SHIMADZU
Excellence in Science

C190-E248

Technical Report

HIC-ESP Anion Chromatograph Equipped with the ICDS-40A High-Performance Suppressor

Katsumasa Sakamoto[1], Masanori Fujiwara[1], Hidetoshi Terada[1], Hiroshi Tanaka[1]

Abstract:

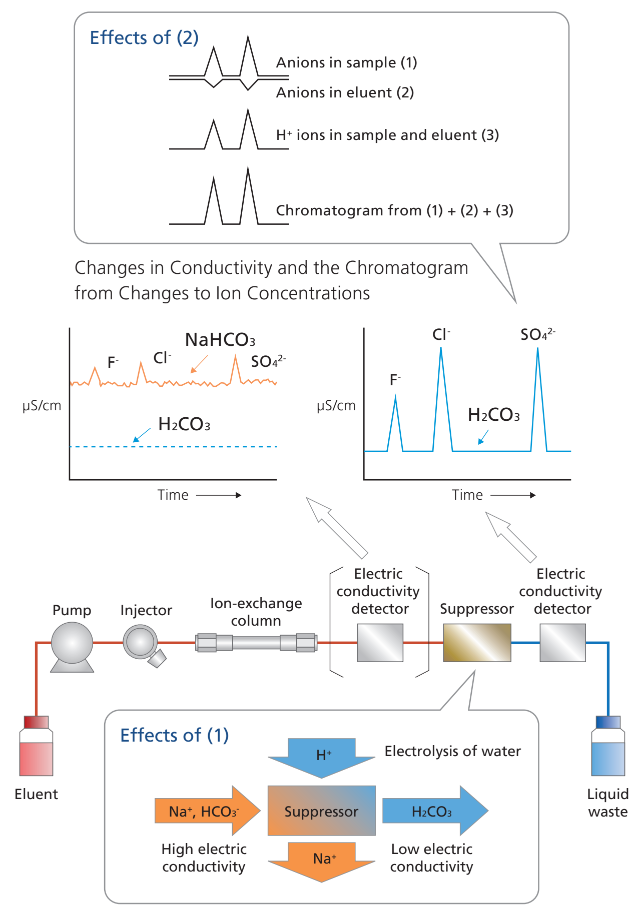
In ion chromatography, the suppressor method is widely used in order to reduce background and noise levels during detection. The newly developed ICDS™-40A electrodialytic suppressor for anion analysis features (1) a dialytic membrane suppressor with a folded structure that reduces the internal volume and inhibits peak dispersion (2) a continuous regeneration method that shortens the analysis cycle time, and (3) a simple system configuration, based on electrodialytic regeneration, that eliminates the need for a regeneration solution. The HIC-ESP anion chromatograph equipped with the ICDS-40A suppressor features a slim oven, which reduces the installation width by 40 % to help utilize laboratory space more effectively. This Technical Report bulletin describes the operating principles and features of the ICDS-40A suppressor and the HIC-ESP anion chromatograph.

Keywords: ICDS-40A, HIC-ESP, suppressor method, electrodialysis, dialytic membrane type

1. Principles of the Suppressor Method

Ion chromatography is a method for analyzing the ions in samples based on a combination of ion-exchange mode separation and electric conductivity detection. However, ions in the mobile phase can interfere with detection. A suppressor is a device that electrically or chemically replaces the background ions in eluted solutions, after separation by a column, with ions that have low electric conductivity, thereby improving the baseline noise level. When analyzing anions, the cations in the sample are replaced with hydrogen ions, which have a higher equivalent electric conductivity. This also improves sensitivity.

In the example shown in Fig. 1, an aqueous sodium hydrogen carbonate solution ($NaHCO_3$) was used as the eluent. Installing the suppressor in front of the detector in the flow line, in order to replace the sodium ions in the eluent with hydrogen ions, changes the composition of highly electrically conductive sodium hydrogen carbonate in the eluent to a slightly acidic composition of aqueous carbonic acid (H_2CO_3). This reduces baseline noise by decreasing the electric conductivity of the background ions. Meanwhile, the sodium counter ions to the anions in the sample are replaced with hydrogen ions, so that the carbon dissociation equilibrium shifts towards the generation of hydrogen ions. (Refer to the chromatogram in Fig. 1 for H^+ ions in the eluent.) Because hydrogen ions have a higher equivalent electric conductivity than sodium ions, this increases the peak intensity.



Effects of the Suppressor

(1) Eliminating the sodium ions just before they reach the detector changes the eluent composition to a carbonic water solution, which decreases the electric conductivity.
(2) Because hydrogen ions have a higher equivalent electric conductivity than other ions, the peak response is increased.

Fig. 1 Suppressor Method

1 Analytical & Measuring Instruments Division

2. Types of Suppressors

The main types of suppressors are column removal suppressors which uses a packing material, and dialytic membrane suppressors.

2-1. Column Removal Suppressors

Column removal suppressors (such as cartridge models) reduce the background electric conductivity by using ion-exchange groups to trap eluent counter ions within a column packed with an ion-exchange polymer. Because separate processes are used for analysis and regeneration, there is no noise from regeneration, which enables low-noise operation.

On the other hand, once the ion-exchange groups become saturated, they can no longer remove ions, so analysis must be stopped in order to regenerate the column by removing the trapped ions. To improve analytical efficiency, it is also possible to switch between multiple suppressors installed in parallel for analysis and regeneration, but this results in a more complicated system. (Refer to Fig. 2.) The regeneration process for column removal suppressors can be performed either electrically by water electrolysis or chemically with a regeneration solution.

2-2. Dialytic Membrane Suppressors

The ion-exchange membrane in dialytic membrane suppressors forms two separate flow channels, with the eluent flowing through one channel and regeneration solution pumped through the other. The ions in the eluent are removed by either chemical or electrodialytic dialysis of ions to the regeneration solution flow channel.

Dialytic membrane suppressors remove ions and regenerate the column at the same time, which eliminates the need to stop analysis when ion-exchange groups become saturated, as required by column removal suppressors, and eliminates the baseline drift associated with switching between processes. This means that the baseline remains stable during measurements, even when analysis takes a long time. Because of this, dialytic membrane suppressors are used for general analysis, including analyses based on official methods.

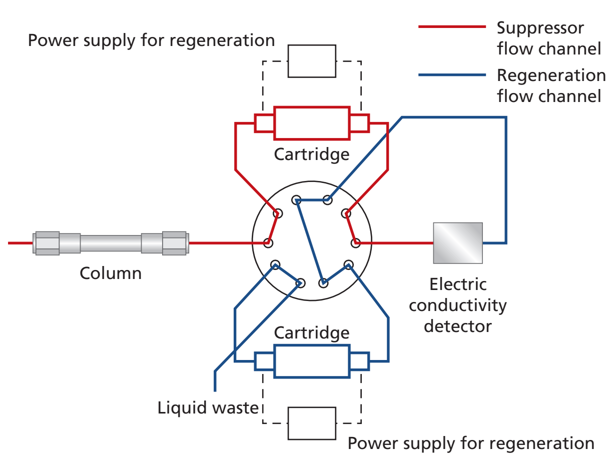


Fig. 2 Example of a Column Removal Suppressor (Electrical Column Regeneration)
In this example, two suppressor cartridges are used alternately, one for analysis (red) and the other for electrical regeneration (blue).

3. Features and Suppressor Effect of the ICDS-40A

The newly developed ICDS-40A anion analysis suppressor is a dialytic membrane type capable of continuous ion dialysis. In order to minimize noise by the efficient dialysis of cations in the eluent, electrodialysis occurs via an internal eluent flow channel designed to reverse directions (patent pending). This heightens dialysis efficiency while reducing internal volume, enabling stable electrodialysis (Fig. 3).

When direct current voltage is applied to the ICDS-40A electrodes, water is electrolyzed to produce hydrogen ions at the anode ($H_2O \rightarrow 2H^+ + 1/2O_2 + 2e^-$) and hydroxide ions at the cathode ($2H_2O + 2e^- \rightarrow 2OH^- + H_2$).

a) When voltage is applied, the hydrogen ions electrolytically generated at the anode move towards the cathode together with the cations (sodium ions) that were contained in the eluent.

b) The hydrogen ions pass through the cation exchange membrane, which only permits the passage of cations. When the ions pass through to the eluent flow channel, the cations from the eluent pass through the cation exchange membrane and are discharged, at which point they move towards the cathode (dialysis). The flow channel in this suppressor is designed to fold back in the opposite direction, so that dialysis is performed twice within the eluent flow channel.

c) Cations discharged on the cathode end combine with electrolytically generated hydroxide ions to form water or salt, which is then discharged from the suppressor.

By reusing the solution discharged from the detector as a regeneration solution, a simple system configuration is achieved that does not require any regeneration solution.

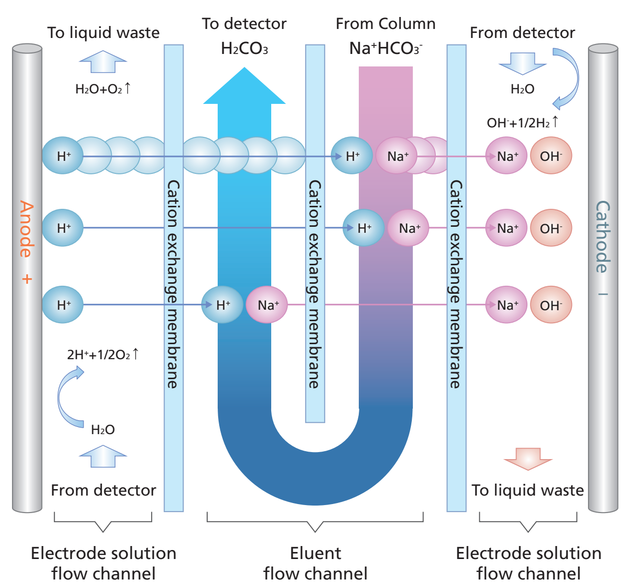


Fig. 3 Structure of the ICDS-40A and Suppressor Effect

4. Inhibition of Peak Dispersion by the ICDS-40

The ICDS-40A not only reduces peak dispersion within the suppressor, but also eliminates any impact from baseline fluctuations due to water in samples (water dip effects). This helps to ensure highly reliable anion analysis (Fig. 4).

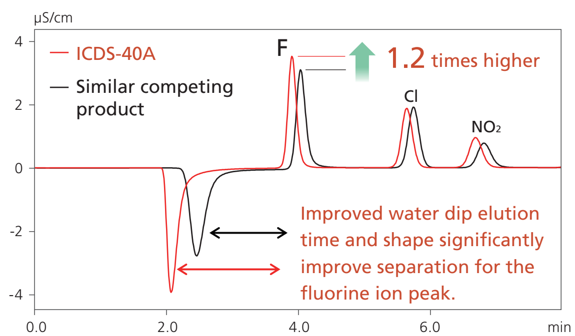
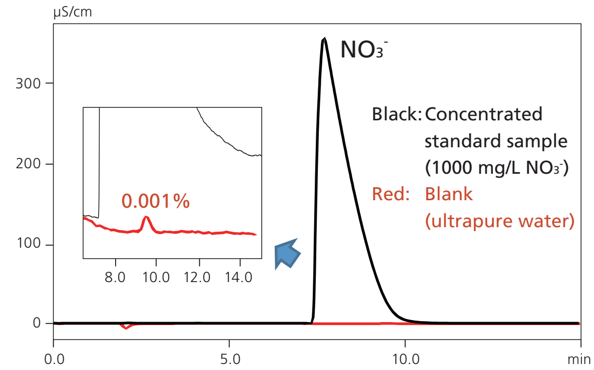


Fig. 4 Comparison of Chromatograms for Standard Anion Samples Resulting from Suppressor Differences

5. High-Performance, Space-Efficient HIC-ESP Design

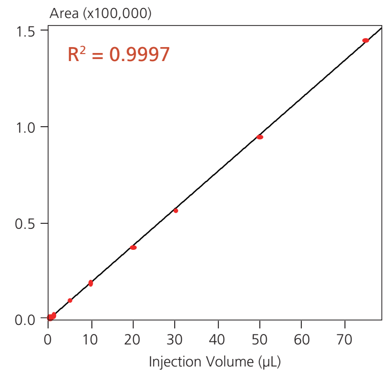
The HIC-ESP anion chromatograph equipped with an ICDS-40A suppressor includes an HPLC module with a reputation for superior performance. The system improves analytical reliability by offering superior solvent delivery performance, sample injection accuracy, injection reproducibility, low carryover precision and oven temperature control accuracy. The narrow oven enables installation in spaces only 420 mm wide.

Low Carryover Performance



Note: Blank (ultrapure water) was injected after injecting a 1000 mg/L NO_3 standard solution.

Injection Volume Accuracy and Reproducibility



Injection Volume (μL)	Area RSD (%) (n = 5)
0.2	1.05
1	0.86
10	0.25
20	0.04
50	0.04
75	0.08

Note: Analyzed while changing the injection volume of a 10 mg/L Br standard solution.

Fig. 5 Low Carryover Performance and Injection Accuracy/Reproducibility

6. Conclusions

- The ICDS-40A suppressor enables continuous, high-efficiency dialysis while achieving a small internal volume.
- The HIC-ESP anion chromatograph equipped with an ICDS-40A suppressor, improves analytical reliability by including an HPLC module with a reputation for superior performance.

ICDS is a trademark of Shimadzu Corporation.

First Edition: January, 2020

SHIMADZU

Shimadzu Corporation

www.shimadzu.com/an/