New On-Line High-Pressure Electrolytic Eluent Generators for Ion Chromatography

Yan Liu, Zhongqing Lu, and Chris Pohl, Thermo Fisher Scientific, Sunnyvale, CA USA

Overview

Purpose: In this work, new high-pressure electrolytic acid and base generation devices are developed.

Methods: The new electrolytic eluent generation devices utilize the electrochemical processes involving the electrolysis of water and charge-selective transport of ions across ion exchange media to generate high-purity acid and base solutions as eluents for use in ion chromatography systems.

Results: The combined use of Reagent-Free™ Ion Chromatography (RFIC™) systems fitted new high-pressure eluent generation devices and new IC columns packed with resins of smaller particle sizes (e.g., 4 μm) provides new opportunities to perform fast and high resolution IC separations.

Introduction

Ion chromatography (IC) is a widely used analytical technique for determination of anionic and cationic analytes in various sample matrices. In modern IC systems, high purity acid, base, or salt eluents are generated electrolytically using deionized water as the carrier. The Reagent-Free Ion Chromatography (RFIC) systems with electrolytic eluent generation make it possible to perform a wide range of ion chromatographic separations using only deionized water as the carrier. For many applications, the RFIC systems provide improved performance with increased sensitivity and the flexibility to perform isocratic and gradient separations. In addition to saving time, labor, and operating costs, the RFIC systems eliminate errors and problems associated with manual eluent preparation and offer users the benefits of simplicity , ease of use, and improved method reproducibility.

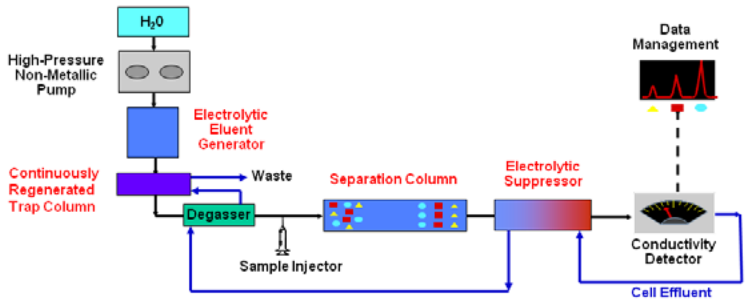
There is growing interest in the development and application of new IC columns packed with resins of smaller particle sizes (e.g., 4 μm or smaller) since these columns bring out new opportunities to perform fast and high-resolution IC separations. The new smaller-particle-size IC columns typically yield pressures higher than 3000 psi, which is the maximum operating pressure of the current generation of electrolytic eluent generators. Therefore, there is a need to develop electrolytic eluent generators capable of operating at elevated pressures. Here, the authors describe the development of a new generation of electrolytic devices for generating high purity acid and base using deionized water as the carrier stream. The new electrolytic eluent generators can be operated under pressures up to 5000 psi. We will describe the principles and operation of the new electrolytic eluent generators, and demonstrate the advantages of using these devices to achieve fast and high resolution ion chromatographic separations under isocratic and gradient conditions**.**

Experimental

All experiments were performed using Thermo Scientific Dionex ICS-5000 RFIC systems with electrolytic eluent generation. A typical Dionex ICS-5000 system consists of a dual pump module (DP), an eluent generator (EG) module, and a detector/chromatography module (DC). The modular design of the Dionex ICS-5000 systems allows users to quickly configure and customize components for a wide range of applications. The system can be configured as a dual-channel capillary RFIC system, a dual-channel conventional RFIC system, or a dual-channel RFIC system supporting both conventional and capillary-scale IC separations. The Dionex ICS-5000 RFIC systems are fully supported by Thermo Scientific Dionex Chromeleon 6.8 and 7 software. Several conventional-scale and capillary-scale anion-exchange and cation-exchange Thermo Scientific Dionex IonPac columns were used. Current capillary-scale systems support high-pressure eluent generation as well as manually prepared eluents; a prototype system was used for conventional-scale high-pressure eluent generation.

The block diagram of key components used in a typical RFIC system is shown in Figure 1. A high-pressure pump is used to deliver a stream of deionized water into an eluent generator cartridge where the high-purity base or acid eluent is generated electrolytically. A continuously regenerated trap column (Thermo Scientific Dionex CR-TC) is the used to remove trace contaminants in the eluent. A high-pressure degasser containing a gas permeable tubing is used to remove hydrogen or oxygen gas formed electrolytically. There are several other downstream system components including a sample injector, a separation column, and an electrolytic suppressor. In the system shown, the conductivity detector effluent is routed through the regenerant chambers of the electrolytic suppressor, the Dionex CR-TC, and the high-pressure degasser assembly before going to waste. Therefore, the RFIC system makes it possible to perform the entire IC separation process using deionized water as the carrier.

FIGURE 1. Block diagram of key components in an RFIC system.



The Dionex ICS-5000 RFIC systems use electrolytic eluent generator cartridges (Dionex EGC) to generate potassium hydroxide (KOH) or methanesulfonic acid (MSA) eluents on-line using deionized water as the carrier stream. Figure 2 illustrates the key components of an conventional-scale high-pressure Dionex EGC-KOH cartridge. The cartridge consists of a low-pressure K^+ ion electrolyte reservoir and two high-pressure KOH generation chambers (EGC pods) connected in series. To generate a KOH solution, deionized water is pumped through the EGC pods and a DC current is applied between the device's anode and cathode. Under the applied electrical field, water is oxidized to form H^+ ions and oxygen at the anode. Water is also reduced to form OH^- ions at the cathode. K^+ ions migrate from the electrolyte reservoir through the ion exchange connector into the KOH generation chamber and combine with OH^- ions generated at the cathode to form a KOH solution. The concentration of KOH formed is directly proportional to the applied current and inversely proportional to the flow rate.

A similar electrochemical process can also be applied to generate an acid eluent electrolytically. Figure 3 illustrates the key components of an conventional-scale high pressure Dionex EGC-MSA cartridge. Compared to the earlier generation of Dionex EGC cartridges, the new high-pressure cartridges can be operated at pressures up to 5000 psi.

FIGURE 2. Electrolytic generation of KOH eluents using a high-pressure Dionex EGC-KOH cartridge.

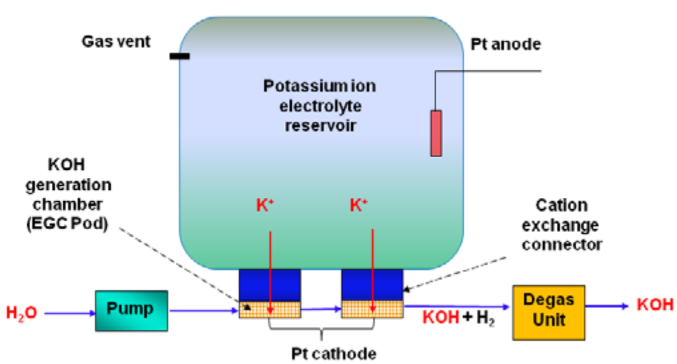


FIGURE 3. Electrolytic generation of methanesulfonic acid eluents using a high-pressure Dionex EGC-MSA cartridge.

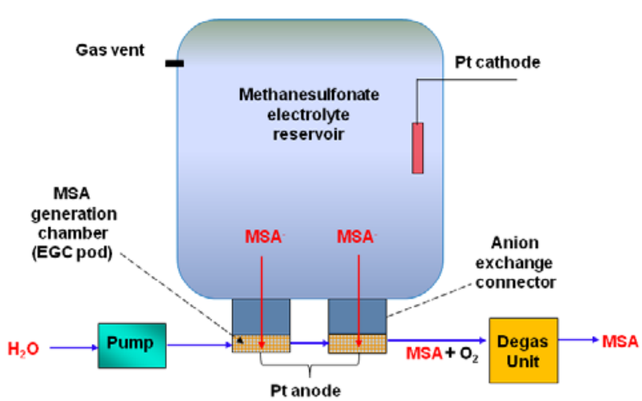


Table 1 summarizes the key operation parameters of conventional-scale and capillary-scale high pressure eluent generator cartridges. In this study, the ICS-5000 systems were modified in order to perform separations using the conventional-scale high-pressure Dionex EGC cartridges. Compared to the conventional-scale Dionex EGC cartridges, the capillary cartridges are capable of generating KOH and MSA eluents over wider concentration ranges and providing significantly longer lifetime. These operation features of high pressure Dionex EGC cartridges enable the RFIC systems to perform highly reproducible isocratic and gradient separations of target analytes.

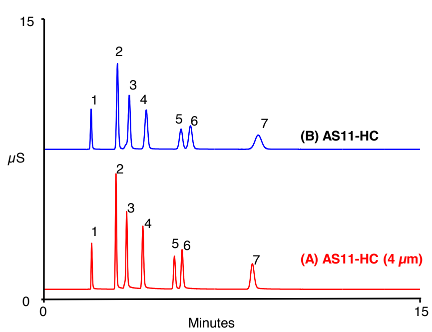
TABLE 1. Operation parameters of high-pressure conventional-scale and capillary-scale Dionex EGC cartridges.

Operation Parameters	Conventional-scale Dionex EGC-KOH and EGC-MSA Cartridges	Capillary-scale Dionex EGC-KOH and EGC-MSA Cartridges
Flow Rate	0.1 mL/min to 3.0 mL/min	1 to 30 µL/min
Concentration	0 to 100 mM	0 to 200 mM
Lifetime	KOH cartridges: 1000 hours at 50 mM and 1.0 mL/min MSA cartridges: 1000 hours at 25 mM and 1.0 mL/min	18 month or 12960 hours at 75 mM and 10 µL/min
Pressure	200 to 5000 psi	200 to 5000 psi

Results and Discussion

The use of RFIC systems fitted with new high-pressure Dionex EGC cartridges and new IC columns packed with resins of smaller particle sizes (e.g., 4 μm) provides new opportunities to perform fast and high resolution IC separations. Figure 4 compares the separation of seven common anions on a conventional 2 mm Dionex IonPac™ AS11-HC column packed with 9 μm resin to the separation on the new 2 mm Dionex IonPac AS11-HC-4μm column packed with 4 μm resin. The new 4 μm column provides significantly higher chromatographic efficiency for the separation of target analytes. For example, the plate number of the sulfate peak was 5988 on the conventional column packed with 9 μm resin and 16111 on the new 4 μm column. The operating pressure of the new 2 mm Dionex IonPac AS11-HC-4μm column is about 4000 psi under the conditions shown.

FIGURE 4. Separation of common anions using 2 mm Dionex IonPac AS11-HC columns and a high-pressure Dionex EGC-KOH cartridge.



Columns:	A: Dionex IonPac AS11-HC-4μm B: IonPac AS11-HC, 2 X 250 mm
Eluent Source:	Dionex EGC-KOH
Eluent:	30 mM KOH
Flow Rate:	0.38 mL/ min
Temperature:	30 ° C
Inj. Volume:	10 μL
Detection:	Thermo Scientific Dionex ASRS 300

Peaks:	Efficiency Column A	Efficiency Column B
1. Fluoride	9151	6019
2. Chloride	15869	7867
3. Nitrite	16784	7634
4. Sulfate	16111	5988
5. Bromide	22645	8558
6. Nitrate	21342	8002
7. Phosphate	14638	4438

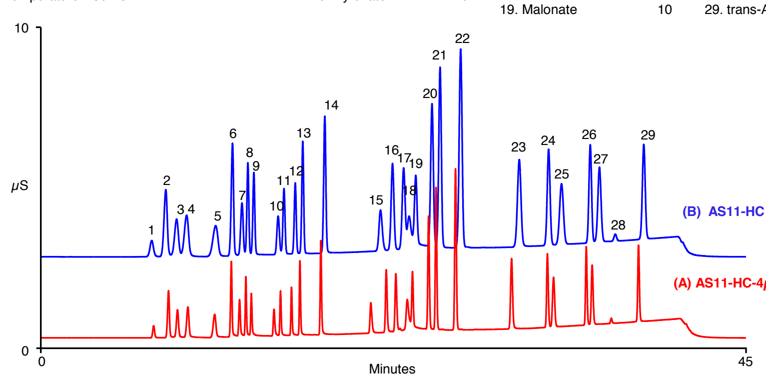
The enhanced chromatographic efficiency provided by the new 2 mm Dionex IonPac AS11-HC-4μm column is highly beneficial in resolving complex mixtures of target analytes. Figure 5 shows a high-resolution separation of 29 inorganic and organic anions obtained using 2 mm Dionex IonPac AS11-HC columns and a high-pressure Dionex EGC-KOH cartridge. Compared to the conventional 2 mm Dionex IonPac AS11-HC, the new 2 mm Dionex IonPac AS11-HC-4μm column significantly improves the resolution of target analytes.

FIGURE 5. Gradient separation of 29 anions using 2 mm Dionex IonPac AS11-HC columns and a high-pressure Dionex EGC KOH cartridge

Columns: A) Dionex IonPac AS11-HC-4μm, 2 × 250 mm
B) Dionex IonPac AS11-HC, 2 × 250 mm
Eluent: 1.0 mM KOH from 0 to 8 min, 1.00 to 30 mM from 8 to 28 min, 30 to 60 mM from 28 to 38 min, 1.0 mM from 38 to 45 minutes
Flow Rate: 0.38 mL/min
Inj. Volume: 2.5 μL
Temperature 30 °C

Peaks: (Concentration in mg/L)

1. Quinate	10	10. Valerate	10	20. Maleate	15
2. Fluoride	3	11. Monochloroacetate	10	21. Sulfate	15
3. Lactate	10	12. Bromate	10	22. Oxalate	15
4. Acetate	10	13. Chloride	5	23. Tungstate	20
5. Propionate	10	14. Nitrite	10	24. Phosphate	20
6. Formate	10	15. Trifluoroacetate	10	25. Phthalate	20
7. Butyrate	10	16. Bromide	10	26. Citrate	20
8. Methylsulfonate	10	17. Nitrate	10	27. Chromate	20
9. Pyruvate	10	18 Carbonate	20	28. cis-Aconitate	20
		19. Malonate	10	29. trans-Aconitate	20



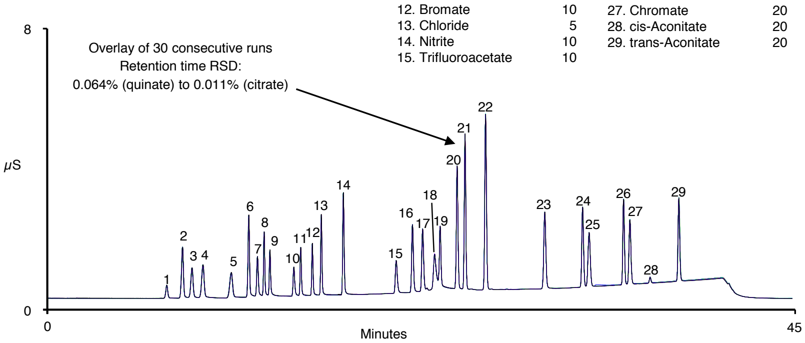
The Dionex ICS-5000 RFIC systems are capable of providing highly reproducible separation of target analytes that are difficult to achieve using standard IC systems. Figure 6 shows an overlay of 30 consecutive high-resolution separations of 29 inorganic and organic anions obtained using a 2 mm Dionex IonPac AS11-HC-4μm column and a high-pressure Dionex EGC-KOH cartridge. A hydroxide gradient from 10 to 60 mM KOH was performed at 10 μL/min. Separations of the relatively large number of target analytes were highly reproducible, with retention time RSD ranging from 0.064% for quinate to 0.011% for citrate over the 30 consecutive runs.

FIGURE 6. Separation of 29 anions using a 2 mm Dionex IonPac AS11-HC-4μm column and a high-pressure Dionex EGC-KOH cartridge.

Column: Dionex IonPac AS11-HC-4μm, 2 x 250 mm
Eluent: 0.1–2 mmol/L KOH in 10 min, 2–25 mmol/L KOH in 30 min, 25–65 mmol/L KOH in 20 min
Flow Rate: 0.38 mL/min
Backpressure: 4250 psi
Inj. Volume: 2.5 μL
Temperature: 35 °C

Peaks(Concentration in mg/L):

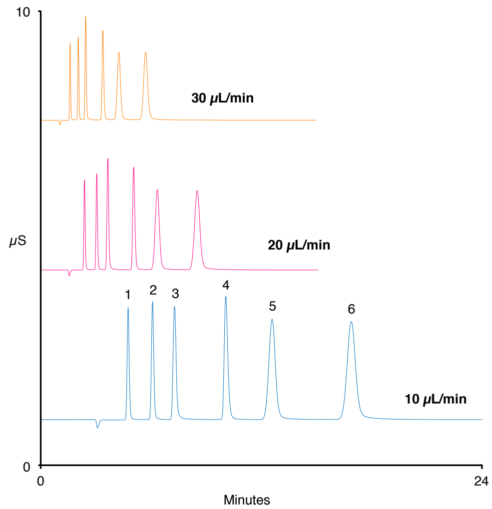
1. Quinate	10	16. Bromide	10
2. Fluoride	3	17. Nitrate	10
3. Lactate	10	18 Carbonate	20
4. Acetate	10	19. Malonate	15
5. Propionate	10	20. Maleate	15
6. Formate	10	21. Sulfate	15
7. Butyrate	10	22. Oxalate	15
8. Methylsulfonate	10	23. Tungstate	20
9. Pyruvate	10	24. Phosphate	20
10. Valerate	10	25. Phthalate	20
11. Monochloroacetate	10	26. Citrate	20
12. Bromate	10	27. Chromate	20
13. Chloride	5	28. cis-Aconitate	20
14. Nitrite	10	29. trans-Aconitate	20
15. Trifluoroacetate	10		



The Dionex ICS-5000 capillary IC system provides an ideal platform to perform fast RFIC separation of common anions and cations. Figure 7 shows the fast separation of common cations using a capillary Dionex IonPac CS16 column. The separation flow rate was varied from 10 to 30 μL/min to influence the separation process. By performing separation using 30 mM MSA at 30 μL/min, six common cations were separated in less than 6 min while maintaining sufficient resolution of target analytes. Compared to conventional-scale IC systems using 4 mm i.d. columns, the capillary IC systems using 0.4 mm i.d. columns provide increased mass sensitivity. This is due to the fact that, for the same amounts of analytes injected onto both columns, the concentrations of separated analytes going through the conductivity detector in the 0.4 mm column systems are 100 times of those in the 4 mm column system.

Because of this increased mass sensitivity, the capillary IC systems offer improved performance in trace analysis of target analytes. A 10 µL injection on a capillary IC system is equivalent to a 1 mL injection on the conventional IC system.

FIGURE 7. Fast separation of six cations on a capillary Dionex IonPac CS16 column.

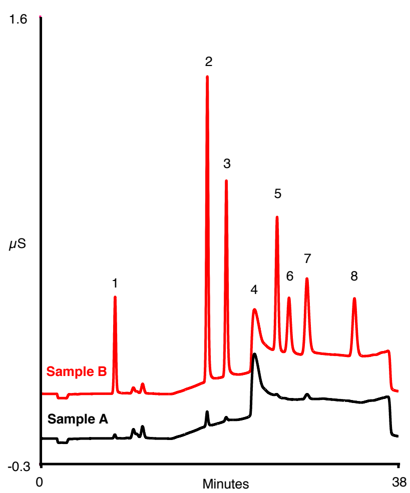


Column:	Dionex IonPac CS16 (0.5 mm x 250 mm)
Eluent Source:	Dionex EGC-MSA Capillary
Eluent:	30 mM MSA
Flow Rate:	10 to 30 µL/min
Temperature:	40 °C
Detection:	Suppressed conductivity, Dionex CCES™ 300, AutoSuppression recycle mode
Inj. Volume:	0.4 µL

Peaks	Retention Time at 30 µL/min (minutes)	Concentration (mg/L)
1. Lithium	1.60	0.1
2. Sodium	2.05	0.4
3. Ammonium	2.45	0.5
4. Potassium	3.38	1.0
5. Magnesium	4.25	0.5
6. Calcium	5.70	1.0

Figure 8 shows the use of a capillary RFIC system in the determination of inorganic anions at trace concentration using a capillary Dionex IonPac AS15 as the separation column. By direction injection of 180 µL of samples, we were able to quantify low ppt levels of target anions.

FIGURE 8. Separation of inorganic anions at trace concentrations on a capillary Dionex IonPac AS15 column.



Column:	Dionex IonPac AS15 (0.4 × 250 mm)
Eluent Source:	Dionex EGC-KOH (Capillary)
Eluent:	7 mM KOH (0 to 10 min), 7 to 32 mM KOH (10 to 16 min), 32 to 50 mM KOH (16 to 30 min), 50 to 65 mM (30 to 33 min), 7 mM KOH (33 to 38 min)
Flow Rate:	12 µL/min
Temperature:	30 °C
Detection:	Suppressed conductivity, Dionex ACES™ 300 AutoSuppression, recycle mode
Concentrator:	Dionex IonSwift™ MAC-100 Concentrator (0.5 mm x 80 mm)
Inj. Volume:	180 µL
Sample:	A: Deionized water B: Deionized water spiked with 0.5 µg/L Fluoride, 2.5 µg/L chloride, nitrite, bromide, nitrate, and phosphate, 5.0 µg/L sulfate

Peaks (concentration in µg/L):

	A	B
1. Fluoride	0.018	0.48
2. Chloride	0.12	2.49
3. Nitrite	0.042	2.53
4. Carbonate	–	–
5. Sulfate	0.075	4.72
6. Bromide	–	2.36
7. Nitrate	0.15	2.58
8. Phosphate	–	2.15

Conclusion

- The development of electrolytic eluent generation technology and RFIC systems has fundamentally changed the practice of ion chromatography
- RFIC systems offer significant benefits in terms of ease of use and improved performance of IC methods
- Capillary RFIC systems provide new platforms to improve the determination of target analytes in different sample matrices
- The combined use of RFIC systems fitted new high-pressure EGC cartridges and new IC columns packed with resins of smaller particle sizes (e.g., 4 µm) provides new opportunities to perform fast and high resolution IC separations.

U.S./Canada	(847) 295 7500	**Denmark**	(45) 36 36 90 90	**Sweden**	(46) 8 473 3380	**India**	(91) 22 2764 2735
Brazil	(55) 11 3731 5140	**France**	(33) 1 39 30 01 10	**Switzerland**	(41) 62 205 9966	**Japan**	(81) 6 6885 1213
Austria	(43) 1 616 51 25	**Germany**	(49) 6126 991 0	**United Kingdom**	(44) 1276 691722	**Korea**	(82) 2 2653 2580
Benelux	(31) 20 683 9768	**Ireland**	(353) 1 644 0064	**Australia**	(61) 2 9420 5233	**Singapore**	(65) 6289 1190
	(32) 3 353 42 94	**Italy**	(39) 02 51 62 1267	**China**	(852) 2428 3282	**Taiwan**	(886) 2 8751 6655

Thermo SCIENTIFIC

Part of Thermo Fisher Scientific

PN70061_E 03/12S