

Configuring a High-Pressure Dedicated Capillary IC System for Electrochemical Detection

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Key Words

HPIC, Setup, Installation, Capillary IC, HPAE-PAD, ICS-4000

Goal

Demonstrate the installation and setup of a Dionex ICS-4000 Capillary HPIC system configured for electrochemical detection.

Introduction

The Thermo Scientific™ Dionex™ ICS-4000 Capillary HPIC™ system is a single channel, compact, dedicated capillary IC with modular detection options designed to meet the needs of high resolution and fast analysis. This system can be configured with conductivity, electrochemical, or charge detectors for different applications. The Dionex ICS-4000 HPIC system can operate at system pressures up to 5000 psi, thereby providing a platform to use 4 μm particle size columns for sample analysis. At a typical flow rate (10 μL/min), the consumption of water is 15 mL/day, which translates into decreased waste generation and reduced overall cost of ownership. This technical note provides information to install and configure the Dionex ICS-4000 HPIC Dedicated system for High Performance Anion-Exchange (HPAE) separations of electroactive analytes at capillary flow rates with Pulsed Amperometric Detection (PAD). The primary focus of this document is to demonstrate the recommended configuration and installation of the Dionex ICS-4000 configured for HPAE-PAD using an electrochemical cell with disposable working electrodes.



Equipment

Dionex ICS-4000 Capillary HPIC system, consisting of:

- Thermo Scientific™ Dionex™ IC Cube™
- Thermo Scientific Dionex Electrochemical Detector (ED)
- Thermo Scientific Dionex Electrochemical Cell, reference electrode with gasket, and working electrode with gasket
- Thermo Scientific Dionex AS-AP Autosampler
- Thermo Scientific™ Dionex™ Chromeleon™ 7 Chromatography Data System (CDS) software, CM 7.1 with SR2 MUa build or later.

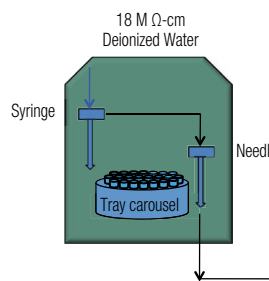
Table 3 in the Appendix lists the consumable products needed for most applications using electrochemical detection on the Dionex ICS-4000 Capillary HPIC system.

Instrument Setup and Installation

Configuring the Dionex ICS-4000 System in Chromeleon CDS

Install the Dionex ED-4000 detector into the Dionex ICS-4000 system while the instrument is powered-off. Then connect the power cables and turn on the system. To configure the system, start the Chromeleon Services Manager program, and then create a new Instrument. Add Dionex AS-AP autosampler and Dionex ICS-4000 system to the Instrument. Each component configuration has additional steps to complete as shown in Table 1.

Dionex AS-AP Autosampler



High-Pressure Dionex ICS-4000 HPIC System

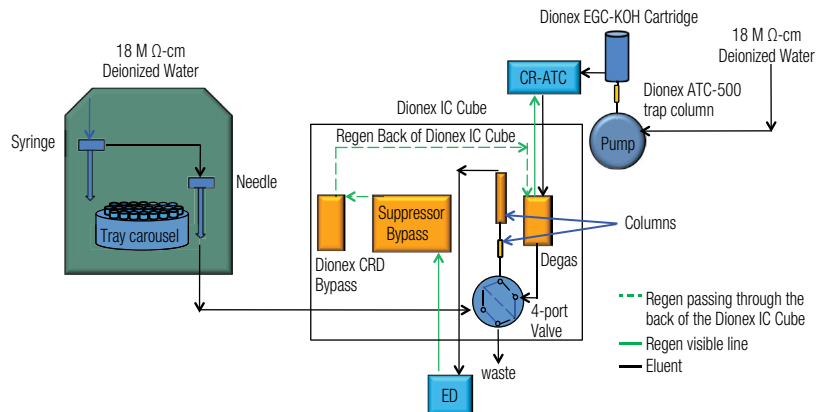


Figure 1. Flow diagram for the Dionex ICS-4000 HPIC System for HPAE-PAD.

Table 1. System configuration for Dionex ICS-4000 HPIC System.

Component	Tab	Action
Dionex ICS-4000 System	General	Select model S/N numbers and download appropriate firmware
	Electrolytics	Check EluentGenerator and CR_TC
	Inject Device	Check Autosampler as Inject Device
	Thermal Controls	Check Column_TC, Compartment_TC, and Damper_TC
Dionex AS-AP autosampler	Sharing	Select Instrument (if more than one instrument is present)
	Segments/Pump Link	Select 1.5 mL vials for "Red", "Blue", and "Green"
	Options	Select "Push" for injection mode, select (250 or 1000 μL) syringe size, enter 0.4 μL loop size, select "1200" (μL) buffer loop size
	Relays	Remove check marks
	Inputs	Remove check marks

Plumbing the Capillary System

Install the 2 mm Thermo Scientific™ Dionex™ IonPac™ ATC-500 Anion Trap Column and the Thermo Scientific Dionex EGC Eluent Generator Cartridge (EGC), Thermo Scientific Dionex CR-TC Continuously Regenerated Trap Column, Thermo Scientific Dionex EG Degas, Thermo Scientific Dionex CRD Carbonate Removal Device Bypass, and Thermo Scientific Dionex Suppressor Bypass capillary devices according to Figures 1 and 2.

Note: The Dionex CRD Bypass and Suppressor Bypass cartridges must be installed because they are needed for the flow path. To achieve the best chromatography with capillary IC, it is important to minimize void volumes in all connections by using precision cut tubing, high pressure connectors and fittings (colored blue), and seating the ferrule > 2 mm above the end of the tubing. These tips are thoroughly discussed in "Technical Note 113 Practical Guidance for Capillary IC".¹ Extra care should be used to prevent introducing air into all consumables or tubing by observing a steady flow before installing the next device in line.

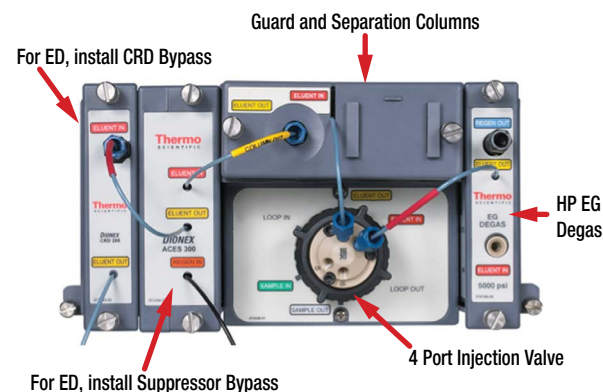


Figure 2. Dionex IC Cube.

To plum the IC, first connect the pump eluent line to the eluent bottle containing deionized water degassed by vacuum filtration. Prime the pump (module or Dionex ICS-4000 Chromeleon panel) until water is flowing out of the pump waste line at a steady rate. Install the Dionex IonPac ATC-500 trap column after the pump transducer with black PEEK tubing (P/N 078497) and before the Dionex EGC-KOH cartridge but temporarily leave the tubing to the Dionex EGC-KOH cartridge disconnected for flushing. To flush the trap column, first initiate the priming function on the pump (1 mL/min), point the Dionex IonPac ATC-500 column upward, and flush for 30 min to flush the resin and to allow air to escape. After 30 min, turn off the the pump prime, and connect the tubing to the Dionex EGC-KOH disconnected for flushing. Hydrate the Dionex EGC capillary cartridge and Dionex CR-TC capillary trap column according to product manuals and the Dionex ICS-4000 Operator's manual.^{2,3}

Plumbing the AS-AP Autosampler

Upon the installation of a Dionex AS-AP autosampler, the needle must be aligned prior to use to avoid needle damage. Select the Sampler tab on the instrument panel and open the align program by pressing the Align Tray button. Follow the commands to align the needle to the Wash Port and Injection Port (Section B.12 in the Operator's Manual) respectively.⁴ Fill up the syringe and buffer wash line with deionized water by priming the syringe. Select 5000 μL volume for the buffer line to speed up the process. Then calibrate the transfer line volume by following the prompts of the TLV Calibration icon. The volume will be recorded automatically. For more information review Section 5.9 in the Dionex AS-AP Operator's Manual.⁴

Electrochemical Cell

Note: Always wear gloves when handling the electrochemical cell. If this is a new ED Cell, disassemble the cell and discard the shipping gasket. Caution: Do not touch the working electrode with any paper products, as this can contaminate the working electrode. The ED Cell is a three-electrode cell: the cell body as the counter electrode, a reference electrode (Ag/AgCl or PdH), and a working electrode (conventional or disposable). The fully assembled cell also includes a Yoke Block Assembly to tighten the cell and gaskets for reference and working electrodes (Figure 3). The installation procedures here describe an electrochemical cell with disposable working electrode; however the procedures are similar when using a conventional working electrode. Different gaskets are specified depending on the application. Additionally, a Support Block is needed when using a disposable working electrode, whereas the conventional working electrode is already installed in a support block.

Note: It is important to use 18 M Ω -cm resistivity, deionized water for standards, eluent, and autosampler flush solution. It is recommended to degas the deionized water intended for eluent in anion determinations. (An appropriate degassing method is vacuum filtration.) Using deionized water with resistivity less than 18 M Ω -cm can reduce sensitivity, introduce contamination, and affect calibration, thereby resulting in inaccurate quantification. Results can vary and contamination introduced from samples can affect the chromatography.

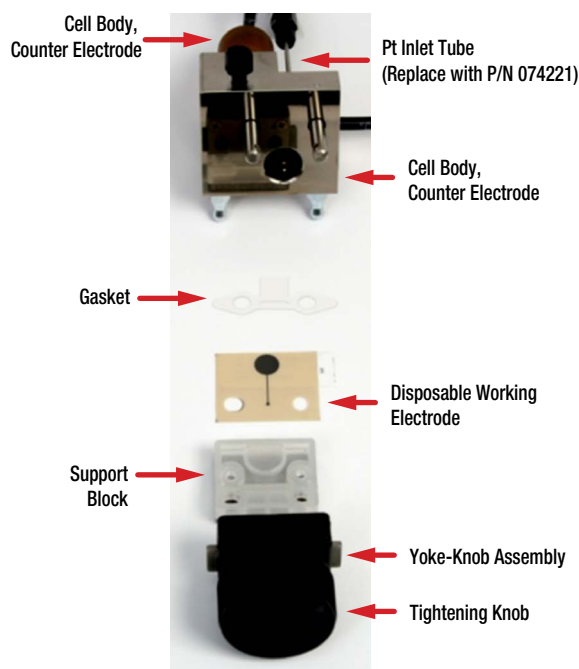


Figure 3. ED Cell with disposable working electrode.

Installing the Electrochemical Cell with a pH-Ag/AgCl Reference Electrode

Tips: Remove all plugs on the cell inlet and cell outlet to prevent cell pressure during the installation. First condition the pH-Ag/AgCl reference electrode by removing the storage cap, rinsing the electrode with deionized water to remove the potassium chloride solution, and then placing the electrode in a solution of pH 7 buffer. The installation procedures are thoroughly discussed in the Dionex ICS-4000 Operator's manual and the ED User's Compendium for Electrochemical Detection.^{4,5}

To prepare the cell body for capillary applications, loosen and unscrew the fitting on the titanium inlet tube and gently, but firmly, pull out the inlet tube from the cell body. Avoid scratching or marring the inlet well as this can cause leaks and poor detection. Rinse the cell body, the wells of the reference electrode, and the inlet tube thoroughly with deionized water. Shake-off the excess water, and dry with a lab wipe. Select the working electrode for the application and corresponding gasket and support block, rinse them with deionized water and shake-off the excess water. Dry the gasket and cell block with an absorbent tissue. Assemble the cell according to the Operator's manual, Figure 3 and ED User's Compendium for Electrochemical Detection by first installing the working electrode gasket flat against cell body.^{4,5} Avoid any wrinkles in the gasket, as this will cause a poor fit and subsequent leaks and poor detection.

Install the disposable working electrode with the metal face down over the gasket and then install the support block firmly over the working electrode. Install the Yoke Block by squeezing the tabs and sliding it on the cell body. Align the Yoke Block parallel to the cell body and rotate the Yoke Block knob clockwise until you hear three "clicks". The cell with a conventional working electrode is assembled similarly with appropriate gasket (Appendix, Table 3). The Support Block is not needed with the conventional working electrode.

To calibrate the reference electrode, select pH buffer 7 and the corresponding buffer for the application, pH 10 for basic eluents and pH 4 for acidic eluents. Install the cell into ED module and connect the yellow cable to the yellow port. Install the reference electrode blue cable into the black port. Immerse the reference electrode in pH 7 buffer to at least mid-level of the electrode. Select the "pH Calibration" button on the ED Panel and follow the instructions to calibrate the electrode. Remove the reference electrode and cell body from the ED module. To install the reference electrode into the cell, first place the gasket for the pH-Ag/AgCl reference electrode in the bottom of the reference electrode well. Rinse the buffer off the electrode with deionized water, remove the o-ring on the reference electrode, and gently, but firmly, screw-in or rotate the reference electrode until it is finger-tight. Immediately complete the final plumbing as described in the second paragraph below.

Installing the Electrochemical Cell with a PdH Reference Electrode

Note: Remove all plugs on the cell inlet and cell outlet to prevent cell pressure during the installation. The PdH reference electrode is a solid-state electrode designed only for capillary flow rates. This electrode does not require storage solutions nor does it need to be calibrated by Chromeleon CDS. This electrode requires a conditioning process when installed, as described in the Conditioning section. Repeat this conditioning process again if it is stored or inactive for more than 1 week.

Install the PdH gasket into the reference electrode well. Align the gasket tabs to fit into the notches at the bottom of the well. Install the PdH electrode by first aligning the tabs with the well, screwing the electrode in place to finger tight, and then with a wrench another 20 to 30 degrees.

Completing the Plumbing

Complete the installation by removing the temporary waste line from the column and installing the 9" piece of blue PEEK tubing ((P/N 071870) to the column outlet. Allow liquid to flow from the end of the tube and then connect the free end to the cell inlet. Wait 60 sec before tightening the connection. Allow liquid to flow through the cell until it flows out the cell outlet. Install the cell in the ED detector module and connect the reference electrode cable (blue to black) and the counter/working electrode cable (yellow to yellow). Finally connect the Dionex Suppressor Bypass tubing to the cell outlet.

When using the pH-Ag/AgCl reference electrode, first turn-on the cell using the ED Panel, and then download the application waveform. Check for leaks by periodically touching an absorbent tissue under the cell. Allow the system to equilibrate until a stable baseline is observed. When using a PdH reference electrode follow the conditioning procedure below.

Conditioning Procedure for PdH Reference Electrode

Set the pump flow rate (Dionex ICS-4000 panel) to 0.008 mL/min. Set the EG concentration to 100 mM (Electrolytics panel), turn-on the Dionex CR-TC (Electrolytics panel), and verify that eluent is flowing out of the cell.

On the ED panel, set reference electrode mode to PdH, select DC amperometry mode, set cell voltage to 0.00 V, and turn-on cell. Select integrated amperometry mode, and download the PdH-referenced carbohydrates waveform. Condition for 1 hour. Then reload the application conditions and allow the system to equilibrate until a stable baseline is observed.

The waveforms are thoroughly discussed in the ED User's Compendium and also listed in the specific application.

Table 2. Additional conditions to create an instrument method using PAD.

Page Title	Page	Mode	Action
Sampler Options	Injection	Injection Mode	PushCap
		Capillary Overfill	50 (times)
		Accept Recommended Values	Click on button
	General Settings	Temperature	Specified if needed
		Accept Recommended Values	Click on button
		Wait for Temperature	Click box if using the temperature option
		Injection Wash Property	After Injection
Temperature	Column	Click on use box	
	Compartment	Click on use box. Select a temperature up to 3 °C lower than column temperature	
EDet Mode Options	Mode	DC or Integrated Amperometry	Click on box for Integrated Amperometry
Integrated Amperometry	Cell Control	On	
	Reference Electrode	Type	Select Ag/AgCl or PdH
	Waveform	Type	Select waveform from pull down menu
	Data Collection	Hz	Enter number of cycles/sec. For carbohydrates, enter 2.0
	pH	Lower and upper	Based on the application. For example, enter 12 and 13 typically for basic eluents and 0 and 2 for acidic eluents
	Temperature	Column	Enter separation temperature
		Compartment	Enter 3 °C below column temperature

Creating an Instrument Method Using Chromeleon Wizard

To create a new instrument method using Chromeleon 7 CDS, select Create, Instrument Method, and specific Instrument. Table 2 describes additional general conditions needed to create an Instrument Method using electrochemical detection. Specific conditions for an application will be described in each individual application document.

Conclusion

This technical note provides recommendations for setting up an electrochemical detection application by HPAE-PAD on a Dionex ICS-4000 HPIC system using Chromeleon 7.1 CDS.

References

1. Thermo Fisher Scientific. Technical Note 113, *Practical Guidance to Capillary IC*, LPN 3043, Sunnyvale, CA, 2012.
2. Thermo Fisher Scientific. *Product Manual for the Continuously Regenerated Trap Column (CR-TC)*. Doc No. 031910, Sunnyvale, CA, 2010.
3. Thermo Fisher Scientific. *Dionex ICS-4000 Operator's Manual*. Doc No. 065468, Sunnyvale, CA, 2013.
4. Thermo Fisher Scientific. *Dionex AS-AP Operator's Manual*. Doc No. 065361, Sunnyvale, CA, 2012.
5. Thermo Fisher Scientific. *ED User's Compendium for Electrochemical Detection*. Doc. No. 065340, Sunnyvale, CA, 2010.

Table 3. Consumables list for the Dionex ICS-4000 System with ED Detection

Product Name	Description of High Pressure Capillary Part	Part Number*
EG Degas HP cartridge	High-pressure EG degas cartridge, up to 5000 psi	AAA-074459
Dionex CRD Bypass cartridge	Bypass (needed for flow path)	072056
Dionex ATC-500	2 mm trap column between pump and EGC cartridge	079018
Black PEEK (Vitrex PLC) Tubing	Tubing from pump to IonPac ATC-500 trap	078497
Dionex Suppressor bypass cartridge	Bypass (needed for flow path)	072055
Dionex high pressure fittings (blue)	Bolts / Ferrules	074449/074373
Dionex AS-AP autosampler	Autosampler vials, packages of 100	
10 mL vial kit, package of 100	Polystyrene vials, caps, blue septa, suitable for applications using strong base eluents.	074228
1.5 mL vial kit, package of 100	Polypropylene vials, caps. Recommended for applications using strong base eluents.	079812*
	Glass vials, caps. Recommended for applications using strong acid eluents.	055427
0.3 mL vial kit, package of 100	Polypropylene vials, caps. Recommended for applications using strong base eluents.	055428
HPAE-PAD, HPAE-IPAD	Using strong base eluents	
Dionex EGC-KOH	Anion Eluent Generator cartridge for capillary flow rates	072076
Dionex CR-ATC	Anion Electrolytic trap column for capillary flow rates	072078
ED-4000 Electrochemical Detector	ED Detector module for capillary or analytical flow rates	072042
pH Buffer solutions	pH 7 buffer and pH 10 buffer	SB108-500** SB115-500**
pH Buffer solutions	pH 7 buffer and pH 4 buffer	SB108-500** SB101-500**
Electrochemical Cell	ED Cell body includes PEEK (Vitrex plc) Yoke Block	072044
ED Cell Inlet Tubing kit	Kit Includes 9" capillary tubing for cell inlet Long neck black PEEK connector, black PEEK split cone ferrule	074221

Reference Electrodes		
Ag/AgCl	Designed for analytical flow rates but can be used in capillary flow rates with the gasket. Also provides pH values.	061879
	Gasket for Ag/AgCl reference electrode in capillary applications	072162
Palladium Hydrogen	Solid-state reference electrode designed for capillary applications. Does not provide pH values.	072075
	Gasket for PdH reference electrode	072214
Disposable Working Electrodes for Capillary and Analytical Flow Rates**		
Gold – Carbohydrates (on polyester)	Carbohydrate applications using < 95 mM hydroxide eluents. Typical life is two weeks.	060139/060216
	Package of six electrodes with two gaskets / Package of 24 electrodes with eight gaskets.**	
Gold on PTFE	Carbohydrates using 100 to 750 mM hydroxide eluents. Typical life is four weeks.	066480
	Package of six with two gaskets.**	
Disposable Working Electrodes for Capillary and Analytical Flow Rates		
Silver	Free cyanide, bromide, and iodide and low concentrations of sulfide optimized using 62.5 mM hydroxide eluents. Typical life is two weeks.	063003
	Package of six with two gaskets.**	
Platinum	Glycols, alcohols, and chelating agents using \leq 100 mM MSA. Typical life is two weeks.**	064440
	Package of six with two gaskets.**	
Gaskets for Disposable Working Electrodes		
0.001" PTFE gaskets	Capillary applications with analytes diluted to μ M concentrations.	072117
	Package of two	
0.002" PTFE gaskets	Analytical flow rates with carbohydrates diluted to μ M concentrations.	060141
	Package of four	
0.015" polypropylene gasket	Applications with carbohydrate concentrations diluted to mg/L concentrations.	057364
0.062" polypropylene gasket	Applications with carbohydrate concentrations diluted to 5–1000 mg/L separated on a high capacity column, such as CarboPac SA10.	075499

* Dionex Product Line P/Ns

** Kits include 0.002" gaskets intended for analytical flow rates.

** Typically using an ion exclusion column which is not yet available in capillary format.

Product Name	Recommended Application/Description	Part Number*
Support Blocks for Disposable Working Electrodes		
Polyester standard block	For use with 0.001", 0.002", 0.015" gaskets.	062158
Polyester block for 0.062" gasket	For use with 0.062" polypropylene gasket.	075501
Conventional Working Electrodes: Designed for Analytical Flow Rates But Can Be Used for Capillary Applications with the Appropriate Column.		
0.001" Ultem® (SAIBC Innovative Plastics) gaskets	Gasket for conventional working electrodes	049722
	Package of one	
ED Au Gold on Kel F® (3M Corporation) block	Especially suitable for applications using > 200 mM hydroxide eluents longer than 5 to 10 min.	079850*
	The kit includes one conventional working electrode, one 0.001" Ultem gasket, and polishing kit	
ED Ag on Kel F block	Designed for free cyanide, bromide, iodide, high cyanide concentration, high sulfide concentration applications and applications using > 100 mM hydroxide based eluents.	079856
	The kit includes one conventional working electrode, one 0.001" Ultem gasket, and polishing kit.	
ED Pt on Kel F block	Designed for applications using acid eluents, especially suitable for applications using eluents > 100 mM.***	061751
	Kit includes one conventional working electrode, one 0.001" Ultem gasket, and polishing kit.	

* Dionex Product Line P/Ns

** Previous P/N was 061749

++ AAA Au disposable and AAA Au conventional electrodes were not included here because the amino acid applications will require other modifications that are not yet available for capillary flow rates.

***Typically the chromatographic separation is on an ion exclusion column which is not yet available in capillary format.

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