A New Hydroxide Selective Anion Exchange Phase for Ion Chromatography

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Overview

Purpose: Development and evaluation of a new anion exchange phase for Ion Chromatography

Methods: Ion Chromatography

Results: Dionex IonPac® AS28-4µm offers superior performance in terms of selectivity, peak efficiency and sensitivity.

Introduction

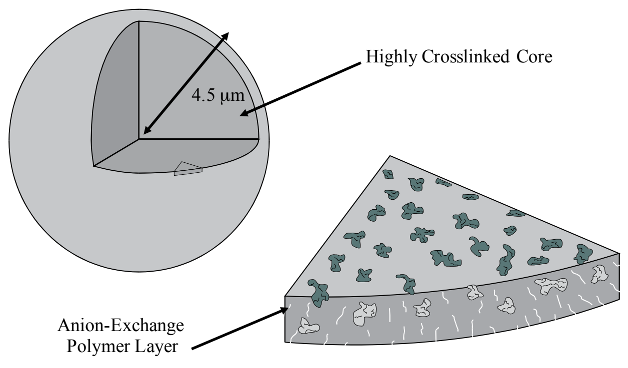
In the area of ion chromatography of anions, hydroxide based eluent systems provide the highest detection sensitivity as well as the lowest noise, resulting in substantially lower detection limits. Hydroxide eluent is ideally suited to the application of gradients in anion exchange ion chromatography in terms of detection properties. As a result, we have developed a series of new hydroxide selective phases over the past 15 years aimed at producing materials well suited to the chemical and chromatographic properties of hydroxide eluents. In this presentation, we will demonstrate recent advances in hydroxide selective stationary phases.

Experimental Conditions

- All separations were performed using an ICS-5000 system (Dionex, Sunnyvale, CA) equipped with dual pump, eluent generator, conductivity detectors and AERS in recycle mode
- Columns used were Dionex IonPac® AS15 and AS28-4µm
- Dionex Chromeleon 6.8 chromatography management software was used for controlling system and data processing

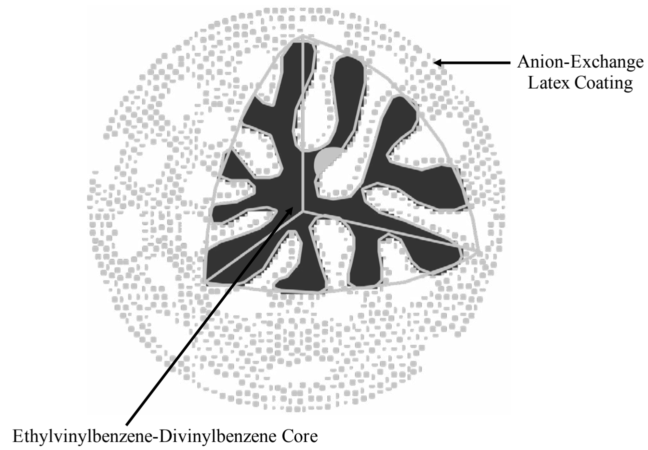
Results

FIGURE 1. Resin Bead Structure for the Dionex IonPac® AS15



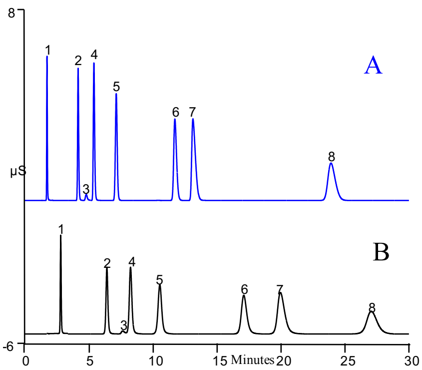
Dionex IonPac® AS15 packing is composed of a highly crosslinked core and an anion-exchange layer grafted to the surface, as shown in Figure 1. The AS15 column substrate is composed of a 9µm macroporous resin bead consisting of ethylvinylbenzene crosslinked with 55% divinylbenzene. The anion-exchange layer is functionalized with alkanol quaternary ammonium groups.

FIGURE 2. Resin Bead Structure for the Dionex IonPac® AS28-4µm



Dionex IonPac® AS28-4µm packing is a unique structure composed of a highly crosslinked core and a MicroBead™ anion-exchange layer attached to the surface, as shown in Figure 2. The AS28-4µm column substrate is a 4µm supermacroporous resin bead consisting of ethylvinylbenzene crosslinked with 55% divinylbenzene. The anion-exchange layer is functionalized with alkanol quaternary ammonium groups and has a controlled thickness, which results in excellent mass transfer characteristics and consequently, highly efficient peaks.

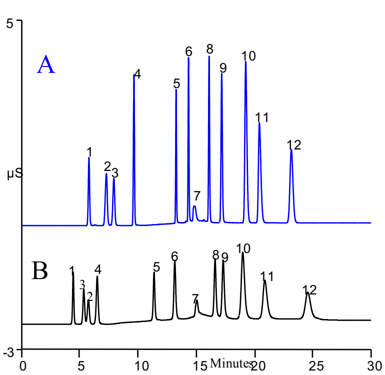
FIGURE 3. Dionex IonPac® AS28-4µm 4x150mm Versus AS15 4x250mm: Comparison of Selectivity Using Isocratic Eluent



Column A:	Dionex IonPac AG28-4µm / AS28-4µm (4 x 150 mm)
Column B:	Dionex IonPac AG15/ AS15 (4 x 250 mm)
Eluent A:	55mM KOH
Eluent B:	38mM KOH
Eluent Source:	Dionex EGC 500 KOH Cartridge
Flow Rate:	1.2mL/min
Inj. Volume:	10 µL
Temperature:	30 ˚C
Detection:	Suppressed Conductivity, Dionex AERS 500 (4 mm) Suppressor, AutoSuppression, Recycle mode
Peaks:	mg/L
1.Fluoride	2.0
2.Chloride	5.0
3.Carbonate	---
4.Nitrite	10.0
5.Sulfate	10.0
6.Bromide	20.0
7.Nitrate	20.0
8.Phosphate	30.0

Figure 3A and B illustrates the common anion selectivity for the IonPac® AS15 and AS28-4µm column using recommended eluent at the same linear velocity. Notice the excellent peak shape for the AS28-4µm due to controlled thickness of MicroBead™ and 4µm supermacroporous resin beads.

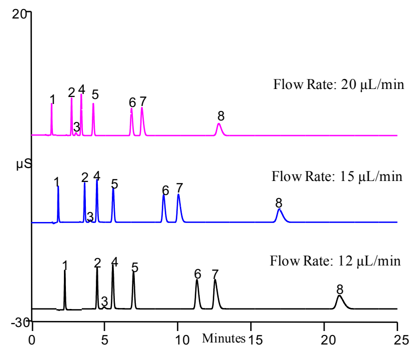
FIGURE 4. Dionex IonPac® AS28-4µm 4x150mm Versus AS15 4x250mm Column: Comparison of Selectivity and Sensitivity Using Gradient Chromatography



Column A:	Dionex IonPac AG28-4µm / AS28-4µm (4 x 150 mm)
Column B:	Dionex IonPac AG15/ AS15 (4 x 250 mm)
Eluent A :	5 mM KOH from 0 to 7 minutes, 5-20 mM KOH from 7 to 9 minutes, 20-72 mM KOH from 9-14minutes 72mM KOH from 14-26 minutes
Eluent B :	10 mM KOH from 0 to 6 minutes, 10-45 mM KOH from 6 to 14 minutes, 45mM KOH from 14-26 minutes
Eluent Source:	Dionex EGC 500 KOH Cartridge
Flow Rate A:	1.2mL/min
Flow Rate B:	1.6mL/min
Inj. Volume:	10 µL
Temperature:	30˚C
Detection:	Suppressed Conductivity, Dionex AERS 500 (4 mm) Suppressor, AutoSuppression, Recycle mode
Peaks:	mg/L (ppm)
1.Fluoride	1.0
2.Acetate	5.0
3.Glycolate	5.0
4.Formate	5.0
5.Chloride	2.5
6.Nitrite	5.0
7.Carbonate	25.0
8.Sulfate	5.0
9.Oxalate	5.0
10.Bromide	10.0
11.Nitrate	10.0
12.Phosphate	15.0

Figure 4A and B demonstrates common inorganic anion and organic acid selectivity for the IonPac® AS15 and AS28-4µm column. The IonPac® AS15 and AS28-4µm are high-capacity, hydroxide-selective anion-exchange columns designed for the determination of trace-level concentrations of inorganic anions and low molecular weight organic acids in high-purity water matrices encountered in the semiconductor and power generation industries. Both columns offer excellent retention of fluoride from the water dip and use a simple hydroxide gradient easily supplied by the Eluent Generator (EG). However, notice the excellent peak shape and better sensitivity offered by the IonPac AS28-4µm column.

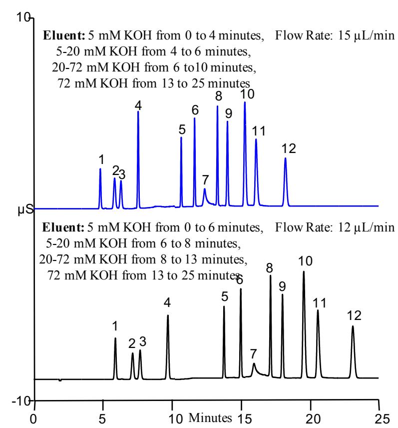
FIGURE 5. Effect of Increasing Flow Rate on Analysis Speed Using Dionex IonPac AS28-4µm and Isocratic Eluent



Column:	Dionex IonPac AG28-4µm / AS28-4µm (0.4 x 150 mm)
Eluent :	55 mM KOH
Eluent Source:	Dionex EGC 500 KOH Cartridge
Flow Rate:	See Chromatogram
Inj. Volume:	0.4 µL
Temperature:	30˚C
Detection:	Suppressed Conductivity, Dionex ACES 300 Suppressor, AutoSuppression, Recycle mode
Peaks:	mg/L
1.Fluoride	0.5
2.Chloride	1.3
3.Carbonate	--
4.Nitrite	2.5
5.Sulfate	2.5
6.Bromide	5.0
7.Nitrate	5.0
8.Phosphate	7.5

Figure 5 shows how analysis time can be reduced by increasing the flow rate without changing the common inorganic anion selectivity.

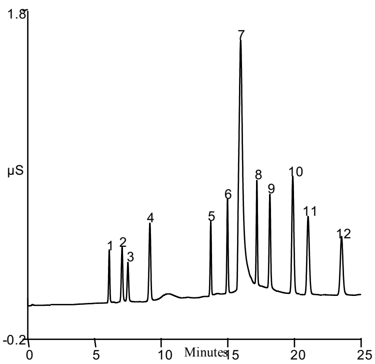
FIGURE 6. Optimization of a Hydroxide Gradient and Flow Rate to Reduce the Analysis Time



Column:	Dionex IonPac AG28-4µm / AS28-4µm (0.4 x 150 mm)
Eluent :	See Chromatogram
Eluent Source:	Dionex EGC 500 KOH Cartridge
Flow Rate:	See Chromatogram
Inj. Volume:	0.4 µL
Temperature:	30˚C
Detection:	Suppressed Conductivity, Dionex ACES 300 Suppressor, AutoSuppression, Recycle mode
Peaks:	mg/L (ppm)
1. Fluoride	0.25
2. Acetate	1.25
3. Glycolate	1.25
4. Formate	1.25
5. Chloride	0.63
6. Nitrite	1.25
7. Carbonate	6.25
8. Sulfate	1.25
9. Oxalate	1.25
10. Bromide	2.50
11. Nitrate	2.50
12. Phosphate	3.75

Figure 6 demonstrates optimization of a hydroxide gradient and flow rate to reduce analysis time for the common inorganic anions and organic acids encountered in the semiconductor and power generation industries.

FIGURE 7. Analysis of Trace Organic Acids and Inorganic Anions Using a Hydroxide Gradient, Large Loop Injection, and Dionex IonPac® AS28-4µm 2 mm Column

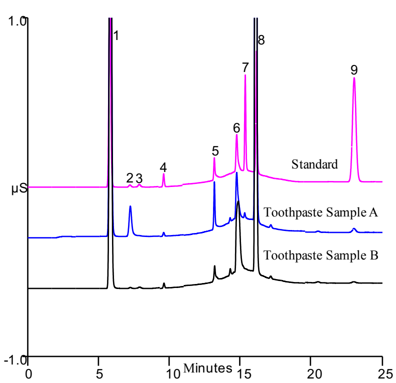


Column:	Dionex IonPac AG28-4µm / AS28-4µm (2 x 150 mm)
Eluent :	7 mM KOH from 0 to 6 minutes, 7-20 mM KOH from 6 to 8 minutes, 20-72 mM KOH from 8 to 13 minutes, 72 mM KOH from 13 to 25 minutes
Eluent Source:	Dionex EGC 500 KOH Cartridge
Flow Rate:	0.3 mL/min
Inj. Volume:	500 µL
Temperature:	30°C
Detection:	Suppressed Conductivity, Dionex AERS 500 (2 mm) Suppressor, AutoSuppression, Recycle mode

Peaks:	µg/L (ppb)
1. Fluoride	1.0
2. Acetate	5.0
3. Glycolate	5.0
4. Formate	5.0
5. Chloride	2.5
6. Nitrite	5.0
7. Carbonate	25.0
8. Sulfate	15.0
9. Oxalate	5.0
10. Bromide	10.0
11. Nitrate	10.0
12. Phosphate	15.0

Figure 7 illustrates the separation of inorganic anions and low molecular weight organic acids in a high-purity water matrix using large loop injection. Separation was achieved using a potassium hydroxide gradient with suppressed conductivity detection at a temperature of 30 °C. Low µg/L (ppb) levels of these analytes can easily be quantified using a 500µL injection on an IonPac® AS28-4µm (2×150 mm) column. The conductivity of the hydroxide eluent can be suppressed to a very low background, facilitating trace-level analysis.

FIGURE 8. Analysis of Toothpaste Samples Using a Hydroxide Gradient and Dionex IonPac® AS28-4µm 4 mm Column

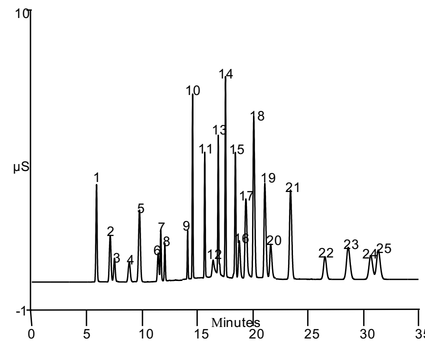


Column:	Dionex IonPac AG28-4µm / AS28-4µm (4 x 150 mm)
Eluent :	5 mM KOH from 0 to 7 minutes, 5-20 mM KOH from 7 to 9 minutes, 20-72 mM KOH from 9 to 13 minutes, 72 mM KOH from 13 to 25 minutes
Eluent Source:	Dionex EGC 500 KOH Cartridge
Flow Rate:	1.2 mL/min
Inj. Volume:	10 µL
Temperature:	30°C
Detection:	Suppressed Conductivity, Dionex AERS 500 (4 mm) Suppressor AutoSuppression, Recycle mode

Peaks (Standard):	mg/L (ppm)
1. Fluoride	1.0
2. Acetate	0.1
3. Glycolate	0.1
4. Formate	0.1
5. Chloride	0.1
6. Carbonate	---
7. Monofluorophosphate	1.0
8. Sulfate	1.0
9. Phosphate	5.0

Figure 8 illustrates that the IonPac® AS28-4µm column can also be used for analysis of tooth paste samples.

FIGURE 9. Separation of Various Environmental Anions Using a Hydroxide Gradient and Dionex IonPac® AS28-4µm 0.4 mm Column



Column:	IonPac AG28-4µm / IonPac AS28-4µm (0.4 x 150 mm)
Eluent :	5 mM KOH from 0 to 7 minutes, 5-20 mM KOH from 7 to 9 minutes, 20-72 mM KOH from 9 to 13minutes, 72 mM KOH from 13 to 35 minutes
Eluent Source:	Dionex EGC 500 KOH Cartridge
Flow Rate:	12 µL/min
Inj. Volume:	0.4 µL
Temperature:	30°C
Detection:	Dionex ACES 300 Suppressor AutoSuppression, Recycle mode

Peaks (Standard):	mg/L
1.Fluoride	1.0
2.Acetate	5.0
3.Iodate	5.0
4.Butyrate	5.0
5.Formate	5.0
6.Valariate	5.0
7.Methylsulfonate	5.0
8.Chlorite	5.0
9. Bromate	5.0
10.Chloride	2.5
11.Nitrite	5.0
12.Carbonate	25.0
13.Monofluorophosphate	10.0
14.Sulfate	5.0
15.Oxalate	5.0
16.Benzoate	10.0
17.Azide	10.0
18.Bromide	10.0
19.Nitrate	10.0
20.Chlorate	10.0
21.Phosphate	15.0
22.Arsenate	10.0
23.Citrate	10.0
24.Chromate	10.0
25.Thiosulfate	10.0

Figure 9 illustrates the separation of various environmental anions using hydroxide gradient.

Conclusion

Dionex IonPac® AS28-4µm offers the following advantages relative to IonPac® AS15 column:

- Improved peak shape, efficiency and resolution
- Superior column selectivity with improved sensitivity
- Superior resolution of early-eluting anions (fluoride, glycolate, acetate, and formate)
- Use large-loop injection for ppb-level analysis
- Recommended column for high-purity water matrices encountered in the semiconductor and power generation industries

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