Patents are pending on this work.
[2] Presented at the International Ion Chromatography Symposium, Reading, 16–19 September, 1996.

these cases, the electric field was used to manipulate the analytes retention by changing the composition of the stationary phase without changing the mobile phase composition. Hern and Strohl [5] discussed the electrochemical generation of H^+ ions to remove metal ions from a modified graphite stationary phase. In their work, the conductive graphite stationary phase acted as the anode.

In electro-elution ion chromatography described here, a nonconductive stationary phase is used and the column itself houses the electrodes. The electric field applied will not change the composition of the stationary phase. Only the mobile phase composition is changed. This technique offers several advantages over the traditional ion chromatography. This paper discusses some of these advantages.

2. Experimental

The chromatography system used was an Alltech (Deerfield, IL, USA) ion chromatograph consisting of a Model 526 HPLC pump, Model 570 autosampler, and Model 550 conductivity detector. A Bertan (Hicksville, NY, USA) high-voltage power supply, Model 105-10R, was used as a constant current or voltage power source. A Thermo Separation Products (San Jose, CA, USA) SP4400 Chromjet integrator was used to record all data.

Low capacity anion and cation-exchange resins packed in specially made columns (30×4.6 mm I.D.) were used for the separation. The packing material was placed between two electrodes within a nonconductive column body. The power supply was connected to both electrodes. For anion separations, an anion-exchanger made of polystyrene–divinylbenzene with a quaternary amine functional group was used. For cation separation, a silica-based cation-exchanger made of silica coated with polybutadiene maleic acid was used [6].

Anion and cation standards were prepared by diluting the 1000 ppm Certified IC Standards from Alltech. The dilute methane sulfonic acid buffer was prepared using the Alltech's EZ-LUTE buffer concentrates. Deionized water was used for preparing all solutions.

3. Results and discussion

It was discovered that when an electric field is applied across two electrodes sandwiching ion-exchange resins, current is carried across the resin with low resistance. The current is believed to be carried via ion transport (or ion-exchange cascade) from one ion-exchange site to another. The resistance across the resin is dependent on the ion-exchange capacity of the resin, the electrode surface area, and also the distance between the two electrodes. The resistance is lower when higher capacity resin is used, or when the electrode surface area is larger, or when the distance between the two electrodes is shorter. The resistance is also dependent on the functional group of the resin. For example, a cation-exchange resin in the hydrogen form has lower resistance than the same resin in the sodium form. This is due to the higher equivalent conductance of the hydrogen ion as compared to the sodium ion. The first application of this discovery was the development of Electrochemically Regenerated Ion Suppressors (ERIS) for ion chromatography [7].

3.1. Electro-elution ion chromatography

When water undergoes electrolysis, the following reactions take place:

Anode: $2H_2O \rightarrow 4H^+ + O_2 + 4e^-$

Cathode: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$
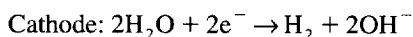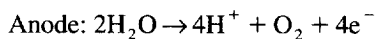
Hydrogen ion and oxygen gas are generated at the anode and hydroxide ion and hydrogen gas are generated at the cathode. When current is applied across the chromatography column, water undergoes electrolysis. The hydrogen or hydroxide ions produced during electrolysis can modify the elution of the sample components from the column. The technique of eluting adsorbed components from a chromatographic bed by electrochemically generating or modifying the mobile phase is referred to as electro-elution.

3.2. Anion electro-elution

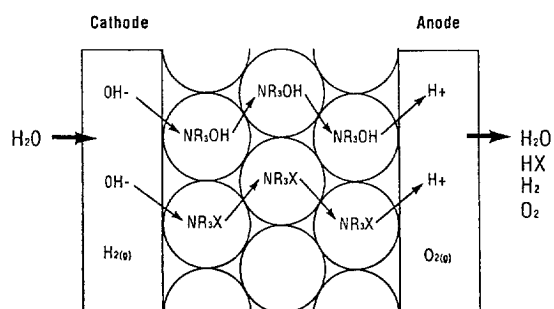In traditional anion analysis by IC, buffers such as sodium carbonate/bicarbonate, sodium hydroxide,

Fig. 1. Effect of anion electro-elution.

sodium phthalate, and p-hydroxybenzoate are used as the mobile phases. In electro-elution, only water is used as the mobile phase. During anion analysis, the column is attached to the power supply with the cathode connected to the column inlet and the anode connected to the column outlet. When the power supply is turned on, hydroxide ions produced at the cathode are believed to be carried through the column by ion-exchange 'cascade' while simultaneously separating the anions retained on the column. Fig. 1 shows the effect of anion electro-elution. Hydrogen ions produced at the anode react quantitatively with the hydroxide ions as they exit the column. This self-suppressing system eliminates the need for a suppressor system as in traditional IC.

Sample anions elute through the column to the detector as their highly conductive acids.

Fig. 2a,b show an electro-elution separation of anions. In Fig. 2a, a current of 10 mA was applied across the column. The voltage drop across the column was 137 V. The nitrate peak elutes in about 18 min. In Fig. 2b, the current was increased to 16 mA and the retention time for nitrate reduced to 9 min. The 16 mA current produced 205 V across the column. The design of the electro-elution column needs further optimization in order to reduce the voltage drop. The selectivity of the anions eluted from the column is identical to the selectivity obtained using ion chromatography. In capillary electrophoresis, ions with highest mobility will migrate first [8]. If the electrophoretic mobility plays a role in the separation the migration order of the anions would be chloride, nitrate, and fluoride. Also, the voltage that was used in the electro-elution is much smaller than the voltage applied in capillary electrophoresis [8]. Based on this, it is believed that electrophoretic mobility plays little, if any, role in the separation.

The electro-elution technique follows Coulomb's law. The amount of hydroxide ion produced is directly proportional to the applied current. Higher current produces more hydroxide and as shown in Fig. 2, this reduces the nitrate retention time. These
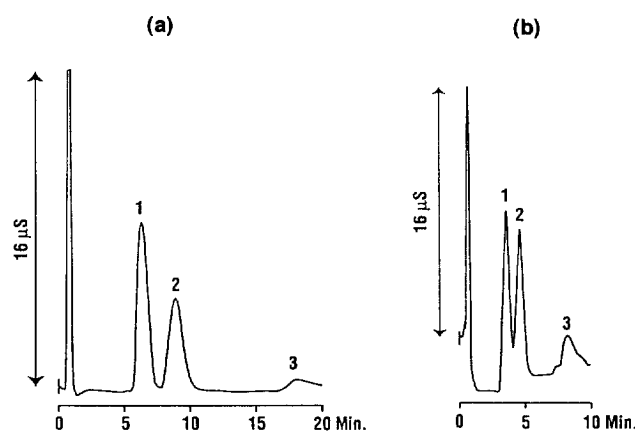

Fig. 2. Electro-elution separation of anions using water as the mobile phase. (a) Constant current at 10 A; (b) constant current at 16 mA. Peak identification: 1 = fluoride (5 ppm), 2 = chloride (10 ppm), 3 = nitrate (10 ppm). Column, anion (30×4.6 mm); mobile phase, deionized water; flow-rate 1.0 ml/min; detection, conductivity.
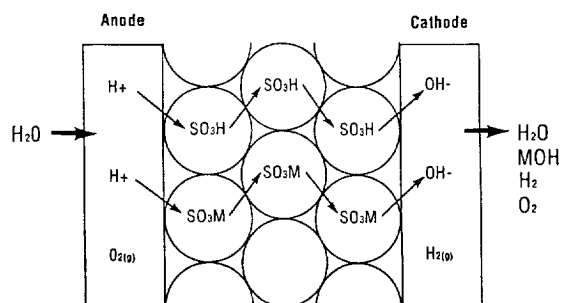
Fig. 3. Effect of cation electro-elution.

results indicate that gradient separations are possible by programming the applied current with time. This eliminates the need for a gradient pump as in traditional ion chromatography.

3.3. Cation electro-elution

In traditional cation analysis by IC, acids such as hydrochloric, methane sulfonic, nitric, or sulfuric are used as the mobile phases. In the electro-elution, only water is used as the mobile phase. During cation analysis, the anode is connected to the column inlet and the cathode is connected to the column outlet. When the power supply is turned on, hydrogen ions produced at the anode are believed to be carried through the column by ion-exchange 'cascade' separating the cations retained on the column. Fig. 3 shows the effect of cation electro-elution. Hydroxide ions produced at the cathode react quan-

titatively with the hydrogen ions as they exit the column, eliminating the need for a suppressor system. Sample cations elute through the column to the detector as their highly conductive bases.

Preliminary results show that the electro-elution separation of cations using water as the mobile phase is possible. However, since the electrodes used in this preliminary study were made of stainless steel, metal ions released during electrolysis bind irreversibly to the sulfonic-acid ion-exchange resin, reducing its capacity with time. Retention times on each successive run decreased and we were not able to obtain reproducible chromatograms with this system. An inert electrode material, such as platinum, would likely overcome this problem.

3.4. Electrochemical mobile phase modification

The technique discussed here may be used to modify the mobile phase concentration. Fig. 4a shows a cation separation using a weakly conductive methane sulfonic acid $(0.1\ M)$. Potassium elutes in approximately 30 min. In this case, the cations are detected by indirect conductivity due to the highly conductive acid mobile phase. By applying 2 V across the column, the potassium retention time is reduced to 22 min as shown in Fig. 4b. The increase in hydrogen ion concentration as a result of the electrolysis elutes the potassium faster. By using a conductive mobile phase, less power is required. Also, a longer column dimension or a lower capacity ion-exchanger may be used.
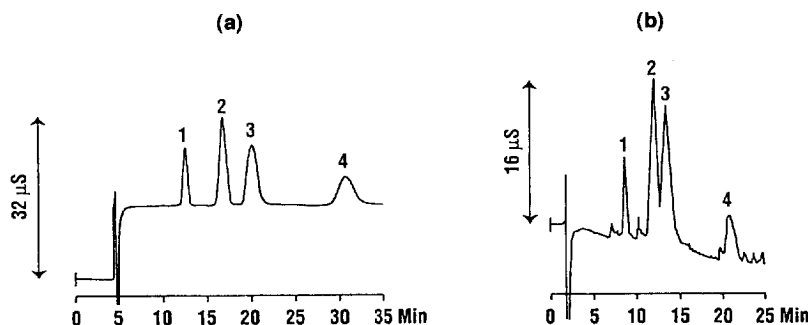

Fig. 4. Electro-elution separation of cation using a weakly conductive mobile phase. (a) No voltage applied; (b) constant voltage at 28 V. Peak identification: 1 = lithium (0.5 ppm), 2 = sodium (1.5 ppm), 3 = ammonium (1.5 ppm), 4 = potassium (2.5 ppm). Column, cation (30×4.6 mm); mobile phase, 0.1 mM methanesulfonic acid; flow-rate, 1.0 ml/min; detection, conductivity.

3.5. Technical hurdles

There are several problems that require further investigations before the electro-elution technology becomes a viable routine technique. For example, significant amount of hydrogen and oxygen gas were generated during the electrolysis and these gases must be removed before entering the detector. These gases can cause spikes and interfere with the detection. In this experiment, a back pressure regulator was added after the detector to eliminate some of the bubbles. Electrodes made of stainless steel were used in this preliminary study. This material caused problems, especially during cation analysis. An inert electrode material, such as platinum, needs to be investigated. Some electrical energy is dissipated as heat within the column (Joule heating). This can also interfere with conductivity detection. The column dimension and design also need to be optimized. Work is being done in our laboratory to overcome these problems.

3.6. Electro-elution liquid chromatography

The technique described here is not limited to ion analysis. It may have applicability to liquid chromatography applications. For example, it may be used in HPLC to elute certain components by changing the pH of the environment. Proteins, for example, retain on ion-exchange packings by charge interactions. By modifying the pH in the column using this technique, the retained protein may be eluted from the column. This possibility is yet to be tested in our laboratory.

4. Conclusion

The electro-elution technique offers several advantages over traditional ion chromatography. For example, only water is required as the mobile phase for anion and cation analysis. This reduces cost and chemical waste. Since the concentration of the electrolysis products are directly proportional to the amount of current applied traditional gradient separation can be accomplished by time-based programming of the current or voltage applied across the column. This eliminates the need for a gradient pump. In IC, this technique is self-suppressing, eliminating the need for a suppressor system.

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