

Improved determination of trace anions in high purity waters by high-volume direct injection with the Dionex EG40 eluent generator

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Introduction

This document describes the use of the Thermo Scientific™ Dionex™ EG40 potassium hydroxide (KOH) eluent generator with the Thermo Scientific™ Dionex™ IonPac™ AS15-5 μ m (3 × 150 mm) column for trace anion analysis. The Dionex EG40 module generates high-purity and carbonate-free hydroxide eluents online to improve the method performance for determination of target analytes at trace levels.^{1,2} The high-volume direct injection technique is used to achieve sensitive detection at low to sub- μ g/L levels without the use of a concentrator column, sample loading pump, and additional valve.³⁻⁵ The Dionex IonPac AS15-5 μ m column is used to separate common inorganic anions and low molecular weight organic acids in less than 20 minutes. This column provides improved peak efficiencies, which results in lower detection limits than the Dionex IonPac AS15-9 μ m column (4 × 250 mm). The analytes are detected by suppressed conductivity with a 2 mm Thermo Scientific™ Dionex™ ASRS™ ULTRA operated in the Gas-Assisted Recycle mode. This Application Update expands on work presented in Technical Note 48, “Determination of Trace Anions in High-Purity Water by High-Volume Direct Injection with the Dionex EG40”.⁶

Experimental

Equipment

- Thermo Scientific™ Dionex™ DX-600 ion chromatography system* consisting of:
 - Dionex GS50 Gradient Pump
 - Dionex CD25 Conductivity Detector
 - Dionex LC30 Chromatography Enclosure equipped with Rheodyne Model 9126 injector PEEK, rear loading
- * Equivalent or improved results can be achieved using the Thermo Scientific™ Dionex™ ICS-5000+ HPIC™ system or the Thermo Scientific™ Dionex™ Integriion™ HPIC™ system.
- Dionex IonPac AS15-5µm analytical column, 3 × 150 mm (P/N 057594)
- Dionex IonPac AG15-5µm guard column, 3 × 30 mm (P/N 057597)
- Thermo Scientific™ Dionex™ IonPac™ ATC-1 trap column, 9 × 24 mm (Replaced by Thermo Scientific™ Dionex™ IonPac™ ATC-3 Trap column, 9 × 24 mm, P/N 059660) placed after pump and Dionex IonPac ATC trap column, 4 × 35 mm (Replaced by Dionex IonPac ATC-3 column, P/N 079932) placed between the EG40 degas module and injector
- Thermo Scientific™ Dionex™ ASRS™ ULTRA 2 mm suppressor. Replaced by Dionex AERS 500 (2 mm), P/N 082541
- Dionex EG40 Eluent Generator with Dionex EluGen™ EGC-KOH cartridge
- Dionex Gas-Assisted Regeneration Kit (P/N 056886)
- Pressurized sample vessel (P/N 037460) and low-pressure 3-way double stack valve (P/N 045009), optional
- 300 cm of green 0.75 mm (0.30 in.) PEEK tubing to make a 1000 µL sample loop
- Thermo Scientific™ Dionex™ PeakNet™ Chromatography Workstation

Reagents and standards

- Deionized water, Type I reagent grade, 17.8 MΩ·cm resistance or better
- Sodium and potassium salts, ACS reagent grade, for preparing anion standards (VWR or other)
- Sodium hydroxide 50% w/w aqueous solution (Fisher Scientific)
- Potassium hydroxide 45% w/w aqueous solution (Fisher Scientific); optional instead of sodium hydroxide
- Thermo Scientific™ Dionex™ Fluoride standard 1000 mg/L, 100 mL (P/N 037158)
- Thermo Scientific™ Dionex™ Chloride standard 1000 mg/L, 100 mL (P/N 037159)
- Thermo Scientific™ Dionex™ Sulfate standard 1000 mg/L, 100 mL (P/N 037160)
- Thermo Scientific™ Dionex™ Nitrate standard 1000 mg/L, 100 mL (P/N 056497)
- Phosphate standard 1000 mg/L, 100 mL (Ultra Scientific, VWR P/N ULICC-005)
- Bromide standard 1000 mg/L, 100 mL (Ultra Scientific, VWR P/N ULICC-001)

Conditions

| | |
|---|---|
| Eluent: | Potassium hydroxide (Dionex EG40 as the source) |
| Temperature: | 30 °C |
| EG40 Offset Volume: | 0 µL |
| Pump Program: | See Table 1 |
| Eluent Flow Rate: | 0.7 mL/min |
| Detection: | Suppressed conductivity, Dionex ASRS ULTRA, Gas-Assisted Recycle mode |
| ASRS Current Setting: | 100 mA |
| Expected Background Conductivity: | 1 µS (60 mM KOH) |
| Expected System Backpressure: | 13.8 MPa (2,000 psi) |
| Sample Volume: | 1 mL |

Table 1. Pump program.

| Time (min) | Flow (mL/min) | A (%) | Valve | EG40 Conc (mM) | Comments |
|------------|---------------|-------|--------|----------------|--|
| Initial | 0.70 | 100 | Load | 60.0 | 60 mM KOH |
| 0.00 | 0.70 | 100 | Load | 7.0 | Load sample loop, equilibrate 7.0 mM KOH for 5 min |
| 5.00 | 0.70 | 100 | Inject | 7.0 | Inject |
| 10.00 | 0.70 | 100 | Inject | 7.0 | |
| 17.00 | 0.70 | 100 | Inject | 60.0 | 60 mM KOH |
| 21.00 | 0.70 | 100 | Load | 60.0 | 60 mM KOH |

Preparation of solutions and reagents

Standard solutions

Stock anion standard solution (1000 mg/L)

Several of the analytes of interest are available as 1000 mg/L ion standard solutions from Thermo Fisher Scientific or other commercial sources. In cases where standards are not available, 1000 mg/L standards can be prepared by dissolving the appropriate amounts of the corresponding mass in 1000 mL of deionized water according to Table 2. We recommend making a 100 mL final volume of 1000 mg/L stock standards in 125 mL high-density polyethylene (HDPE) containers. Concentrated standards are stable for at least one month when stored at 4 °C.

Table 2. Amounts of compounds used to prepare 1 L of 1000 mg/L ion standards

| Anion | Compound | Mass (g) |
|---|---|----------|
| F ⁻ | Sodium fluoride (NaF) | 2.210 |
| C ₂ H ₃ O ₃ ⁻ | Glycolic acid (C ₂ H ₄ O ₃) | 1.000 |
| CH ₃ COO ⁻ | Sodium acetate (CH ₃ COONa•3H ₂ O) | 2.305 |
| HCOO ⁻ | Sodium formate (HCOONa) | 1.511 |
| Cl ⁻ | Sodium chloride (NaCl) | 1.648 |
| NO ₂ ⁻ | Sodium nitrite (NaNO ₂) | 1.499 |
| SO ₄ ²⁻ | Sodium sulfate (Na ₂ SO ₄) | 1.479 |
| C ₂ O ₄ ²⁻ | Sodium oxalate (Na ₂ C ₂ O ₄) | 1.522 |
| NO ₃ ⁻ | Sodium nitrate (NaNO ₃) | 1.371 |
| PO ₄ ³⁻ | Potassium phosphate, monobasic (KH ₂ PO ₄) | 1.433 |

Composite standard solution

Composite standards of the target analyte at lower concentrations are prepared from the 1000 mg/L standards above. Select a range similar to the expected analyte concentrations in the samples. Take aliquots from this dilute standard to make working standards at the low-µg/L (ppb) down to the high-ng/L (ppt) range. Dilute stock standards at the low-mg/L (ppm) levels should be prepared fresh weekly. Working standards at the low-µg/L (ppb) range should be made fresh daily.

Dionex ATC regeneration solution

2 M sodium hydroxide

Dilute 160 g of 50% (w/w) sodium hydroxide with degassed, deionized water (with a specific resistance of 17.8 MΩ·cm or greater) to a final weight of 1080 g in an eluent bottle. Avoid the introduction of carbon dioxide from air. *Note: 2 M potassium hydroxide can be used instead of 2 M sodium hydroxide. Preparation is the same as above except that 249 g of 45% potassium hydroxide is used for a final weight of 1090 g.*

System preparation and setup

This section describes the procedures for the initial installation and start-up of the Dionex ASRS ULTRA Suppressor, Dionex IonPac ATC columns, and Dionex EGC-KOH EluGen cartridge. Prepare the Dionex ASRS Suppressor according to the *Quickstart Instructions for the ASRS ULTRA* (Document No. 031368). Prepare the Dionex IonPac ATC columns for use by rinsing with 200 mL of 2 M KOH or 2 M NaOH at 2.0 mL/min. This can be done offline without the Dionex GS50 Gradient Pump by pressurizing an eluent bottle with helium at 34.5 kPa (5 psi). Rinse the two Dionex IonPac ATC columns with deionized water at 2.0 mL/min for 20 min.

Install the Dionex EGC-OH EluGen cartridge according to the instructions in the *Operator's Manual for the EG40 Eluent Generator System* (Document No. 031373). Place the 4 mm Dionex IonPac ATC-1 column between the Dionex GS50 outlet and the Dionex EGC-KOH cartridge inlet and the 2 mm Dionex IonPac ATC column between the Dionex EG40 degas unit outlet and the injection valve inlet, as shown in Figure 9, "EG40 Flow Path Diagram", in the EG40 Eluent Generator System Manual.

Program the Dionex EG40 Eluent Generator to generate the highest concentration of KOH (60 mM) that will be used by the method and rinse the second Dionex IonPac ATC column and the separation column for 30 minutes at the method flow rate. For the Gas-Assisted Recycle mode, connect the Regen In line (shorter tubing from the tee) to the SRS Regen In port. Connect the line from the Cell Out on the conductivity cell to the From Cell line (longer tubing from the tee). Connect a gas line to the regulator. Compressed air can be used in place of helium or nitrogen if it is purified with suitable traps to remove moisture, hydrocarbons, carbon dioxide, and other particulate matter. (For more information see the *SRS Gas-Assisted Regeneration Kit Installation and Use Instructions* (Document No. 031665-02).

Make a 1000 μL sample loop by cutting a 220 cm portion of the green 0.030 in. (0.75 mm) i.d. PEEK tubing. If a different loop or tubing with a different internal diameter is desired, refer to Table 3 to calculate the length needed. The volume of a loop can be verified by measuring the weight difference between the sample loop filled with deionized water and the empty loop. The inside diameter of tubing varies by as much as 20% (for example, 0.010 ± 0.002 in.).

Table 3. Volume per unit length for various tubing internal diameters.

| Material | Color | Internal Diameter | | Estimated Volume ($\mu\text{L}/\text{cm}$) |
|----------|--------|-------------------|-------|--|
| | | Inches | mm | |
| PEEK | Red | 0.005 | 0.125 | 0.126 |
| PEEK | Black | 0.010 | 0.250 | 0.506 |
| PEEK | Orange | 0.020 | 0.500 | 2.022 |
| PEEK | Green | 0.030 | 0.750 | 4.550 |

System operation

Turn on the gradient pump to begin the flow of eluent through the system. If the system backpressure is below 14 MPa (1000 psi), a portion of yellow PEEK 0.003 in. (0.075 mm) tubing should be added between the outlet of the degas assembly in the Dionex EG40 Eluent Generator and the inlet of the injection valve. For optimal Dionex EG40 Eluent Generator performance, maintain a system backpressure of 15.2 to 16.6 MPa (2200 to 2400 psi). Confirm that there are no leaks anywhere in the chromatographic pathway. For more information see the *Operator's Manual for the EG40 Eluent Generator System* (Document No. 031373).

After stable eluent flow has been established, apply 10–15 psi gas pressure to the Regen In port of the Dionex ASRS ULTRA Suppressor. A mixture of gas and liquid will be observed exiting the Regen Out port. Turn the power on to supply current to the Dionex ASRS Suppressor; the gas flow rate across the regenerant chamber will be about 100 mL/min at a set pressure of 10–12 psi.

Turn on the Dionex EG40 Eluent Generator using PeakNet software to deliver the highest eluent concentration required by the method. Allow the Dionex LC30 oven to stabilize at the 30 °C operating temperature. Assess the quality of the blank by measuring the short-term noise. In a representative 1 minute level portion of the chromatogram, a "peak-to-peak" measurement should be less than 10 nS. It will take at least 4 hours for the system to equilibrate to a stable background conductivity for trace analysis. It is a good practice to run a system overnight to equilibrate for use the following day.

The sample is loaded with either a syringe or a pressurized reservoir. When using a syringe, take care not to introduce contamination by contact of the sample with the syringe. The black rubber plunger in disposable plastic syringes can be a source of significant contamination. To avoid contamination, the syringe should be placed at the waste port and used to pull sample into the loop. Pulling too hard will introduce unwanted bubbles into the sample loop.

When loading sample with a pressurized reservoir, a low-pressure double stack valve at the waste port regulates when the sample is loaded into the loop. More details about sample loading strategies can be found in Technical Note 48, "Determination of Trace Anions in High-Purity Water by High-Volume Direct Injection with the EG40". A Dionex AS40 or AS50 autosampler is not suitable for the determination of anions at concentrations below 10 µg/L (ppb) because the pathway of an autosampler contributes unwanted anionic contamination.

Results and discussion

The Dionex EG40 Eluent Generator electrolytically produces high-purity KOH eluents using deionized water as the carrier stream.¹ It can generate hydroxide eluents that are free of carbonate contamination. For gradient separations, the use of the Dionex EG40 Eluent Generator provides negligible baseline shifts, greater retention time reproducibility, and better method precision. Background conductivity is lower, providing the best signal-to-noise ratio. These features enhance method performance at trace levels.²

The Dionex IonPac AS15-5µm (3 × 150 mm) column is well suited for trace-level analysis of common inorganic anions and low molecular weight organic acids. For trace analysis a large loop injection was used with a weak beginning eluent concentration. The column provides improved peak efficiencies, which results in lower detection limits than the Dionex AS15-9µm (4 × 250 mm) column. The use of a shorter column provides the advantage of a faster run time. The Dionex ASRS ULTRA Suppressor delivers low background and noise for sensitivity at trace levels.

The Gas-Assisted Recycle mode was chosen to supply the regenerant solution to the Dionex ASRS Suppressor. It provides the benefit of low noise without the need for external water, significantly reducing water usage and waste. Gas-Assisted Recycle mode reduces peak-to-peak noise from the suppressor by a factor of 4 to 10 when using the eluent as the source for regenerant. A Thermo Scientific™ Dionex™ DS-3 Detection Stabilizer minimizes the effects of cell drift due to temperature fluctuations.

The separation begins with an eluent concentration of 7 mM KOH to elute the weakly retained ions such as fluoride, glycolate, acetate, and formate. A gradient from 7 mM to 60 mM KOH is used to separate the more strongly retained ions such as sulfate and phosphate. The chromatographic baseline shift is typically less than 200 nS. The separation is performed at 30 °C to provide consistent retention times during trace analysis. Figure 1 shows a typical chromatogram for a standard 11 anions at trace levels.

| | | | |
|----------------|--|---------------|------|
| Column: | Dionex IonPac AG15, AS15, 3 mm | | |
| Eluent: | 7 mM Potassium hydroxide for 5 min, 5–12 min gradient to 60 mM | | |
| Eluent Source: | Dionex EG40 | | |
| Flow Rate: | 0.7 mL/min | | |
| Injection: | 1 mL | | |
| Temperature: | 30 °C | | |
| Detection: | Suppressed conductivity, Dionex ASRS ULTRA, Gas-Assisted Recycle mode | | |
| Peaks: | 1. Fluoride 0.32 µg/L (ppb) | 7. Carbonate | — |
| | 2. Glycolate 0.84 | 8. Sulfate | 0.83 |
| | 3. Acetate 1.1 | 9. Oxalate | 0.82 |
| | 4. Formate 1.2 | 10. Bromide | 2.9 |
| | 5. Chloride 0.34 | 11. Nitrate | 0.87 |
| | 6. Nitrite 0.35 | 12. Phosphate | 2.9 |

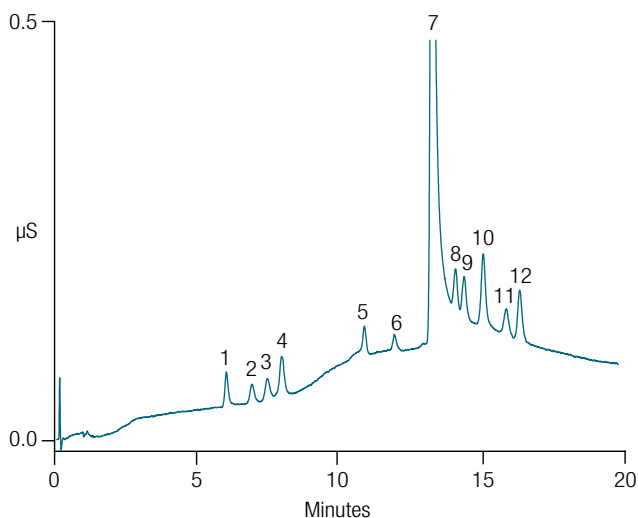


Figure 1. Trace anion determination using the Dionex IonPac AS15-5µm (3 × 150 mm) column.

A representative blank for this method is shown in Figure 2. Trace levels of fluoride, acetate, and formate originated from the point-of-use deionized water system. Determining a blank establishes a starting point above which anion determinations can be made.

Column: Dionex IonPac AG15, AS15, 3 mm
 Eluent: 7 mM Potassium hydroxide for 5 min,
 5–12 min gradient to 60 mM
 Eluent Source: Dionex EG40
 Flow Rate: 0.7 mL/min
 Injection: 1 mL
 Temperature: 30 °C
 Detection: Suppressed conductivity, Dionex ASRS ULTRA,
 Gas-Assisted Recycle mode

Peaks: 1. Fluoride 0.32 µg/L (ppb)
 2. Acetate 1.1
 3. Formate 1.2
 4. Carbonate —

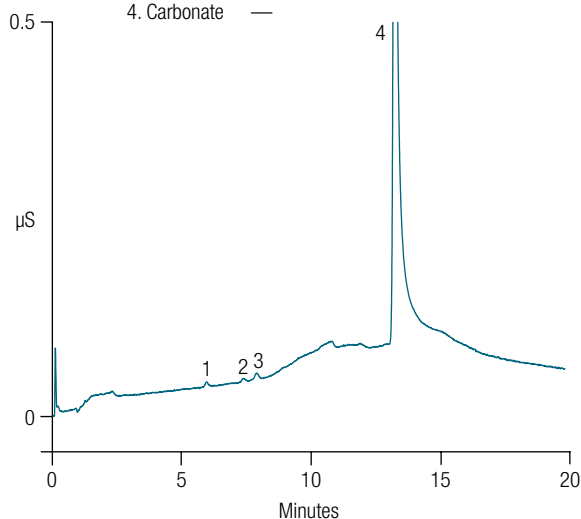


Figure 2. Representative blank for trace analysis using the Dionex IonPac AS15-5µm (3 × 150 mm) column.

Method detection limits (MDLs) established for the target anions are listed in Table 4. The MDLs for the target analytes were determined by multiplying the standard deviation of seven replicate injections for the lowest level standard with the Student's *t* value for the 99% confidence level.⁷ Calibration curves were obtained with standards prepared in deionized water using the concentrations listed in Table 5. Calibration curves for the anions of interest were linear and had coefficients of determination (*r*²) greater than 0.99.

Table 4 Method detection limits^a for anions by high-volume direct injection ion chromatography with the Dionex EG40 Eluent Generator and the Dionex IonPac AS15-5µm (3 × 150 mm) column.

| Anion | MDL ^a µg/L (ppb) |
|-----------|-----------------------------|
| Fluoride | 0.040 |
| Glycolate | 0.065 |
| Acetate | 0.49 |
| Formate | 0.42 |
| Chloride | 0.17 |
| Nitrite | 0.13 |
| Sulfate | 0.12 |
| Oxalate | 0.11 |
| Bromide | 0.27 |
| Nitrate | 0.25 |
| Phosphate | 0.18 |

^aMDL = (S.D.) × (*t*_{99%}), where (*t*_{99%}) is for a 99% single sided Student's *t*-test distribution for *n* = 7.

Table 5. Calibration curve concentrations (µg/L) for anions by high-volume direct injection ion chromatography with the Dionex EG40 Eluent Generator and the Dionex IonPac AS15-5µm (3 × 150 mm) column.

| Anion | Levels | | |
|-----------|--------|-----|-----|
| | 1 | 2 | 3 |
| Fluoride | 0.1 | 0.3 | 1.0 |
| Glycolate | 0.3 | 1.0 | 3.0 |
| Acetate | 0.3 | 1.0 | 3.0 |
| Formate | 0.3 | 1.0 | 3.0 |
| Chloride | 0.1 | 0.3 | 1.0 |
| Nitrite | 0.1 | 0.3 | 1.0 |
| Sulfate | 0.3 | 1.0 | 3.0 |
| Oxalate | 0.3 | 1.0 | 3.0 |
| Bromide | 1.0 | 3.0 | 10 |
| Nitrate | 0.3 | 1.0 | 3.0 |
| Phosphate | 1.0 | 3.0 | 10 |

Precautions

Special care must be taken to minimize contamination when performing trace analysis. It is very important to use only the highest quality deionized water. When conducting analyses at trace levels, the sources of contamination are numerous. To minimize contamination, wear disposable, powder-free PVC gloves. After putting them on, rinse with deionized water and air dry. Do not dry with paper towels. All containers should be dedicated for this analysis and copiously rinsed with 17.8 MΩ·cm or better deionized water before use. Exercise caution when handling anything that could have contact with the blank, unknown, or standards. The flow path of the chromatographic instrumentation (eluent containers, injector, pump, valves, tubing, columns, suppressor, and conductivity cell) are all potential sources of contamination. Take care when switching from a system set-up that had previously seen significant concentrations of anions. Rinse with high purity water to reduce residual contamination.

The Dionex ATC columns should be periodically regenerated with the procedure described in the System preparation and setup section. Monitoring the blank for any significant increase in anionic contamination will indicate when regeneration is necessary. Monitoring the baseline shift during the Dionex EG40 Eluent Generator hydroxide gradient will also indicate when regeneration is necessary. A significant increase beyond 200 nS indicates that the Dionex ATC column has exceeded its capacity to trap ionic contaminants and should be regenerated. The frequency of regeneration depends on the quality of the deionized water and the usage rate of the instrument.

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