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The Thermo Scientific Dionex IonPac AS29-Fast-4µm column, and why it is time to upgrade to this new carbonate eluent column

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Background: drinking water and regulations

Let's review drinking water regulations and regulated methods before I compare the Thermo Scientific™ Dionex™ IonPac™ AS4A-SC column which is similar to the 1984 state-of-the art column (the Thermo Scientific™ Dionex™ IonPac™ AS4 column), to the modern 2019 column, the Thermo Scientific™ Dionex™ IonPac™ AS29-Fast-4µm column.

Everyone wants clean drinking water, however drinking water has not always been clean. In the U.S, municipal drinking water regulations were enacted in 1972 under the 1972 Clean Water Act and the National Primary Drinking Water Regulation.[1] The test methods for determining contaminants in drinking water are also regulated. Bottled water is regulated as a food item under the U.S. Food and Drug Administration. In contrast, the European Union (EU) groups all forms of drinking water together, municipal, bottled, and mineral water. The EU regulates drinking water under EU Council Directive 98/83/EC.[2]

Which contaminants are regulated? Not every contaminant needs to be regulated. The U.S. EPA has criteria for adding contaminants into the contaminant regulations: 1) The contaminant poses a health risk; 2) The contaminant is present or frequently present, and present at a concentration that impacts health; and 3) Removal of the contaminant is possible and removal reduces the health risk.[3] In addition, we need a viable test for them. Sensitive analytical methods must be available to determine those contaminant concentrations below the regulatory limits. Ideally, it would also be great if the method can separate the contaminants of interest from everything else in the sample.

Test methods

In 1972, the water testing methods weren't quite ready; water analysis methods were spot tests, titration, or colorimetric methods.[4] Many of the ions of interest are poor chromophores, and therefore not suitable for colorimetry. Do you remember spot tests and titration, and how tedious they were to perform? All that changed, when in 1975 Dionex introduced "Ion Chromatography (IC)" instruments using anion-exchange chromatography with a carbonate buffer mobile phase (eluent) and suppressed conductivity

detection. The ions of interest were resolved from each other and from other anions in the sample. As the ions eluted from the column, they were detected using another new invention "suppressed conductivity detection".

U.S. EPA Methods 300.0 and 300.1

In 1984 the U.S. EPA and Dionex Corporation jointly developed EPA Method 300.0, and later Method 300.1 Part A and Part B[5], to determine anions and disinfection byproducts in drinking water. U.S. EPA Method 300.0 specified the Dionex IonPac AS4, 4 x 250 mm column and required the determinations of fluoride, chloride, nitrite, bromide, nitrate, phosphate, and sulfate in drinking water. Fluoride, nitrate, and nitrite are health concerns when concentrations are present in the drinking water at part per million (mg/L). Phosphate and nitrate are nutrients, which at high levels can cause algae blooms that poison the water. In contrast, chloride and sulfate are regulated as a secondary contaminant for aesthetic reasons, because the water tastes salty or disagreeable at high concentrations. Bromide is not a regulated contaminant but is monitored as the source of bromate, a toxic disinfection byproduct regulated at parts per billion (µg/L) concentrations. The EU has similar water quality test methods, ISO 10304-1 for common anions and ISO 10304-4 for disinfection byproducts.[6]

The maximum contamination level (MCL) and the maximum contamination goals (MCLG) for each anion and regulation are summarized in Table 1

Table 1. Drinking water standards

	U.S. EPA		E.U. Directive 98/83/EC
	MCLG (mg/L)*	MCL (mg/L)**	MCL (mg/L)**
Fluoride***	4.0	4.0, 2.0***	1.5
Nitrite	1.0	1	0.5
Nitrite	10	10	50
Chloride***	250	250	250
Sulfate***	250	250	250

* MCLG: Maximum contamination level goal

** MCL: Maximum contamination level

*** Fluoride is listed as a primary and secondary contaminant; Chloride and sulfate are secondary contaminants.

Thermo Scientific Dionex IonPac AS29-Fast-4µm Column

I'll quickly summarize the advantages of the latest carbonate eluent column, the Dionex IonPac AS29-Fast-4µm (4 x 150 mm), over the Dionex IonPac AS4A-SC column (4 x 250 mm) to determine anions using U.S. EPA Method 300.1 Part A. For more information on this topic, please visit the Water Analysis section of our Environmental Learning Center.

The Dionex IonPac AS29-Fast-4µm column has (as compared to the Dionex IonPac AS4A-SC column):

1. Similar run times at 50% the flow rates which saves manual eluent preparation time and costs
2. Improved selectivity optimized to elute fluoride well out of the void volume, which allows accurate reporting of fluoride concentrations
3. Improved selectivity optimized to resolve acetate from fluoride, resulting in accurate reporting of fluoride in the presence of acetate (an anion sometimes found in spring water)
4. Buffered column substrate to manage high pH and low pH samples (and buffered eluent)
5. Higher capacity to allow improved tolerance of higher concentrations of matrix ions without column overload
6. Higher column and peak efficiencies which result in narrower peaks, improved integration, and more accurate reporting

In Table 2, I show a comparison of the two columns.

Table 2. Comparing the modern column against the 1980's column

	1980's Dionex IonPac AS4A-SC column	2019 Dionex IonPac AS29-Fast-4µm column
Run times for 7 or 8 common anions	8 min	9 min
Manual eluent consumption*	Lasts ~ 32 h for 4 L	Lasts ~ 65 h for 4 L
Selectivity: Fluoride resolution from void dip**	Sometimes in the dip	~0.5 min after dip
Selectivity: Resolution of acetate and formate from fluoride*	No	√
Buffered column and eluent	Only eluent	√
Column Capacity (4 mm i.d.)	20 µEquivalence/column	126 µEquivalence/column
Column Efficiency	2000-4000 plates/column	8000-12000 plates/column
Peak Efficiency (sulfate)*	≥ 3600	≥ 8100

* Based on QAR report specifications

** This issue was solved decades ago

Resin and column improvements

Some of the process advancements made after 1984 are not visible, however the resin size and type are very different. In 1984, state of the art anion-exchange columns used non-porous, 13-µm latex-resin particles with their surfaces covered in anion-exchange beads (Figure 1). Since then, the columns are created with much smaller and highly porous resin particles (Figure 2)[7]. Table 3 shows a side-by-side comparison of the two columns. The Dionex IonPac AS29-Fast-4µm column has very porous 4 µm polymer beads, composed of ethylvinylbenzene cross-linked with 55% divinylbenzene. These highly porous resin beads are coined supermacroporous beads.

The anion-exchange process starts with sulfonating the surface similar to our other anion-exchange columns. The next stage creates a novel layer structure coined as "hyper-branched" on the surface of the resin particle.[6] The structures are grown directly off the substrate by alternating condensation reactions with epoxy and amine monomers. Using this process, the Dionex IonPac AS29-Fast-4µm column is optimized for selectivity of common inorganic anions in diverse sample matrices. The final column is very robust, optimized to buffer extremely acidic or basic samples with minimum loss of performance.

Figure 1. Anion exchange beads on non-porous resin beads used on Dionex IonPac AS4A-SC column

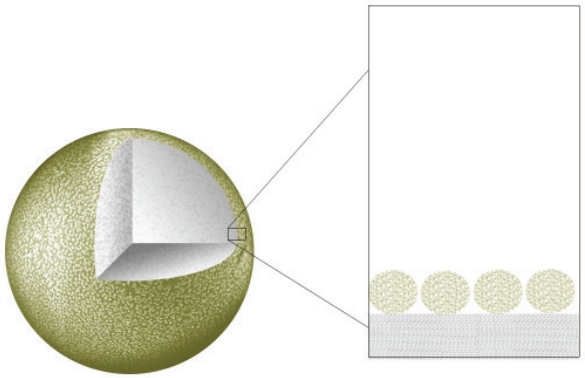


Figure 2. Hyper branched anion exchange structure on supermacroporous resin beads used on Dionex IonPac AS29-Fast-4µm column

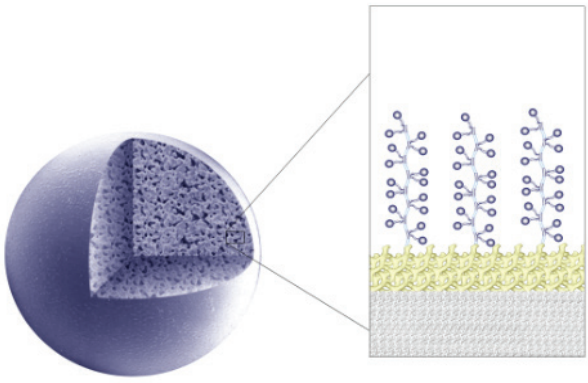


Table 3. Column resin comparison

	1980s Dionex IonPac AS4A-SC column	2019 Dionex IonPac AS29-Fast-4µm column
Resin bead type	Non-porous	Highly porous. 2000 Å
Cross-linked	55% divinylbenzene	55% divinylbenzene
Anion-exchange structure	Small latex beads on outside of resin bead	Hyper-branched structure on outside and in pores
Resin bead size (µm)	13	4

Column selectivity, improving the quantitation of early eluting peaks

The differences and advantages of column selectivity are demonstrated in Figures 3 and 4. Carbonate is considered a strong eluent, noticeably impacting the early eluting anions: the barely retained fluoride, followed by acetate and formate that elute between fluoride and chloride. In the earlier columns, such as the Dionex IonPac AS4A-SC column, fluoride elutes in or on the edge of the column void volume (also called the water dip) (Figure 3), making integration difficult and inconsistent. Additionally, on this column, chloride elutes immediately after fluoride with little to no elution window available for acetate and formate. Acetate is ubiquitous so likely it is co-eluting with fluoride. As a result, higher and inconsistent reporting of fluoride concentrations may occur. Whereas on the modern the Dionex IonPac AS29-Fast-4µm column, Figure 4 shows that the fluoride peak is well resolved from the water dip, and acetate is present as a nearly baseline resolved peak. Chloride, nitrite, bromide, and nitrate are evenly spaced rather than grouped together. With these selectivity advantages, fluoride is easier to quantify because the peak is on a flat baseline making the integration easier and consistent run-to-run. Thus, the results are more likely to be reported accurately. In addition, the acetate peak is not hidden under fluoride as in Figure 3. Acetate is a separate peak, making it much easier to report fluoride accurately. Of course, many columns were invented between 1984 and the present, and those columns also corrected the fluoride and acetate selectivity. The 150 mm long Dionex IonPac AS29-Fast-4µm column is also designed to have a similar run time of 8-9 min (Figure 4) as the 250 mm long Dionex IonPac AS4A-SC column at half the flow rate. The lower flow rate saves eluent and eluent preparation time.

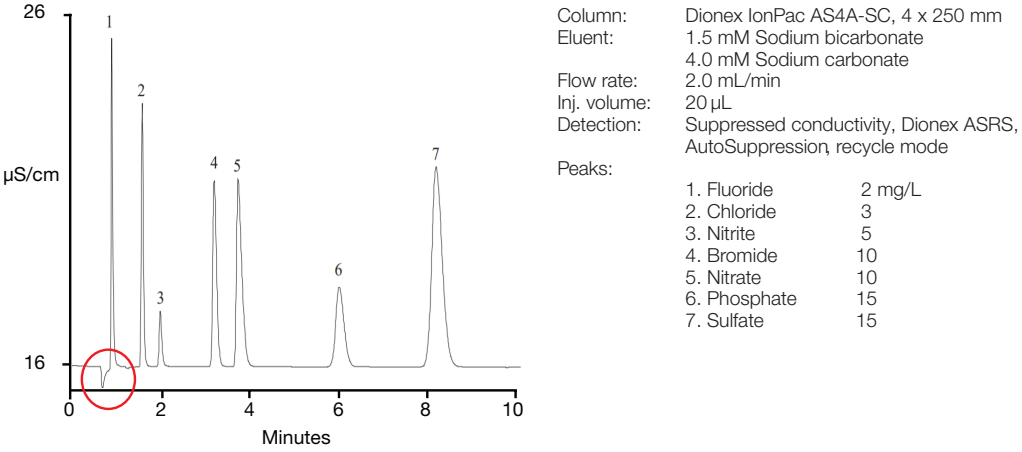
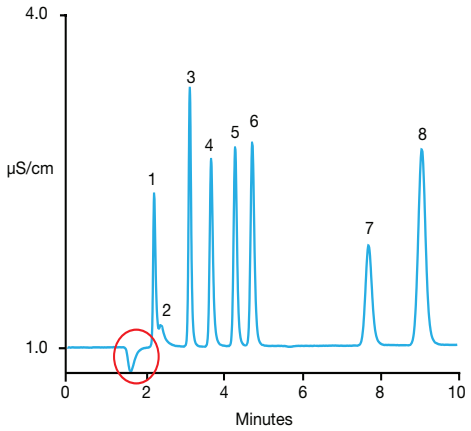


Figure 3. Separation of seven anions on Dionex IonPac AS4A-SC column in 9 min

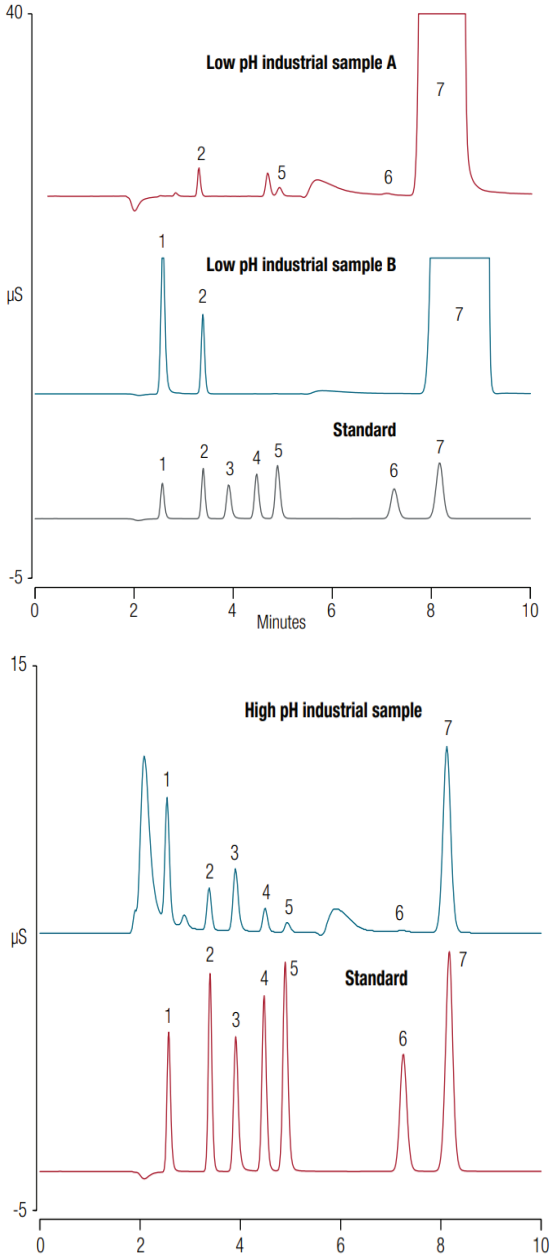


Column:	Dionex IonPac AS29-Fast-4µm, 4 x 150 mm
Eluent:	2.0 mM Sodium bicarbonate 4.5 mM Sodium carbonate
Flow rate:	1.0 mL/min
Inj. volume:	10 µL
Temperatures:	Column: 30 °C, Detector: 20 °C
Detection:	Suppressed conductivity, Dionex AERS 500 Carbonate, 4 mm, 28 mA, recycle mode

Peaks:

1. Fluoride	5 mg/L
2. Acetate	10
3. Chloride	10
4. Nitrite	15
5. Bromide	25
6. Nitrate	25
7. Phosphate	40
8. Sulfate	30

Figure 4. Eight anions separated on a 4 x 150 mm Dionex IonPac AS29-Fast-4µm column in 9 min



Column:	Dionex IonPac AS29-Fast-4µm, 4 mm i.d.
Eluent:	2.0 mM Sodium Bicarbonate 4.5 mM Sodium Carbonate
Flow rate:	1.0 mL/min
Inj. volume:	10 µL
Temperatures:	Column: 30 °C, Detector: 20 °C
Detection:	Suppressed conductivity, Dionex AERS 500 Carbonate, 4 mm, 28 mA, recycle mode

Standard peaks:

1. Fluoride	5 mg/L
2. Chloride	10
3. Nitrite	15
4. Bromide	25
5. Nitrate	25
6. Phosphate	40
7. Sulfate	30

Figure 5. Stable retention times with low and high pH samples

Dionex IonPac AS29-Fast-4µm column buffering and capacity

Strongly acidic (low pH) and strongly basic (high pH) samples can impact the anion-exchange properties of the column and can also impact the buffering capacity of the eluent. The chromatogram will have disturbances in the baseline or changes in the retention times (Figure 5). As a result, the automatic peak selection and concentrations can't be trusted. For accurate results, this usually requires multiple standard addition experiments to confirm the peak identity and to recalculate the peak concentrations. The Dionex IonPac AS29-Fast-4µm column has unique buffering by the substrate as well as buffering by the eluent which reduces manual corrections. In addition, the column has ~6x higher column capacity (125 µEq versus 20 µEq) than the 1980's column. The higher column capacity results in less column overload and more tolerance to those "real" samples, the high salt matrix samples.

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Column and peak efficiencies

Integrating a large peak is easier than a miniscule peak. The peak response and peak shape are important to quantitation and determining sensitivity, and generally easier quantitation and more sensitivity are achieved by higher peak response. Peak response is augmented by narrow peak widths which are a hallmark of smaller stationary phase particles. Thus, when comparing the same ion and the same amount on column, the Dionex IonPac AS29-Fast-4µm delivers higher peak efficiency compared to the Dionex IonPac AS4A-SC column. Therefore, the chromatogram shows narrower and taller peaks. In this way, higher efficiency results in better quantitation and thus better reporting.

Summary

In summary, the Dionex IonPac AS29-Fast-4µm column is a modern carbonate-eluent column with 4 µm diameter highly porous resin particles. This column has the same elution order as the Dionex IonPac AS4A-SC column with improved selectivity so that fluoride is resolved from the void volume and acetate and formate are resolved from fluoride. The Dionex IonPac AS29-Fast-4µm column has higher capacity, peak efficiencies, and buffering by the substrate and eluent which result in less manual peak identifications and little or no pH adjustments. See related application documents on Thermo Scientific AppsLab Digital Library.

References

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Find out more at **thermofisher.com/ICColumns**

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