

Configuring the Dionex Integrion HPIC system for trace anion determinations in ultrapure water

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Keywords

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Goal

Provide instructions for installing a trace anion application using the Thermo Scientific™ Dionex™ AutoPrep™ and Thermo Scientific™ Dionex™ EWP Electrolytic Water Purifier modules on the Thermo Scientific™ Dionex™ Integrion™ HPIC™ system

Introduction

The latest advancement in ion chromatography (IC) instrumentation, the high pressure (HP) Thermo Scientific™ Dionex™ Integrion™ HPIC™ system, can operate continuously up to 5000 psi for both 4 mm and 2 mm i.d. column formats when using electrolytic eluent generation.

When combined with the advantages and ease-of-use of a Reagent-Free™ (RFIC™) system with automated calibration and water purification, this system permits low baseline contamination with excellent reproducibility, thereby yielding greater quantification accuracy, greater sensitivity, and consistently reliable results.



Dionex Integrion HPIC system

The Dionex Integrion HPIC system includes recent advances in IC instrument technology, including high pressure capabilities for eluent generation (up to 5000 psi), column heater control, and new features designed to increase ease of use for customers. It features:

- Compact, fully integrated system design
- Easy access to eluent generator and electrolytic trap column
- Separate compartments for pump, column heater with injection valve, and detection-suppressor to provide separate temperature control and faster equilibration
- Thermo Scientific™ Dionex™ IC PEEK Viper™ fittings, replacing standard fitting connections in specified positions to minimize void volume problems, thereby improving chromatography and increasing reporting accuracy
- Components tracking by cable and radio frequency technologies for GMP compliance and to assure installation of compatible devices (i.e. installation of non-compatible devices is prevented)
 - Independent tablet control for convenient continuous chromatography monitoring, independent manual control, and the online instrument manual and troubleshooting guides
 - Optional add-ons, such as an auxiliary injection valve and additional electrolytic device channels
 - Thermo Scientific™ Chromeleon™ 7 Chromatography Data System (CDS) software features that provide easy instrument configuration, monitoring of consumable devices, and online video instructions for conditioning columns, suppressors, and other electrolytic devices

In this technical note, we provide installation recommendations for the Dionex Integrion HPIC system configured for trace anion determinations (ng/L to µg/L) using the Thermo Scientific™ Dionex™ AutoPrep™ module and the Dionex™ EWP Electrolytic Water Purifier. The results will highlight using the Thermo Scientific™ Dionex™ EWP and Dionex AutoPrep modules to achieve ng/L sensitivity, as well as some of the instrument, column, and suppressor features.

Experimental Equipment

- Thermo Scientific™ Dionex™ Integrion™ HPIC™ system, including:
 - Eluent generation
 - CD Conductivity Detector
 - Column oven temperature control
 - Detector-Suppressor compartment temperature control
 - Tablet control
 - Consumables Monitoring
 - Integrion Auxiliary Power Supply Control option, P/N 22153-62023
- RFIC-ESP™ Water Purifier option
 - Dionex Anionic Electrolytic Water Purifier with installation kit, P/N 072629
 - Dionex AutoPrep (large loop, small loop kit), P/N 066342
- Auxiliary 10-port injection valve option, P/N 22153-62025
- Thermo Scientific™ Dionex™ AS-HV Autosampler with 250 mL culture flask tray



Thermo Scientific™ Dionex™ AS-HV Autosampler

Software

- Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) software, CM 7.2 SR4

Table 1 lists the consumable products recommended for the Dionex Integrion HPIC system configured for suppressed conductivity detection and trace analysis with the Dionex EWP and Dionex AutoPrep module.

Table 1. Consumables list for the Dionex Integrion HPIC system.

Product name	Description	Part Number
Dionex IC PEEK Viper fitting tubing assembly kits	Dionex IC PEEK Viper fitting assembly kit for the Dionex Integrion HPIC system configured for eluent generation and conductivity detection: Includes one each of P/Ns: 088815–088821	088798
Dionex IC PEEK Viper fitting tubing assemblies (included in kit P/N 088798)	Guard outlet to separator column: 0.007 × 4.0 in (102 mm)	088805
	Injection Valve, Port C to guard column: 0.007 × 5.5 in (140 mm)	088806
	EGC Eluent Out to CR-TC Eluent In: 0.007 × 6.5 in (165 mm)	088807
	Separator to Suppressor Eluent In: 0.007 × 7.0 in (178 mm)	088808
	Suppressor Eluent Out to CD In: 0.007 × 9.0 in (229 mm)	088810
Dionex AS-HV Autosampler items	CR-TC Eluent Out to Degasser In: 0.007 × 9.5 in (241 mm)	088811
	Thermo Scientific™ Nunclon™ sample flasks, 250 mL, with caps and septa (pkg. of 50)	064235
	Nunclon sample flasks, 250 mL (pkg. of 50)	064053
	Additional peristaltic tubing, Santoprene™ (Exxon Mobile): 2.06 mm i.d.	064521
	Additional peristaltic tubing, Santoprene: 0.64 mm i.d.	064825
	Alternative septa: food grade aluminum foil which is cleaner than most septa	
Thermo Scientific™ Dionex™ EGC 500 KOH Eluent Generator cartridge	Eluent generator cartridge recommended for this application	075778
Thermo Scientific™ Dionex™ CR-ATC 600 Electrolytic trap column	Continuously regenerated trap column used with Dionex EGC KOH 500 cartridge and the Dionex Integrion HPIC system	088662
Thermo Scientific™ Dionex™ HP degasser module	Degasser installed after Dionex CR-TC trap column and before the Injection Valve. Used with eluent generation. Included with an Integrion HPIC system configured for eluent generation.	075522
Thermo Scientific™ Dionex™ AERS™ 500e suppressor	Recommended suppressor for 4 mm and 5 mm columns, using external water mode	SP6952
Dionex AERS 500 suppressor	Alternative suppressor for 4 mm and 5 mm columns	082540
Thermo Scientific™ Dionex™ IonPac™ AG17-C column	Anion guard column, 4 × 50 mm	066295
Dionex IonPac AS17-C column	Anion separation column, 4 × 250 mm	066294
Dionex IonPac UTAC-LP2 column	Anion concentrator column, 4 × 35 mm	079917
Dionex Anionic EWP Electrolytic Water Purifier	Provides continuous purified water for eluent generation, to the suppressor, transfer water, and diluent. The installation kit is included.	072629
Dionex AutoPrep system (large loop, small loop)	The small loop allows for automated calibration. The large loop is used for sample loading.	066342
Auxiliary 10-port Injection Valve	Second injection port for Dionex EWP	22153–62025
Thermo Scientific™ Dionex™ CRD 300 Carbonate Removal Device, 4 mm	Inline sample degasser. Removes carbonate prior to sample concentration	064637

Chromatographic conditions	
Columns:	Dionex IonPac AG17-C guard, 4 × 50 mm Dionex IonPac AS17-C separation 4 × 250 mm
Eluent:	KOH gradient, See Table 2
Eluent Source:	Dionex EGC 500 KOH eluent cartridge, Dionex CR-ATC 600 trap column and high pressure degas module
Flow Rate:	1.0 mL/min
Column Temperature:	35 °C
Detection/ Suppressor Compartment:	15 °C
Detection:	Suppressed conductivity, Dionex AERS 500e suppressor, 4 mm, external water mode (driven by system pump)
Concentrated Volume:	Standards: Incremental additions of 10 µL
Sample Volume:	10 mL
Sample Flow Rate:	~3.5 mL/min (Dionex AS-HV Autosampler pump)
Standard Flow Rate:	~0.5 mL/min (Dionex AutoPrep small loop, gravity)
Concentrator:	Dionex IonPac UTAC-LP2, 3 × 35 mm
Run Time:	Calibration standards: 41.5 min
Samples and Check Standards:	51.5 min
Background Conductance:	< 1 µS
Noise:	< 1 µS
System Backpressure:	~2200 psi

Table 2. Gradient conditions

Equilibration Starts	Time (min)	KOH (mM)
Samples and check standards	-21.5	50
	-11.5	50
	-7.0	50
	-7.0	1
	0.0	1
Calibration/Dionex EWP	4.0	1
	10.0	12.5
	20	20
	25.5	35
	30.0	35

Reagents and standards

- 18 MΩ·cm resistivity or higher degassed deionized (DI) water
- Thermo Scientific™ Dionex™ Combined Seven Anion Standard II, NIST traceable (P/N 057590) for a second source standard
- Fisher Scientific reagents, Certified ACS grade
 - Sodium bromide, P/N S255-500
 - Sodium chloride, P/N S271-500
 - Sodium fluoride, P/N S299-500
 - Sodium nitrite, P/N S347-500
 - Sodium nitrate, P/N S343-500
 - Sodium sulfate, P/N S421-500
- Fisher BioReagents: Sodium phosphate, monobasic, P/N BP329-500

Standard preparation

For trace analysis using the Dionex AutoPrep module, it is convenient to use a combined stock standard prepared at the same concentration. To prepare individual 1000 mg/L stock standards, the reagent is dissolved in DI water. Table 3 shows the amount of reagent needed to prepare 100 mL of individual 1000 mg/L stock standards.

Add the compound (shown in Table 3) to a 100 mL HDPP bottle, add 100 g of DI water, cap the bottle, and shake until the reagent is fully dissolved. Label and store at 20 °C.

Table 3. Amount of reagent needed to prepare 100 mL of 1000 mg/L individual stock standards.

Anion	Compound	Amount of Reagent (mg)	Amount of Deionized Water (g)
Fluoride	Sodium fluoride (NaF)	221	100
Chloride	Sodium chloride (NaCl)	165	100
Nitrite	Sodium nitrite (NaNO ₂)	150	100
Bromide	Sodium bromide (NaBr)	129	100
Nitrate	Sodium nitrate (NaNO ₃)	137	100
Phosphate	Sodium phosphate, monobasic (NaH ₂ PO ₄)	126	100
Sulfate	Sodium sulfate (Na ₂ SO ₄)	148	100

The Dionex AutoPrep module allows standards to be prepared at 100–1000× higher concentrations than needed for ppb and ppt calibration standards, thereby minimizing the impact of contamination. For calibration standards needed at ppb concentrations, prepare one working standard at 100× higher concentration than the lowest calibration concentration. For ppt calibrations, prepare a 1000× higher concentration standard than the lowest calibration concentration.

To prepare the 10 mg/L combined intermediate standard, add 1 g of each 1000 mg/L individual stock standard to a 100 mL HDPP bottle. Add DI water to a final weight of 100 g. Cap the bottle and invert to mix. Store the standard at 20 °C until it is needed.

To prepare 1 L of 50 ppb stock standard, add 5 g of the 10 mg/L combined standard. Add DI water to 1000 g total weight. Connect the solution to the small loop.

Place a 1 ft piece of black backpressure tubing (or sufficient length to result in a 0.5 mL/min flow rate) on the Dionex AutoPrep module small loop waste line. Use a syringe on the waste line to start gravity feed. Measure the flow rate with a timer and a 5 mL graduated cylinder. Adjust the backpressure tubing to achieve a 0.5 mL/min flow rate.

To calibrate the large loop to small loop ratio, prepare a 50 ppt working standard of bromide, by diluting the 50 ppb stock standard, 1000-fold with DI water. Prepare this calibration standard just prior to use.

Instrument Setup and Installation

The Dionex Integrion HPIC system is a high pressure integrated IC system. This system and the Dionex EGC 500 KOH cartridge and Dionex CR-ATC 600

Continuously Regenerated Trap Column consumable products are designed for high pressure conditions up to 5000 psi.

To set up this application, connect the Dionex AS-HV Autosampler and the Dionex Integrion HPIC system, the Dionex EWP Electrolytic Water Purifier, and Dionex AutoPrep module as shown in Figure 1. The flow path is similar to that of most IC systems, from the pump to the CD Conductivity Detector.

- After the conductivity detector, connect the Eluent Out line to Port 1 of the Dionex EWP Electrolytic Water Purifier module (purified water is flowing out of Port 4 of the EWP)
- Connect Port 4 of the Dionex EWP Electrolytic Water Purifier, which produces purified water, to Port 4 of the 10-port valve (contents of large or small loop are flowing out of Port 9 of the 10-port valve)
- Connect Port 9 of the 10-port valve to Eluent In of the Dionex CRD 300 Carbonate Removal Device
- Connect the Eluent Out of the Dionex CRD 300 Carbonate Removal Device to Port 5 of the 6-port valve
- Connect Port 6 of the 6-port valve to Port 2 of the Dionex EWP Electrolytic Water Purifier (water will flow out of Port 5 of the Dionex EWP Electrolytic Water Purifier module)
- Connect Port 5 of the Dionex AERS 500e suppressor and then the Dionex CRD 300 Carbonate Removal Device, and the Dionex CR-ATC 600 Continuously Regenerated Anion Trap Column. The Regen Out from the Dionex CR-ATC 600 is then connected to Port 3 of the Dionex EWP device.

Note that the injection valve is plumbed through different ports than that of previous Dionex IC systems.

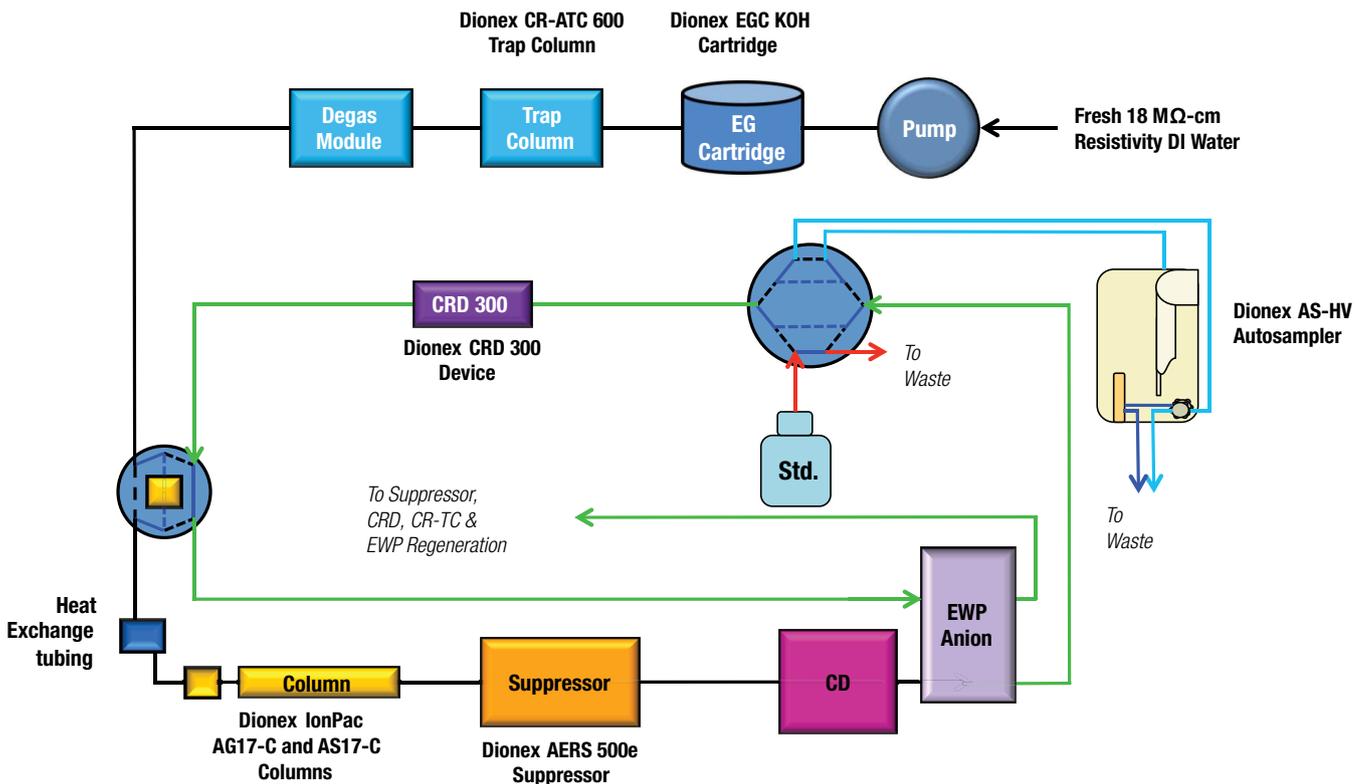


Figure 1. Flow diagram of Dionex Integrion HPIC system for trace anion determinations.

Connect the USB cable from the Dionex Integrion HPIC system to the computer and the RS232 cable from the Dionex AS-HV Autosampler to the Dionex Integrion system. Connect the cable of the Dionex EWP Electrolytic Water Purifier into the additional Aux Power Port. Connect the power cables and power-on the IC instrument and the autosampler.

Configuring the modules in Chromeleon CDS software

To configure the IC system:

1. Start the Chromeleon Instrument Controller program.
2. Select the link, *Configure Instruments* The Chromeleon Instrument Configuration Manager will open.
3. Right-click on the computer name.
4. Select *Add an Instrument*.
5. Enter an appropriate name (for example: Integrion_Trace_1).

Three modules are added to this instrument configuration: the Dionex Integrion HPIC system, Dionex Integrion HPIC Pump Wellness, and Dionex AS-HV Autosampler.

Dionex Integrion HPIC system module

1. Select *Add a Module, IC: Dionex Integrated Modules, and Integrion HPIC System* (Figure 2).

The configuration for each module is summarized at the end of this section in Table 3.

A multi-tabbed program will automatically open up (Figure 3).

2. Select *Model Serial No.* in the General tab.

The Chromeleon CDS software will automatically detect all electrolytic devices, detectors (Figure 3), Pump Degasser, and Seal Wash (not shown).

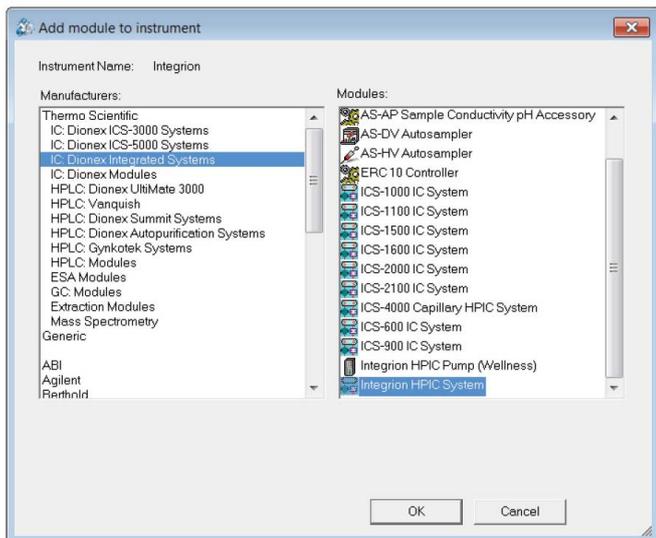


Figure 2. Creating a configuration.

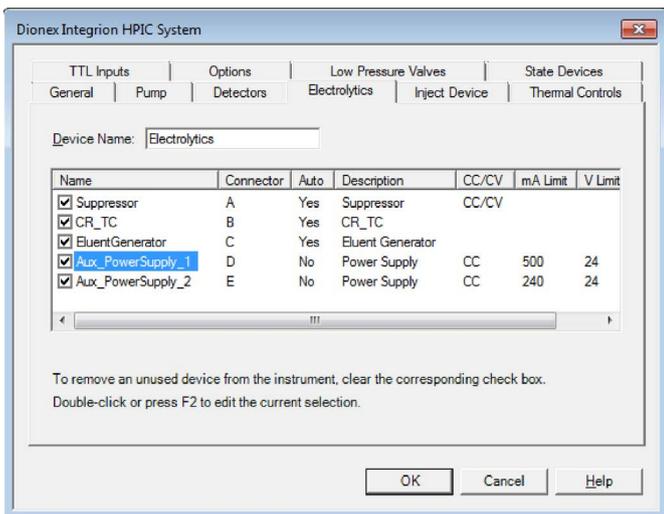


Figure 3. Automatic detection of electrolytic devices.

Dionex EWP Electrolytic Water Purifier

The Dionex Integrion HPLC system includes three channels for electrolytic devices as a factory default (eluent generator cartridge, CR-TC, and suppressor). For the Integrion HPLC system used in this technical note, the Auxiliary Power Supply option was installed, allowing the system to power two additional electrolytic devices for sample preparation purposes.

In this configuration, the auxiliary power supply on the Dionex Integrion system will be used to power the Dionex EWP Electrolytic Water Purifier (30 mA). It is prudent to limit the current to 30 mA to prevent over-voltage errors and to prevent unintentional damage to the device. To set the limit, double click (left) on Aux_PowerSupply_1 line highlighted in Figure 3, which opens a Device Configuration window. Enter 30 in the Current Limit (Figure 4).

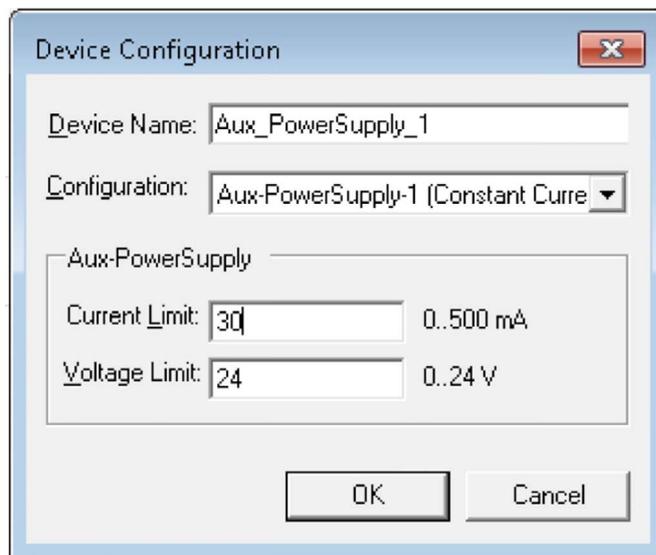


Figure 4. Setting the Dionex EWP Electrolytic Water Purifier current limit of the auxiliary power supply.

Dionex AutoPrep module

In the Dionex AutoPrep module, samples (10 mL, large loop) and standards (10 µL, small loop) use different injection loops requiring valve switches during loading and concentrating. To set control of both valves (InjectValve and HP_Valve) of the Integrion IC system, select the Inject Device tab. Double-click on InjectValve and select Integrion (Figure 5). The HP_Valve is controlled by the IC system by default.

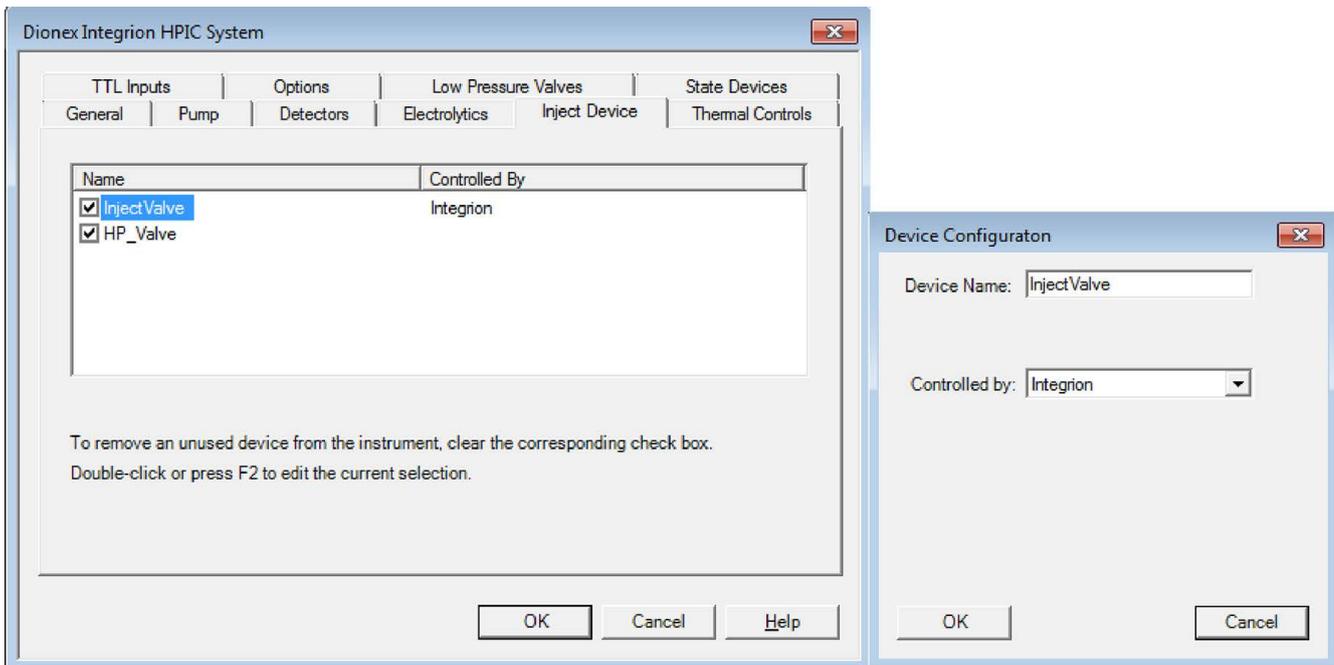


Figure 5. Setting control of the injection valve on the Dionex Integrion IC system.

Dionex Integrion HPIC Pump Wellness module

To add pressure monitoring capabilities, it is necessary to add another virtual module:

1. Right-click and select Add a Module, IC: Dionex Integrated Modules, Integrion HPIC Pump Wellness module
2. Select the USB address to link the module to the configuration.
3. Select the Devices tab and click on the Pressure Signal(s) box (Figure 6).

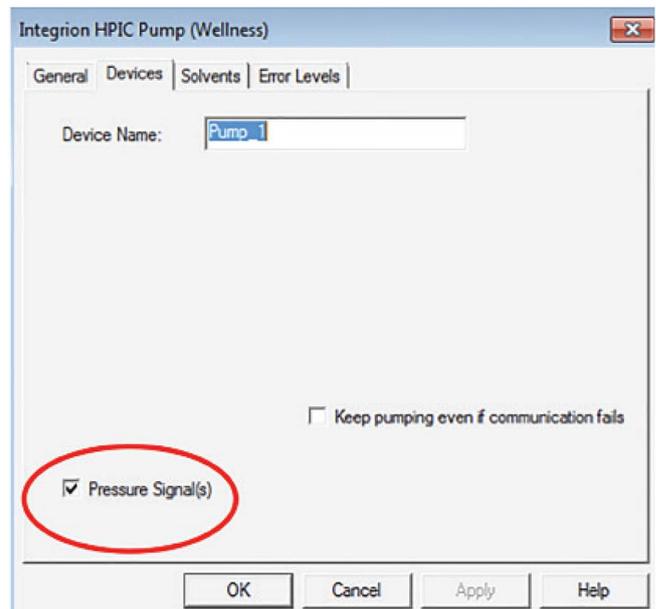


Figure 6. Adding the Dionex Integrion HPIC Pump Wellness Module to the instrument configuration.

Add the Dionex AS-HV Autosampler to the configuration

Add the Dionex AS-HV Autosampler as a module, and select the COM1 or COM2 address (see the AS-HV Operator's manual for more information¹). On the Options tab, enter in the values shown in Table 4.

Plumbing the Dionex Integrion HPIC system

To plumb the Dionex Integrion HPIC system:

1. Loosen the waste lines, including the metal-wrapped waste line, in the back of the instrument and direct the free ends to a waste container.

2. Connect the pump eluent line to the eluent bottle containing DI water previously degassed (vacuum filtration and ultrasonic agitation).
3. Prime the pump by opening the priming knob 1/4 turn and press the priming button. Prime the pump until no bubbles are visible and water is flowing at a steady rate out of the pump waste line.
4. Close the priming knob to finger tight.

For more information, review the product manual.²

Table 4. Summary of system configurations for the Dionex Integrion HPIC system.

Tab	Action	Result
Dionex Integrion HPIC System		
General	Link to USB address	
Pump		Flow rate and pressure limitations are displayed
Detectors		Automatically detected
Electrolytics		Automatically detects Dionex EGC Eluent Generator Cartridge, and Dionex CR-TC Continuously Regenerated Trap Column, suppressor, and two auxiliary power supplies (Figure 3)
	Double-left-click on Aux-PowerSupply_1	Opens the Device Configuration information on the Auxiliary Power Supply (Figure 3)
	Enter 30 in current limit	Limits current draw of the EWP module to 30 mA. (Figure 4)
Inject Device	Double left click on Inject Valve	Opens the Device Configuration information on the injection valve on the injection valve
	Select Integrion	Changes control of the injection valve from the autosampler to a programmed command by the Dionex Integrion IC system (Figure 5)
Thermal Controls		Automatically detects thermal control options for column, detector, and suppressor
Low Pressure Valves		Automatically detected
Options		Automatically detects Pump Degasser and Seal Wash pump
Pump Wellness Module		
Devices	Click pressure signal box	Activates pressure monitoring feature (Figure 6)
Add Dionex AS-HV Autosampler		
Add Module	Select Com port	Typically COM 1 or COM 2. See Dionex AS-HV Autosampler manual ¹
Options	Select rack sizes	11-position standard rack, 24-position sample rack (Figure 7)
	Select Sample Loading pump	Internal Peristaltic
	Select Rinse Source	External
	Select Sample loading type	Sample Loop
	Select Loading mode	Pull
	Not applicable	Delay volume

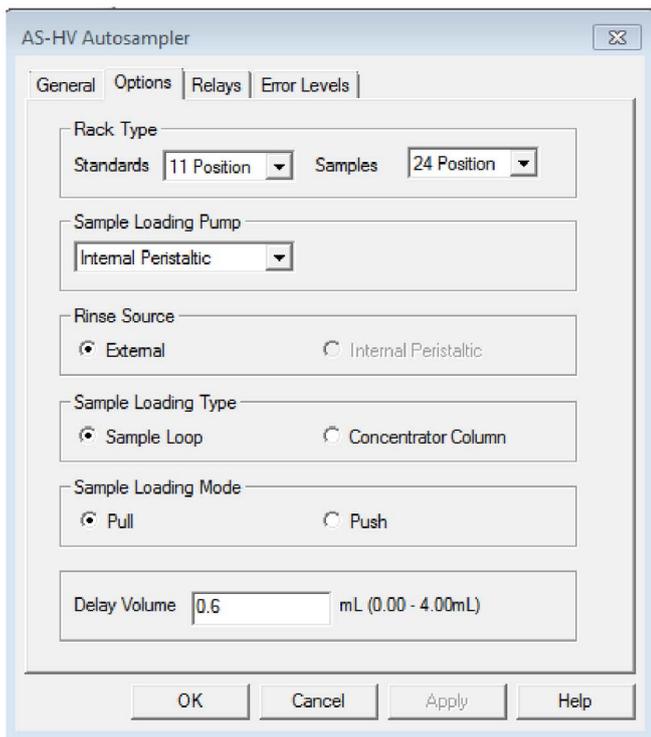


Figure 7. Configuring the Dionex AS-HV Autosampler.

Dionex IC PEEK Viper fittings

To achieve the best chromatography, it is important to gently tighten the Dionex IC PEEK Viper fittings to finger tight and to use the Dionex IC PEEK Viper fitting assemblies (Figure 8):

- Dionex EGC 500 KOH Eluent Generator Cartridge—Eluent Out to Eluent In on Dionex CR-ATC 600 Continuously Regenerated Anion Trap Column
- Dionex CR-ATC 600 Continuously Regenerated Anion Trap Column—Eluent Out to Eluent In on the Dionex Degas Module
- Injection Valve—Column port to the guard column
- Between the guard and separation columns
- Separation column to Eluent In on the Dionex AERS 500e Anion Electrolytically Regenerated Suppressor
- Dionex AERS 500e Anion Electrolytically Regenerated Suppressor—Eluent Out to Eluent In on CD Conductivity Cell.

Dionex IC PEEK Viper fittings (Figure 8) minimize void volume in critical chromatography components, such as the columns and suppressor. Dionex IC PEEK Viper fittings are also recommended for use in consumable devices, such as the eluent generator cartridge and trap column to minimize installation issues. The tubing can be used for both standard bore and microbore column applications. The tubing length is specified for each connection (Table 1). The recommended practice is to tighten the Dionex IC Viper fittings to finger tight. If leaking is observed, tighten an additional 1/16 to 1/8 turn clockwise.



Figure 8. Dionex IC PEEK Viper Fittings.

Caution: Using a wrench or any other tool to tighten the Dionex IC PEEK Viper fittings may permanently damage the fitting, making it inoperable.

Conditioning electrolytic devices and columns

Important: Do not remove consumable tracking tags on the columns and consumable devices. These tags are required for consumables monitoring functionality.

Install the Dionex EGC 500 KOH cartridge and Dionex CR-ATC 600 Continuously Regenerating Anion Trap Column in the reservoir tray compartment. Condition the devices according to instructions in the drop-down menu under Consumables, Install (Figure 9). (This information is also available in the product manuals and the system installation manual.²⁻⁴) Install the black PEEK (0.010 in i.d. tubing) backpressure loop (exerting an additional ~40 psi) from the slotted compartment next to the CD Conductivity Detector to the suppressor Regen In port.

To hydrate the Dionex ERS 500e Electrolytically Regenerated Suppressor:

1. Follow the QuickStart Instructions received with the suppressor and also in suppressor product manual.⁵
2. Wait 20 min for the suppressor to fully hydrate before installing it in the detector compartment.
3. Install the backpressure loop between the CD outlet and the suppressor Regen In port.
4. Condition the columns for 30 min according to the instructions from the *Consumables, Install Column section* (Figure 9).

General practice is to follow the eluent and flow rate conditions listed in the QAR report while directing the eluent exiting the column to a waste container.^{6,7}

5. Complete the installation according to the Figure 1 flow diagram.

Installing the Dionex AS-HV Autosampler

The Dionex AS-HV Autosampler is a high volume autosampler designed for trace ion applications. This autosampler is a low-pressure autosampler, therefore samples are loaded into a sample loop and then the sample is transferred to a concentrator column.

Plumb the Dionex AS-HV Autosampler in Pull mode through the waste and sampler ports in the Dionex AutoPrep valve according to Figure 1 and the autosampler Operator's Manual.¹

The Dionex AS-HV Autosampler uses a peristaltic pump (Dionex AS-HV Rinse Pump) to push or pull samples by compressing flexible tubing. This flexible tubing will need to be examined every week to ensure that it is still flexible. A typical replacement cycle is every month. The flexible tubing can be a source of contamination when plumbed in "push" mode. However as shown here in Pull mode, the sample flows through the peristaltic tubing after filling the sample loop, and therefore does not contribute to baseline contamination.

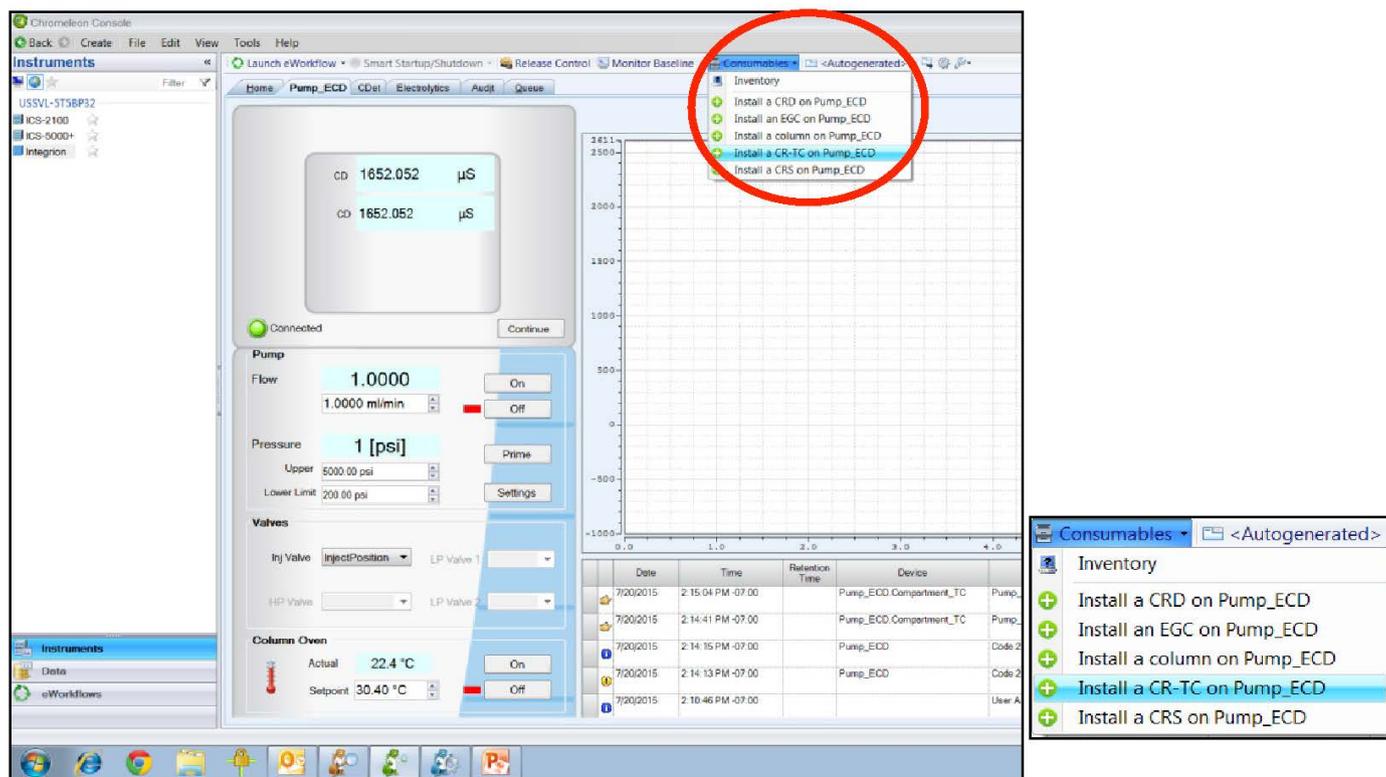


Figure 9. Consumables online installation instructions.

To control the speed of the pump, rotate the Rinse Pump Speed Knob clockwise until the flow rate is ~3 mL/min (> 2× overflow), determined empirically. It is prudent to measure the flow rate periodically to ensure it remains stable.

Starting the Dionex Integrion HPIC system

To start the system, turn on the pump. As the pump pressure reaches 2000 psi, turn on the Dionex EGC 500 cartridge by entering “7” (mM KOH). Turn on the Dionex CR-ATC 600 Continuously Regenerated Anion Trap Column and the AERS 500e Anion Electrolytically Regenerated Suppressor (and input the suppressor current) when liquid is flowing through the devices.

The suppressor regenerant flow rate is supplied as part of the system pump flow rate in this configuration. Therefore, it is not defined as an independent flow rate. The system backpressure is dependent on the flow rate and type of column but the system must be above 2000 psi to ensure sufficient degassing of the electrolytically produced eluent.

If additional pressure is needed to achieve system pressures >2000 psi:

1. Install yellow PEEK backpressure tubing (yellow PEEK, 0.076 mm i.d., 0.003 in i.d.) between the HP Degasser module and the injection port (Pump position).
2. Set the eluent concentration, column oven, compartment oven, and cell temperatures as shown in the Conditions section in the application.
3. Allow the system to equilibrate for 30 min. For optimum chromatography equilibrate until the total background is stable, 1–2 $\mu\text{S}/\text{cm}$.

For standard and sample introduction, verify the flow rates of the 50 $\mu\text{g}/\text{L}$ (ppb) standard and the samples as discussed in the Standard Preparation and Installing the Dionex AS-HV Autosampler sections.

Creating instrument methods

AutoPrep templates can be downloaded.

1. Download the datasource and user-defined columns
2. Follow the AutoPrep Installation Instructions.
3. Mount the AutoPrep datasource listed in the Chromeleon CDS software DVD. Import the AutoPrep user-defined columns into the local datasource (refer to the AutoPrep Installation Instructions for details).
4. Copy the AutoPrep template files to the local datasource.

The AutoPrep instrument methods can also be created using the Chromeleon Wizard for a basic method. The Chromeleon Wizard will also insert the commands needed for switching the valves to load standards through the small loop and samples through the large loop. To create a new instrument method using the Chromeleon Wizard:

1. Select *Create, Instrument Method*, and select Instrument.
2. Enter the values from the Chromatographic Conditions section.
3. Save the instrument method.

This provides a basic instrument method which will be used to create a separate instrument method for samples, and for each of the calibration standards.

The Dionex AutoPrep module loads multiple 10 μL aliquots of a 50 ppb standard onto the concentrator column. The standard solution can be prepared at 1000× the calibration concentrations because the small loop/ large loop ratio (10 $\mu\text{L}/10\text{ mL}$) is 1/1000×, which acts as 1000× dilution. Using a 1000× higher concentration standard for these calibrations minimizes the effects of environmental contamination and inaccurate manual dilutions.

To determine the amount of time needed to fill and overflow the small sample loop, first measure the flow rate as described in the standard preparation section. A minimum of 3x overflow should be used, in this case we use a 10x overflow for the standard.

To calculate the time needed to fill the 10 µL loop (small loop volume):

$$\text{Time (min)} = \frac{\text{standard loop } (\mu\text{L}) \times 10 \text{ (overflow)}}{\text{flow rate } (\mu\text{L}/\text{min})}$$

Example: $\text{time} = (10 \times 10) / 500 = 0.2 \text{ min}$

This calculation shows that 0.2 min is sufficient time to overflow the small loop more than 10x. This time is transferred into the program, as shown in Tables 5 and 6.

Table 5 summarizes the commands needed to load and concentrate a single aliquot of the 50 ppb standard (Calibration Standard 1, 50 ng/L (ppt)). Name this instrument program as Calibration Standard 1.

Table 5. Timing for loading, concentrating, and injecting a single standard aliquot.

Timing (min)*	Valve	Position	Command
-11.5	Inject Valve	Load	Pump_ECD.InjectValve.LoadPosition
-10.5	HP Valve	A	Pump_ECD.HP_ValveA
-10.3	HP Valve	B	Pump_ECD.HP_ValveB
0	HP Valve	A	Pump_ECD.HP_ValveA
	Inject Valve	Inject	Pump_ECD.InjectValve.InjectPosition

* Determined empirically, described in the “Creating instrument methods” section.

Figure 10 shows the script of the instrument program for Calibration Standard 1.

Enter “1000” into the dilution factor column in the sequence temporarily until the ratio of the two AutoPrep loops are determined.

31	-11.500	Equilibration	Duration = 11.500 [min]
		Pump_ECD.InjectValve.LoadPosition	Flushing KOH out of the concentrator for a minute
32			
33		Electrolytics.EluentGenerator.Concentration	50.00 [mM]
*		Click here to append a new command	
34	-10.500		
		Pump_ECD.HP_ValveA	Loading small loop with standard
35			
*		Click here to append a new command	
36	-10.300		
		Pump_ECD.HP_ValveB	Concentrating standard x1
37			
*		Click here to append a new command	
38	-7.000		
39		Electrolytics.EluentGenerator.Concentration	50.00 [mM]
40		Electrolytics.EluentGenerator.Concentration	1.00 [mM]
*		Click here to append a new command	
*		New Time Step	
41	0.000	Start Run	
42		Pump_ECD.HP_ValveA	
43		Pump_ECD.InjectValve.InjectPosition	
44		Pump_1.Pump_1_Pressure.AcqOn	
45		CDet.CD.AcqOn	
46		CDet.CD_Total.AcqOn	
47		CDet.Autozero	
*		Click here to append a new command	
48	0.000	Run	Duration = 30.000 [min]

Figure 10. Dionex AutoPrep section of instrument program for Calibration Standard 1.

Table 6 summarizes the commands needed to load and concentrate four aliquots of the 50 ppb standard (Calibration Standard 4, 200 ppt). These commands can be inserted into the script of the program (Insert time, insert command). Save this instrument program as Calibration Standard 4. Create instrument programs for Calibration Standards 2, 3, and 5 in a similar way.

Table 7 summarizes the commands needed to load and concentrate a 10 mL sample. These commands can be inserted into the script of the program (Insert time, insert command). Name this program "Sample".

Table 6. Timing for loading, concentrating, and injecting four standard aliquots.

Timing (min)*	Valve	Position	Loading 10 µL of Standard	Command
-11.5	Inject Valve	Load		Pump_ECD.InjectValve.LoadPosition
-10.5	HP Valve	A	1x	Pump_ECD.HP_ValveA
-10.3	HP Valve	B		Pump_ECD.HP_ValveB
-10.1	HP Valve	A	2x	Pump_ECD.HP_ValveA
-9.9	HP Valve	B		Pump_ECD.HP_ValveB
-9.7	HP Valve	A	3x	Pump_ECD.HP_ValveA
-9.5	HP Valve	B		Pump_ECD.HP_ValveB
-9.3	HP Valve	A	4x	Pump_ECD.HP_ValveA
-9.1	HP Valve	B		Pump_ECD.HP_ValveB
0	HP Valve	A		Pump_ECD.HP_ValveA
	Inject Valve	Inject		Pump_ECD.InjectValve.InjectPosition

* Determined empirically, described in the "Creating instrument methods" section.

Table 7. Timing for loading, concentrating, and injecting 10 mL samples.

Timing (min)	Valve	Position	Command	Action
9.5	Sampler Relay A	Closed	SamplerRelay_A.Closed	Loads 3x sample loop (~30 mL)
0.5	Inject Valve	Load	Pump_ECD.InjectValve.LoadPosition	Rinses Concentrator column
0.5	Sampler Relay A	Open	SamplerRelay_A.Open	Concentrate
0	HP Valve	A	Pump_ECD.HP_ValveA	Inject
	Inject Valve	Inject	Pump_ECD.InjectValve.InjectPosition	Inject



Dionex ERS 500 Electrolytically Regenerated Suppressor



Dionex EWP Electrolytic Water Purifier

Determining the Dionex AutoPrep large loop to small loop ratio (ppt concentrations)

The small Dionex AutoPrep loop is approximately 10 µL. The large loop is 10 mL.

Use the freshly prepared 50 ppt working standard. Concentrate 10 mL of the working standard by overfilling the Dionex AutoPrep large loop with ~12 mL total volume. Then concentrate 10 µL in the Dionex AutoPrep small loop by overfilling 10x. Record the peak area responses. Repeat both measurements in triplicate. Determine the ratio by comparing the average peak area response for each loop. Add the factor in the dilution factor column in the sequence.

Consumables device tracking

A new feature of the Dionex Integriion HPIC system is consumables device monitoring and tracking. This feature automatically detects electrolytic devices and the columns. Review and approval of the devices is required to start the first sequence on the Dionex Integriion system. and when new consumable devices are installed. To access this approval, select *Consumables* and then *Inventory* (Figure 11). The device monitoring shows the

device history, tracking: Part No., size, serial numbers, manufacture lot, installed location (On Device), and best-if-used-by date (Figure 11, top). Additionally, device monitoring will provide warnings if there is incompatibility between the devices installed (Figure 11, bottom left). An action to either approve or correct an incompatibility between devices is required to start a sequence after installing any new consumable device. To start the sequence:

1. Correct any errors
2. Review the inventory
3. Approve
4. Close the page (Figure 11, bottom right).
5. Select the Instrument Queue tab and conduct a Ready Check on the sequence.
6. Start.

Tracked	Part No.	Description	Size	Chemistry	Serial No.	Lot No.	Detected By	On Device	Best If
<input checked="" type="checkbox"/>	059660	Dionex ATC-3 (4 mm) (9 x 24 mm)	Standard	Anion	150924323	12345678I	RFID	Pump_ECD	09/24/2017
<input type="checkbox"/>	064637	Dionex CRD 300 (4 mm)	Unknown	Unknown	150924323	12345678I	RFID	Pump_ECD	09/24/2017
<input checked="" type="checkbox"/>	072076/074532/075778	EGC 500 KOH		Anion			cable	Electrolytics	07/21/2017
<input checked="" type="checkbox"/>	075550	Unknown	Analytical	Anion	150819017	01427099I	cable	Electrolytics	08/19/2020

Compatibility Check Results:

⚠ Instrument contains consumables of more than one size.

Rescan Approve Close

Figure 11. Consumables tracking.

Results and discussion

Determinations of trace anions (ppb to ppt) in ultrapure water are important to the power and the electronics industries to prevent corrosion failures resulting from anionic contamination. Consequently, the ASTM International limits ionic contamination to ppt concentrations, per the ASTM D 5127.⁷ However, trace anion determinations can prove to be a challenging analysis. Water samples easily absorb contaminants from the environment, including the instrument itself, providing misleading results. In some cases, the contamination may be higher than the analyte concentrations.

In this technical note, determinations of anions at ppt concentrations were achieved using the Dionex AutoPrep module and the Dionex EWP Electrolytic Water Purifier on the Dionex Integrion HPIC system. This approach increases the sensitivity and reduces the baseline contamination of the analysis. More information on this technique can be found in the Dionex Integrion HPIC system Product Spotlight discussion of trace analysis.⁸

Sensitivity was increased by:

- Loading a large volume, 10 mL sample

Baseline contamination was reduced by:

- Selecting a column with a low residual sulfate, such as the Dionex IonPac AS17-C column for separations
- Operating the Dionex AS-HV Autosampler in Pull Mode
- Using the Dionex EWP Electrolytic Water Purifier as the purified water source for the transfer of water and to supply the regenerant for the electrolytic devices
- Preparing working standards inline using the Dionex AutoPrep small loop from the manually prepared 50 ppb stock standard
- Removing carbonate using the Dionex CRD 300 Carbonate Removal Device prior to concentrating the sample
- Selecting a suitable gradient that results in low baseline drift (< 100 nS/cm per min)

For sample analysis and analysis of check standards, the Dionex AS-HV Autosampler delivers a 10 mL sample (12 mL with overflow) in Pull mode to the AutoPrep large loop. The sample is collected in the sample loop before it passes through the peristaltic pump, eliminating introduction of contamination by the pump. The sample is transferred from the large loop through the Dionex CRD 300 Carbonate Removal Device and to the concentrator column by the Dionex EWP Electrolytic Water Purifier using the inline purified water.

In trace analysis, the carbonate peak from carbon dioxide absorption is typically the largest peak in the chromatogram, overshadowing the very small analyte peaks of interest. However, the Dionex CRD 300 Carbonate Removal Device prevents poor chromatography by significantly reducing carbonate contamination in the sample prior to concentration. Check standards are treated in the same manner as samples.

The most challenging aspect of trace ion analysis is controlling and minimizing environmental contamination during manual preparation of low ppb and ppt standards. The contamination effects are often higher than the intended concentration of the working standard, resulting in poor calibration curves, poor sensitivity, and incorrect results.

Using the Dionex AutoPrep module and Dionex EWP Electrolytic Water Purifier eliminates much of the potential environmental contamination by having a closed loop calibration process and use of a 1000× higher concentration stock calibration standard. For calibration working standards, a single stock standard at 1000× higher concentration is needed.

The calibration curve is created from 10 µL incremental additions by the Dionex AutoPrep small loop and multiple valve switches to load and concentrate the aliquot or multiple aliquots of the stock standard. In this configuration (using a large loop for samples and a 1000× smaller loop for standards), manual preparation of ppt working standards is no longer needed. The Dionex EWP device transfers the aliquots of the stock standard in the sample loop to the concentrator column using the purified water for transfer.

Method evaluation

To evaluate this technique, calibration curves were generated from 50 to 400 ppt for seven anions using a single injection of multiple 10 μL aliquots of the 50 ppb stock standard (Figure 12). The other 5 inorganic anions (fluoride, nitrate, nitrite, bromide, and phosphate) had similar results (not shown). The peak responses of the anions to concentration-exhibited coefficients of determination > 0.999 .

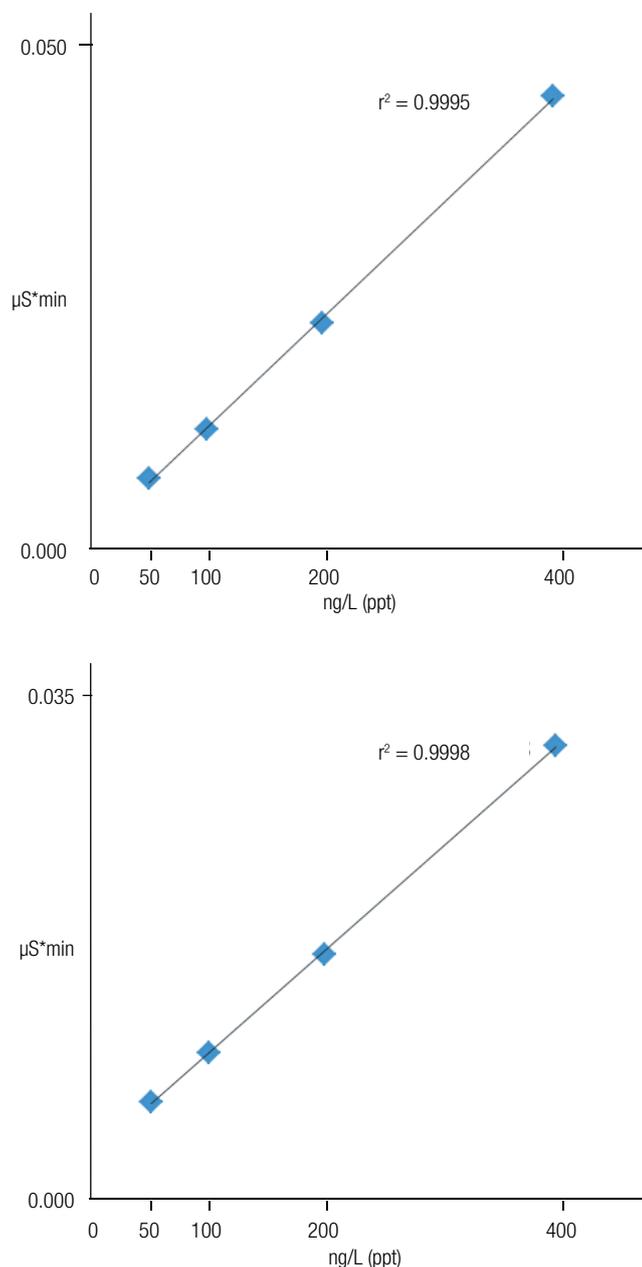


Figure 12. Calibration curves for chloride (top) and sulfate (bottom).

As previously mentioned, in trace anion analysis the carbonate peak typically dominates the sample chromatograms, which is problematic because the peak tailing can affect accurate integration of nearby analyte peaks.

Both the 4 mm Dionex CRD 200 Carbonate Removal Device, recommended for most hydroxide applications, and the Dionex CRD 300 Carbonate Removal Device, recommended for carbonated samples, were evaluated as inline carbonate removal devices.

The experiments were conducted to determine the highest carbonate removal efficiency of a 10 mL DI water sample and a 200 ppt standard. The results, shown in Figure 13, demonstrate higher efficiency of the Dionex CRD 300 Carbonate Removal Device, which was used for this application.

Baseline contamination

A comparison of water produced by the Dionex EWP Electrolytic Water Purifier and a lab water sample is shown in Figure 14. A 50 ppt standard is included for comparison. The 50 ppt standard has excellent S/N from 40 to 600 (Table 8), indicating that considerably lower LODs can be achieved. Trace fluoride, chloride, nitrite, and nitrate contamination were detected in both the system blank and the lab water, with estimated values of 5 to 20 ppt.

In trace ion analysis, the detection limit is often restricted to the baseline contamination. In this configuration, the system blank is the base-line contamination because the Dionex EWP Electrolytic Water Purifier and the Dionex AutoPrep module exclude the environment and the subsequent environmental contamination. The estimated limits of detection (LODs) were determined at $3 \times$ S/N of the baseline contamination and, where not present, at the estimated $3 \times$ S/N from the 50 ppt standard (Table 8). In all cases, the estimated LODs are single- to double-digit ppt.

Columns: Dionex IonPac AS17-C set, 4 mm i.d.
 KOH Gradient: 50 mM wash (4.5 min); 1 mM (-7 to 4 min),
 1–12.5 mM (4–10 min); 12.5–20 mM
 (10–20 min); 20–35 mM (20–30 min)
 Eluent Source: Dionex EGC 500 cartridge, CR-ATC
 600 trap, high pressure degasser
 Flow Rate: 1 mL/min
 Column Temp.: 35 °C
 Detection: Suppressed conductivity,
 Dionex AERS 500e, 4 mm, 87 mA
 external water mode
 Det. Compart.: 15 °C
 Sample Prep.: Dionex CRD inline degassing,
 Dionex AutoPrep, EWP, 30 mA
 Concentrator: Dionex UTAC-LP2, 4 mm
 Sample Vol.: Sample (10 mL)
 Sample Flow Rate: ~ 3.5 mL/min (Dionex AS-HV)
 CRD: A, B: Dionex CRD 300
 C: Dionex CRD 200
 Samples: B, C: DI water blank
 A: 400 ppt standard (~0.5 mL/min)

Peaks: 1. Fluoride 5. Nitrate
 2. Chloride 6. Carbonate
 3. Nitrite 7. Sulfate
 4. Bromide 8. Phosphate

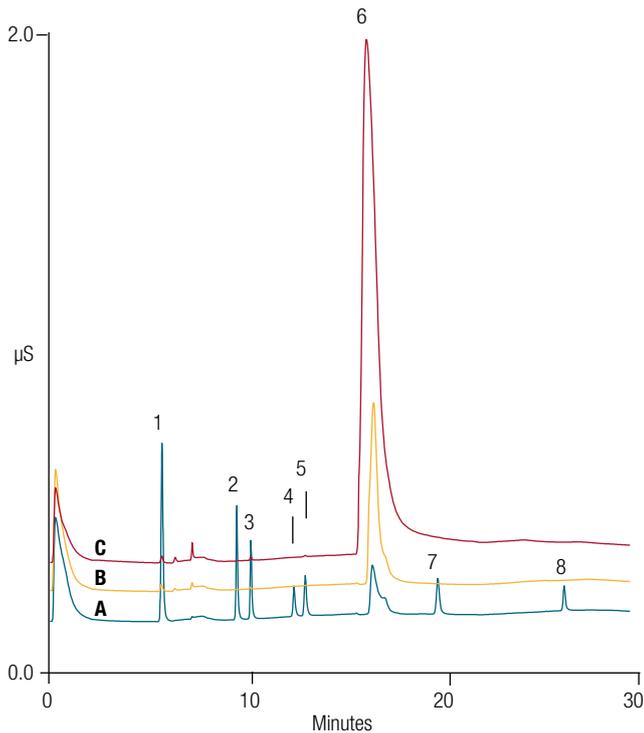


Figure 13. Selection of the appropriate Dionex CRD Carbonate Removal Device.

Columns: Dionex IonPac AS17-C set, 4 mm i.d.
 KOH Gradient: 50 mM wash (4.5 min); 1 mM (-7 to 4 min),
 1–12.5 mM (4–10 min); 12.5–20 mM
 (10–20 min); 20–35 mM (20–30 min)
 Eluent Source: Dionex EGC 500 cartridge, Dionex CR-ATC
 600 trap, Dionex high pressure degasser
 Flow Rate: 1 mL/min
 Column Temp.: 35 °C
 Detector Compart.: 15 °C
 Detection: Suppressed conductivity,
 Dionex AERS 500e, 4 mm, 87 mA,
 external water mode
 Sample Prep.: Dionex CRD 300 inline degassing,
 Dionex AutoPrep, EWP, 30 mA
 Concentrator: Dionex UTAC-LP1, 4 mm
 Sample Vol.: Sample (10 mL); Standard (10 µL)
 Sample Flow Rate: Dionex AS-HV: ~3.5 mL/min
 Standard Flow Rate: Dionex AutoPrep small loop: ~0.5 mL/min
 Samples: A: EWP water, System blank
 B: 50 ppt standard
 C: DI water

Peaks:	A	B	C (ppt)
1. Fluoride	11	54	18
2. Acetate	--	--	--
3. Formate	--	--	--
4. Chloride	12	55	13
5. Nitrite	13	55	18
6. Bromide	--	54	--
7. Nitrate	5	53	7
8. System	--	--	--
9. Carbonate	--	--	--
10. Sulfate	--	53	--
11. Oxalate	--	--	--
12. Phosphate	--	53	--

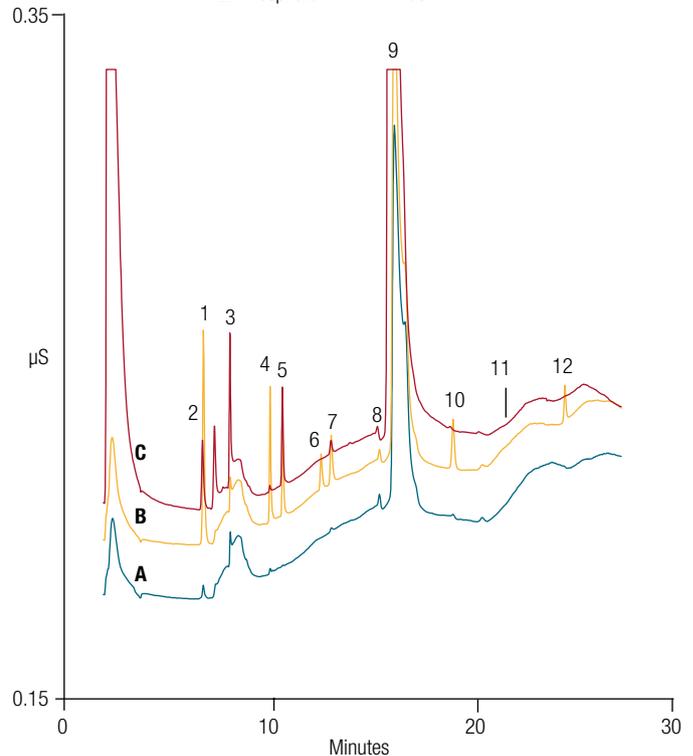


Figure 14. Comparison of the system blank, DI water, and a 50 ppt standard.

Table 8. Estimated limits of detection.

Anion	System Blank (ppt, S/N)	50 ppt Standard (S/N)	Estimated LOD (ppt) (3× S/N)
Fluoride	11 (100)	300	33*
Chloride	12 (6)	630	36*
Nitrite	13 (6)	120	40*
Bromide	ND	30	5**
Nitrate	5 (2)	41	15*
Sulfate	ND	100	2**
Phosphate	ND	83	2**

* 3× S/N above system blank

** 3× S/N based on 50 ppt standard

Conclusion

This technical note shows how the combination of RFIC-EG and the Dionex AutoPrep system minimizes the time and labor needed for sensitive determinations of anions in ultrahigh purity water as required by ASTM D5127.

The Dionex AutoPrep application is used to calibrate the method and automate sample delivery in a closed system that minimizes sample contamination.

In addition, this technical note describes the installation and setup of the Dionex Integrion HPIC system with the Dionex AutoPrep module and Dionex EWP Electrolytic Water Purifier for trace anion determinations.

Trace anion quantification is demonstrated using a Dionex Integrion HPIC system with an integrated, auxiliary 10-port valve, and a Dionex EWP Electrolytic Water Purifier. The Dionex EWP Electrolytic Water Purifier paired with eluent generation and a high-performance ion chromatography system work together to provide low backgrounds and single-digit ppt detection limits.

The system represents a cost-effective solution for the ultratrace analysis of anions. Determination of anions at these levels is necessary to characterize impurities in the ultrahigh purity water produced by the semiconductor manufacturing industry.

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