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S C I E N T I F I C

Ion chromatography

Combustion ion chromatography with a Dionex Integrion HPIC System

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Goal

To provide instructions to set up a combustion ion chromatography (IC) system using a Thermo Scientific™ Dionex™ Integrion™ HPIC™ system, a Nittoseiko AQF-2100H combustion system, and the Thermo Scientific™ Chromeleon™ 7 Chromatography Data System (CDS) software

Introduction

A combustion IC system can be used for automated qualitative and quantitative analysis of halogens and sulfur in samples comprised of difficult matrices – intractable solids, semisolids, liquids, and even gases. These samples are very difficult to analyze using conventional ion chromatography (IC): sample preparation is required to extract analytes or remove interfering matrices, and these sample preparation techniques are costly and labor intensive. Automated combustion IC reduces the time and labor required for this analysis. The samples are pyrolyzed in an oxidizing atmosphere, the resultant vapors are absorbed in an aqueous solution, and then introduced directly into the IC system for analysis. This automated method is highly sensitive, easy to use, saves time, and produces fewer environmental contaminants than other sample preparation procedures, such as acid digestions or back extractions from organic solutions.

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Equipment

The combustion IC system described in this note includes the following:

- Dionex Integrion HPIC system (Firmware 1.3.2 and later), including:

  – Eluent generation capability

  – CD conductivity detector

  – Column oven temperature control

  – Thermostatted detector compartment

  – Tablet control

  – Consumables device monitoring capability

- Thermo Scientific™ Dionex™ AXP Auxiliary Pump (optional)

- Nittoseiko AQF-2100H system, comprised of:

  – Electric furnace, HF-210

  – Gas absorption unit, GA-210

  – External solution selector, ES-210 (optional)

  – Autosampler options

    • Automatic boat controller, ABC-210 (optional)

    • Liquid autosampler, ASC-250L (optional)

    • Solid autosampler, ASC-240S (optional)

- Computer, including:

  – At least three USB ports for computer peripherals and Dionex Integrion HPIC system

  – At least one RS232 port for the AQF-2100H system

Software

Chromeleon CM7.2 SR4 MUb CDS software and Nittoseiko NSX-2100 software.

Process overview

Samples are introduced into the AQF-2100H by one of the autosampler options. Pyrolysis occurs between 800 and 1100 °C. The samples are oxidized by O_2 at high temperature, the vapors are sparged through the absorbing solution in the Nittoseiko GA-210 module, and the solution is transferred to the IC system for analysis.

Phosphate may be added to the absorbing solution as an internal standard to calibrate the analytical results. Hydrogen peroxide is added in the absorbing solution to oxidize hydrogen sulfite, resulting from the incomplete oxidation of sulfur, which will be quantified as sulfate in aqueous solution.

Instrument set up and installation

The Dionex Integrion HPIC System is configured with a CD Conductivity Detector, eluent generation, and temperature control of the column oven and detector compartment. This system has consumables device monitoring, optional manual control via the Dionex Integrion HPIC system tablet, and can operate at pressures up to 5000 psi with eluent generation. To set up this application:

1. Plumb the Dionex Integrion HPIC system based on the intended application (refer to schematics)

2. Connect the USB cable from the Dionex Integrion HPIC system to the computer

3. Connect the RS232 cables from the Nittoseiko GA-210, ES-210 and autosampler to the Nittoseiko HF-210 module

4. Connect the RS232 cable from the Nittoseiko HF-210 module to the computer

5. Connect the power cables and turn on all the modules

Configuring the modules in the Chromeleon CDS software

To configure the IC system:

1. Start the Chromeleon Instrument Controller program.

2. Select the link, Configure Instruments, to open the Chromeleon Instrument Configuration Manager.

3. Right-click on the local computer name.

4. Select Add an Instrument.

5. Enter an appropriate name (for example: IntegrionCIC).

6. Add the following modules to this instrument configuration: Integrion HPIC system, Integrion HPIC Pump (Wellness), and Remote Inject, as detailed below.

Integrion HPIC system module

1. Select *Add a Module, IC: Dionex Integrated Modules, and Integrion HPIC System* (Figure 1). A window with multiple tabs will automatically open up (Figure 2).

2. Select the Model Serial No. on the General tab. The Chromeleon CDS software will automatically detect all electrolytic devices, detectors (Figure 2), Pump Degasser, and Seal Wash pump (not shown).

The Nittoseiko AQF-2100H system communicates with the Dionex Integrion HPIC system using TTL signals.

3. InjectDevice tab. Assigning control of the injection valve.

4. Open the TTL Inputs tab, and ensure that the designated TTL input is checked (Figure 3).

In this note, TTL Input 3 is used. Upon receiving the signal, the Dionex Integrion system can perform other tasks such as flipping the inject valve, autozero, turning the pump on, and/or making a recorder mark. Depending on the requirements of the application, one or more of these tasks can be checked. In this note, none of the tasks are required (Figure 4).

Note: Other TTL inputs may also be used, but the Remote Inject settings and Physical TTL Connections need to be updated accordingly.

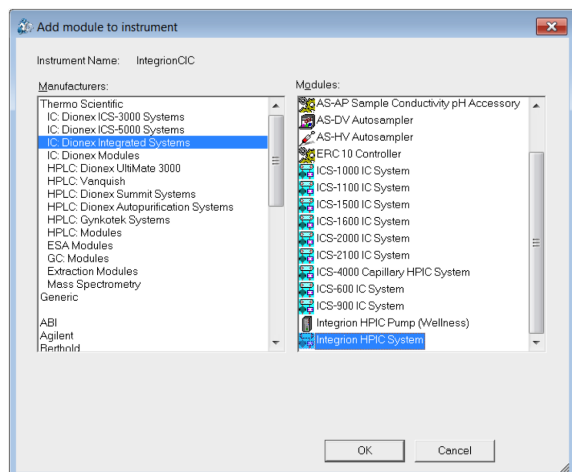| Mode	Assign Control of Integrion Injection Valve
Direct injection using the injection valve in the Mitsubishi GA-210 Module	No assignment is necessary
Direct injection – using injection valve in Dionex Integrion System	Assign to Integrion control
Preconcentration	Assign to Integrion control

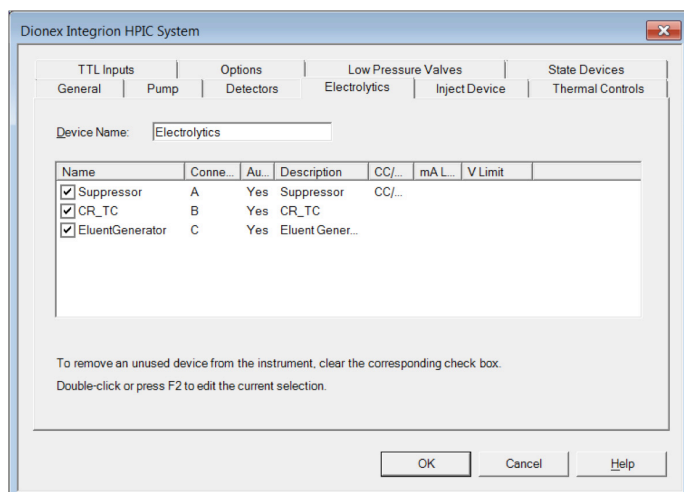Figure 1. Creating a configuration

Figure 2. Automatic detection of electrolytic devices
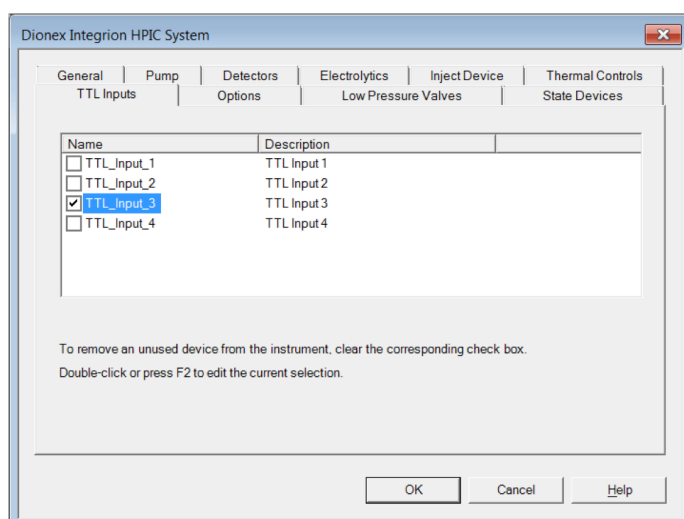

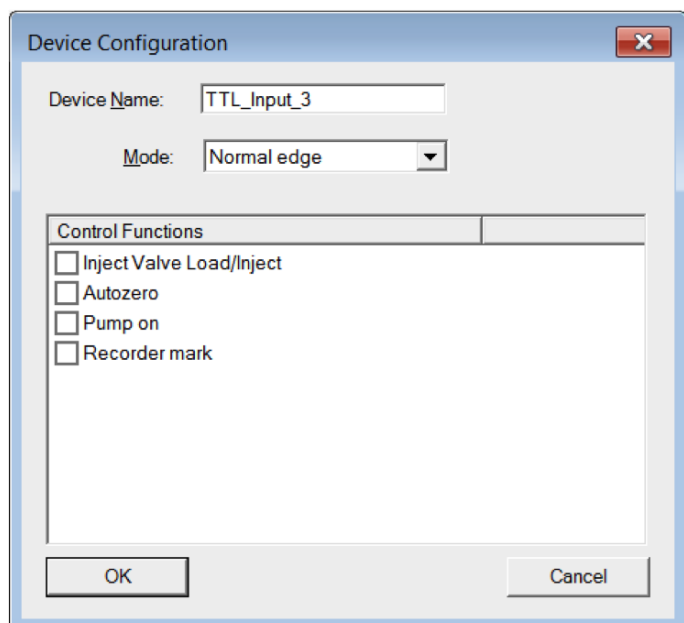Figure 3. Dionex Integrion TTL input

Figure 4. Configuring Dionex Integrion TTL input

Integrion HPIC pump (Wellness) module

To add pressure monitoring capabilities, it is necessary to add another module. To do this:

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.

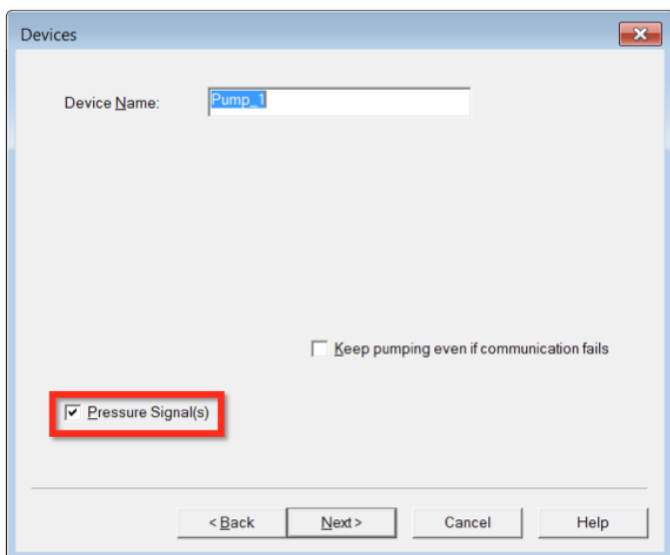3. Select the Devices Tab and click on the Pressure Signal(s) box (Figure 5).

Figure 5. Adding the Integrion HPIC Pump Wellness Module to the instrument configuration

Remote inject

1. Select *Add a Module, Generic, and Remote Inject* (Figure 6). The default device name is InjectValve and needs to be renamed (for example: InjectValve_CIC).

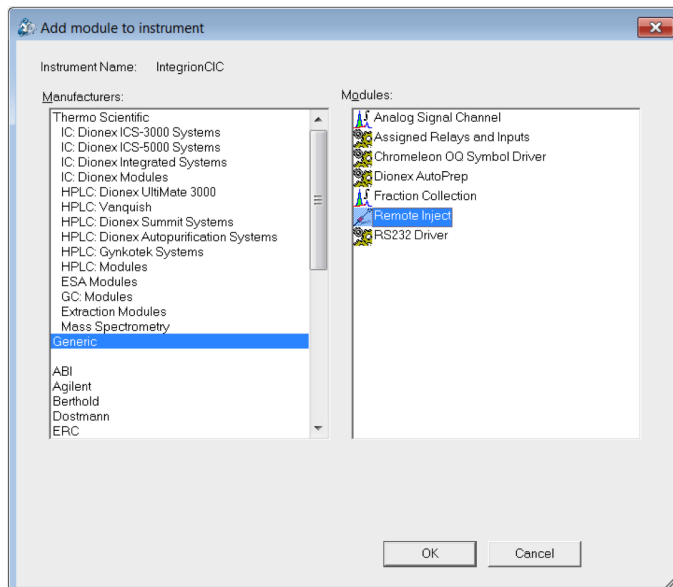2. Select the TTL signal to be used (Figure 7).

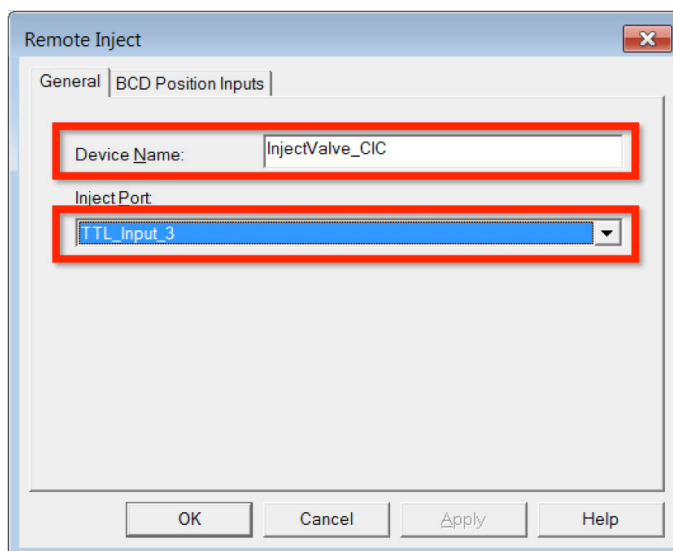Figure 6. Adding the Remote Inject Module to the instrument configuration

Figure 7. Configuring the Remote Inject Module

Table 1. TTL connections

	Dionex Integrion System	Nittoseiko AQF-2100H System
Red Wire	TTL-3 IN	1
Black Wire	Ground	2

Physical TTL connections

With a pair of twisted wires, make the connections in Table 1 (Figures 8 and 9).
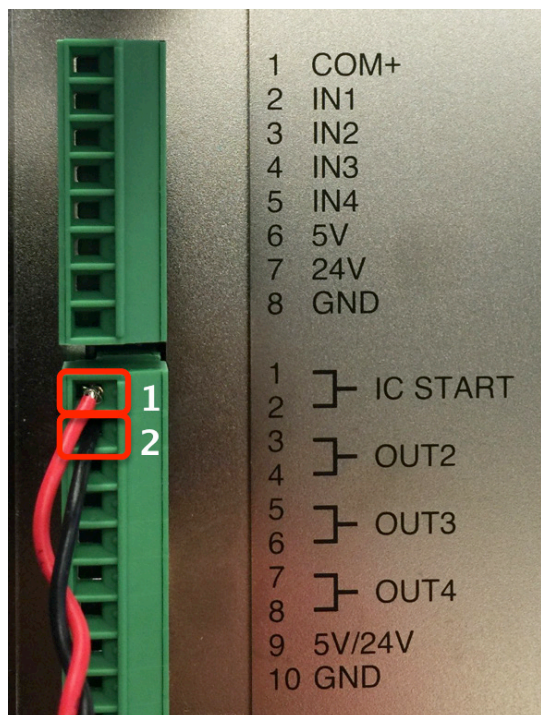

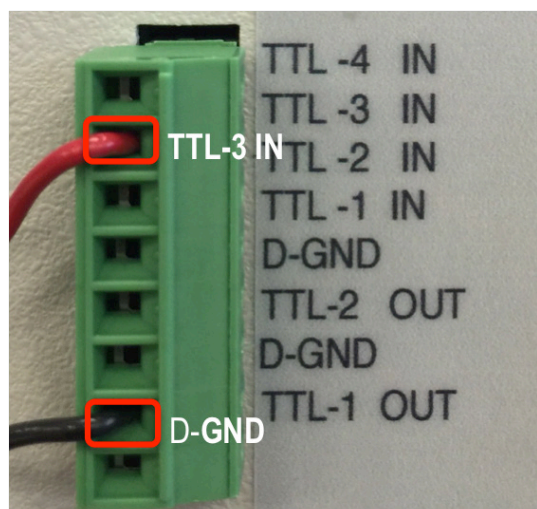Figure 8. TTL connections at the rear panel of Mitsubishi GA-210 Module

Figure 9. TTL connections at the rear panel of the Dionex Integrion HPIC System

Plumbing the high-pressure Dionex Integrion HPIC system

To plumb the HPIC system:

1. Loosen the waste lines, including the metal-wrapped waste line, at 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 ¼ turn and press the priming button.

4. Prime the pump until no bubbles are visible and water is flowing at a steady rate out of the pump waste line.

5. Close priming knob to finger tight.

Schematics

Direct injection using the injection valve in the Nittoseiko GA-210 Module

The sample loop is installed on the Nittoseiko GA-210 injection valve. When the sample is ready for IC analysis, the Nittoseiko GA-210 module loads the sample loop. The schematic is shown in Figure 10.
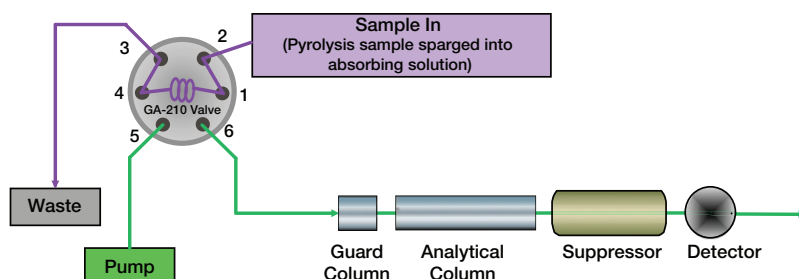

Figure 10. Combustion IC application - direct injection using the injection valve in the Nittoseiko GA-210 Module

Preconcentration

This setup is used when detection of analytes in the low mg/L concentrations is required, or when the early eluting peaks are affected by the matrix effect from hydrogen peroxide. In this setup, the sample loop is installed on the Nittoseiko GA-210 injection valve, and a concentrator column is installed on the Dionex Integrion HPIC system injection valve. When the sample is ready for IC analysis, the Nittoseiko GA-210 module loads the sample loop. The sample is transferred to the concentrator column by the auxiliary pump, and flushed with 3 times the concentrator column volume of deionized water before starting the IC analysis.

Plumb the system as shown in Figure 11: Nittoseiko AQF-2100H system injection valve on GA-210 unit

- Connect the sample loop to Ports 1 and 4

- Connect the tubing from the auxiliary pump to Port 6

- Connect Port 5 and Dionex Integrion system injection valve Port S with 0.010 in. (0.25 mm) i.d. PEEK tubing

- Connect the sample transfer line from Nittoseiko GA-210 system to Port 2

- Connect the sample waste line from Nittoseiko GA-210 system to Port 3 and route this tubing to a waste container

Dionex Integrion system injection valve

- Connect the tubing from the IC pump to Port P

- Connect the concentrator column to Ports L

- Connect the column to Port C

- Connect the 0.030 in. (0.75 mm) i.d. PEEK tubing waste line to Port W and route this tubing to a waste container

Tip: Add enough backpressure tubing just after the auxiliary pump, and before the injection valve, to produce a back pressure of at least 1000 psi at the desired flow rate.

Dionex IC PEEK Viper fittings
To achieve the best chromatography, it is important to gently tighten the Thermo Scientific™ Dionex™ IC PEEK Viper™ fittings to finger-tight and to use the fitting assemblies in the following locations.

- Dionex EGC 500 KOH eluent generator cartridge – Eluent Out to Eluent In on Thermo Scientific™ 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 Thermo Scientific™ Dionex™ Degas Module

- Between the valve – "Column" port to the guard column

  – This Dionex IC PEEK Viper fitting is used in the setup shown in Figure 11 (preconcentration), but not in Figure 10 (direct injection using the Nittoseiko GA-210 injection valve).

- Between the guard and separation columns

- Separation column to Eluent In on the Thermo Scientific™ Dionex™ AERS 500 Anion Electrolytically Regenerated Suppressor

- Dionex AERS 500 Anion Electrolytically Regenerated Suppressor – *Eluent Out* to *Eluent In* on the CD Conductivity Cell

Dionex IC PEEK Viper fittings 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 is common for both standard bore and microbore column applications and is specified for each connection. The recommended practice is to tighten the Dionex IC PEEK Viper fittings to finger-tight and then, if leaking is observed, do an additional 1/16 to 1/8 turn clockwise.

Caution: Overtightening, or using a wrench or any other tools to tighten the Dionex IC PEEK Viper fittings, may permanently damage the fitting.

Important: Do not remove consumables tracking device tags from the columns or consumable devices. These tags are required for monitoring functionality.

Conditioning electrolytic devices and columns
Install the Thermo Scientific™ Dionex™ EGC 500 KOH Potassium Hydroxide Eluent Generator Cartridge and Dionex CR-ATC 600 Continuously Regenerating Anion Trap Column in the Dionex Integrion HPIC system Reservoir Tray compartment. Condition the devices according to instructions in the Chromeleon Instrument Panel, drop-down menu (Consumables, Install) (Figure 12). This information is also available in the product manuals and the Dionex Integrion HPIC System Operator's manual.

To hydrate the Dionex AERS 500 Electrolytically Regenerated Suppressor, follow the QuickStart instructions received with the suppressor and also in the suppressor product manual.
1. Wait for 20 min for the suppressor to fully hydrate before installing the suppressor in the detector compartment.

2. Install the backpressure loop from the slotted compartment next to the CD detector (exerting an additional ~40 psi) between the CD outlet and the suppressor *Regen In* port.
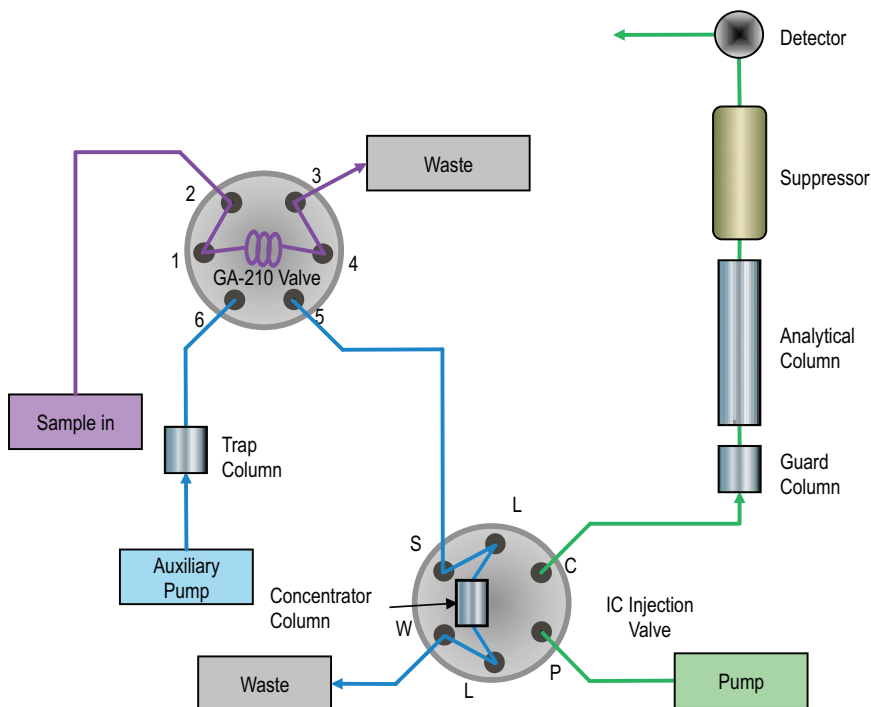
Figure 11. Combustion IC application - preconcentration with matrix elimination
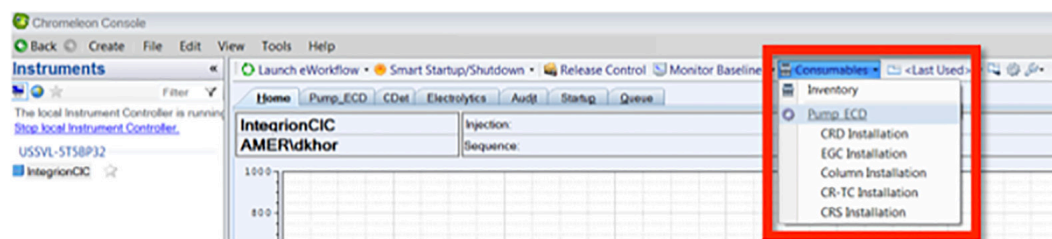

Figure 12. Consumables installation instructions on instrument panel

3. Condition the columns for 30 min according to the instructions from the Consumables, Install Column section in the Chromeleon CDS software (Figure 12).

The general practice is to use the eluent and flow rate conditions listed in the column's QAR report while directing the eluent exiting the column to a waste container.

4. Complete the installation according to flow diagram in Figure 10 or 11.

Starting the Dionex Integrion HPIC system

To start the system:

1. Turn on the pump.

2. Immediately turn on the Dionex EGC 500 Eluent Generator Cartridge.

3. Turn on the Dionex CR-ATC 600 Continuously Regenerated Anion Trap Column and Dionex AERS 500 Anion Electrolytically Regenerated Suppressor when liquid is flowing through the devices. The system backpressure is dependent on the flow rate and type of column, but the system pressure must be above 2000 psi to support the Dionex EGC cartridges. Typically, columns with 4 µm resin particles operate above 2000 psi and, therefore, do not require additional backpressure tubing. However, if additional pressure is needed to achieve system pressures above 2000 psi, install yellow 0.003 in. (0.076 mm) i.d. PEEK backpressure tubing between the Dionex High Pressure Degasser and the injection port (Pump port position).

4. Set the eluent concentration, column oven, compartment oven, and cell temperatures, and allow the system to equilibrate for 30 min.

Creating an instrument method

To create a new instrument method using the Chromeleon Wizard:

1. Select Create, Instrument Method, and select an Instrument.

2. Enter the values from the Chromatographic Conditions section.

3. Save the instrument method. Example instrument methods for direct injection and preconcentration/matrix elimination are shown in Figure 13, 14, and 15. For direct injection, the InjectValve_CIC.inject is in the Inject stage. If HPIC, or gradient separations, are required, the injection on the Dionex Integrion IC system needs to be used. To facilitate this, additional commands are required, as shown in Figure 14. The initial Pump_ECD.InjectValve.LoadPosition command puts the sample loop in the load position and upon receiving the signal, the latter Pump_ECD.InjectValve.InjectPosition puts the sample loop in the inject position for separation and detection.

For preconcentration matrix elimination, the InjectValve_CIC.inject is in the Equilibration stage. Additional commands, such as Pump_ECD.InjectValve.LoadPosition and Pump_ECD.InjectValve.InjectPosition, are added to prepare the concentrator column for pre-concentration (load position) and elution (inject position).

Consumables device monitoring

A new feature of the Dionex Integrion HPIC system is consumables device monitoring and tracking. This feature automatically detects the electrolytic devices and the columns. Review and approval of the devices is required to start the first sequence on the Dionex Integrion HPIC system when new consumable devices are installed. To access this approval:

Select Consumables and then Inventory (Figure 16). 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 16). Additionally, the device monitoring will provide warnings if there is incompatibility with the devices installed (Figure 16),

- To start the sequence, correct any errors, review the inventory, Approve, and Close the page.

- Select the Instrument Queue tab and conduct a Ready Check on the sequence.

- Select Start.

	Time	Command	Value
0	{Initial Time}	Instrument Setup	
1		Pump_ECD.Pressure.UpperLimit	5000.00 [psi]
2		Pump_ECD.%A.Equate	"DI"
3		Pump_ECD.Pressure.LowerLimit	200.00 [psi]
4		Pump_ECD.Compartment_TC.Mode	On
5		Pump_ECD.Compartment_TC.TemperatureSet	20.0 [°C]
6		Pump_ECD.Column_TC.Mode	On
7		Pump_ECD.Column_TC.TemperatureSet	30.0 [°C]
8		Electrolytics.Suppressor.CurrentSet	15 [mA]
9		Electrolytics.Suppressor.Type	AERS_2mm
10		Electrolytics.EluentGenerator.Concentration	23.00 [mM]
11		CDet.Rise_Time	0.5 [s]
12		CDet.Data_Collection_Rate	5.0 [Hz]
13		CDet.CellHeater.Mode	On
14		CDet.CellHeater.TemperatureSet	35.0 [°C]
15		CDet.Temperature_Compensation	1.7 [%]
16		Pump_ECD.Flow.Nominal	0.25 [ml/min]
17		Electrolytics.CR_TC.CR_TC	On
18		Wait	Pump_ECD.Ready
19		Wait	Compartment_TC.TemperatureState
20		Wait	Column_TC.TemperatureState
21	0.000	Inject	
22		InjectValve_CIC.Inject	
23	0.000	Start Run	
24		Pump_1.Pump_1_Pressure.AcqOn	
25		CDet.CD.AcqOn	
26		CDet.CD_Total.AcqOn	
27		CDet.Autozero	
28	0.000	Run	Duration = 20.000 [min]
	New Time Step		
29	20.000	Stop Run	
30		Pump_1.Pump_1_Pressure.AcqOff	
31		CDet.CD.AcqOff	
32		CDet.CD_Total.AcqOff	
33		End	

Figure 13. Example instrument method for direct injection using GA-210 valve.

	Time	Command	Value
0	{Initial Time}	Instrument Setup	
1		Pump_ECD.Pressure.UpperLimit	5000.00 [psi]
2		Pump_ECD.%A.Equate	"DI"
3		Pump_ECD.Pressure.LowerLimit	200.00 [psi]
4		Pump_ECD.Compartment_TC.Mode	On
5		Pump_ECD.Compartment_TC.TemperatureSet	20.0 [°C]
6		Pump_ECD.Column_TC.Mode	On
7		Pump_ECD.Column_TC.TemperatureSet	30.0 [°C]
8		Electrolytics.Suppressor.CurrentSet	15 [mA]
9		Electrolytics.Suppressor.Type	AERS_2mm
10		Electrolytics.EluentGenerator.Concentration	23.00 [mM]
11		CDet.Rise_Time	0.5 [s]
12		CDet.Data_Collection_Rate	5.0 [Hz]
13		CDet.CellHeater.Mode	On
14		CDet.CellHeater.TemperatureSet	35.0 [°C]
15		CDet.Temperature_Compensation	1.7 [%]
16		Pump_ECD.Flow.Nominal	0.25 [ml/min]
17		Electrolytics.CR_TC.CR_TC	On
18		Wait	Pump_ECD.Ready
19		Wait	Compartment_TC.TemperatureState
20		Wait	Column_TC.TemperatureState
21		Pump_ECD.InjectValve.LoadPosition	
22	0.000	Inject	
23		InjectValve_CIC.Inject	
24		Pump_ECD.InjectValve.InjectPosition	30
25	0.000	Start Run	
26		Pump_1.Pump_1_Pressure.AcqOn	
27		CDet.CD.AcqOn	
28		CDet.CD_Total.AcqOn	
29		CDet.Autozero	
30	0.000	Run	Duration = 20.000 [min]
31	20.000	Stop Run	
32		Pump_1.Pump_1_Pressure.AcqOff	
33		CDet.CD.AcqOff	
34		CDet.CD_Total.AcqOff	
35		End	

Figure 14. Example instrument method for direct injection using injection valve in the Dionex Integrion IC system.

Figure 15. Example instrument method for preconcentration/matrix elimination.

Figure 16. Consumables tracking.

Figure 17. Step Editor in the Nittoseiko NSX-2100 software.

Starting the combustion IC analysis

Both the Chromeleon CDS software and the NSX-2100 software are used in this analysis to control the respective systems. To ensure that the signal from Nittoseiko GA-210 system is always received by the Dionex Integrion HPIC system, it is crucial to provide a time buffer of at least one minute. For example, if the total cycle time of the IC system is 23 min, then the IC Analysis Time should be 24 min in the NSX-2100 software (Figure 17). In the example in Figure 15 the total cycle is 23 min (3 min for preconcentration and matrix elimination, and 20 min for separation).

Always start the Chromeleon CDS software sequence before starting the NSX-2100 schedule.

Caution: If the wait ready setting (Figure 18) is checked, do not open the column oven or thermostatted detector compartment (if available) after the analysis has started. In addition, ensure that the IC system is ready and is waiting for the Inject Signal (Figure 19) before starting the NSX-2100 schedule.

Figure 18. Temperature options in the instrument method.

Figure 19. Waiting for inject response from Nittoseiko AQF-2100H.

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Conclusion

This technical note describes the installation and setup of a combustion IC system consisting of a Dionex Integrion HPIC system and a Nittoseiko AQF-2100H system for determination of sulfur and halogens in particularly complex matrices.

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