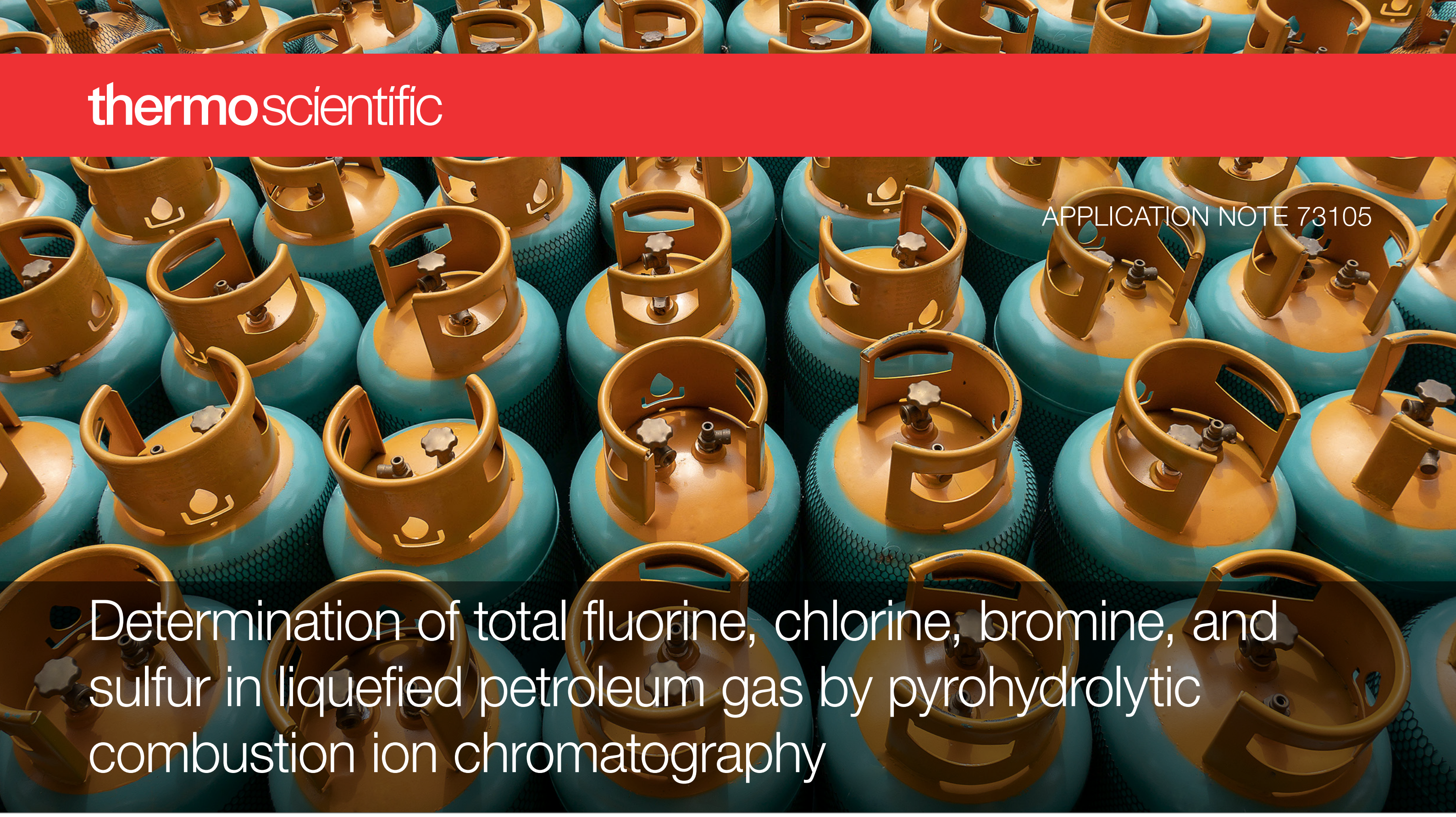

APPLICATION NOTE 73105

Determination of total fluorine, chlorine, bromine, and sulfur in liquefied petroleum gas by pyrohydrolytic combustion ion chromatography

Authors

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Keywords

IonPac AS20 column, RFIC, Reagent-Free IC, Integrion, CIC, combustion IC, LPG, ASTM D7994

Goal

Demonstrate fast determinations of total halides and total sulfur in n-butane liquefied petroleum gas using pyrohydrolytic combustion IC

Introduction

Natural gas is an important energy resource, accounting for 29% of the total energy consumed in 2017.[1] Natural gas is composed predominantly of methane but it can include other C_2 to C_5 hydrocarbons such as butane. The primary uses of natural gas are to generate electricity and as feed stock for plastic materials. Natural gas is withdrawn from traditional and hydraulic fracking petroleum wells. The gas obtained from traditional wells generally needs limited purification prior to selling it as a natural gas product. In contrast, wet natural gas withdrawn from wells using hydraulic fracturing requires additional processing to remove the water, other hydrocarbons, and sometimes hydrogen sulfide (H_2S) and carbon dioxide (CO_2) before it can be sold.[2] Amine gas treatment (also named amine scrubbing, gas sweetening)[3] typically uses percent concentrations of alkanolamines to remove these dissolved gases. These neutralizing processes result in dissolved sulfur species, organic acids, amine degradation products, and salt build-up in the amine gas treatment solutions. Determination of these contaminants and the alkanolamines by ion chromatography (IC) and IC-MS has been thoroughly discussed in previous applications.[4-10]

For more convenient storage and transportation, natural gas is often pressurized to a liquid state to produce liquefied petroleum gas (LPG). Determinations of halogen- and sulfur-containing compounds in LPG are needed because these contaminants can foul the catalysts during processing and because low halogen content LPG has greater market value.[11] Analysis of LPG hydrocarbons is commonly done by GC-MS; however, the quantification of numerous halogen- and sulfur-containing compounds can be challenging. The other common approach is combustion followed by titration or an ion selective electrode, which are labor-intensive and prone to analysis errors from matrix interferences.[11] Analysis of LPG in its gaseous and liquid form can be challenging for IC. As with other challenging samples, pyrolytic combustion ion chromatography (CIC) is an ideal approach to eliminate the sample matrix and increase sample homogeneity. Pyrolytic CIC has been previously demonstrated for halide determinations in other challenging samples, such as wastewater,[12] crude oil, aromatic hydrocarbons, and fuels,[13-19] including gas and liquefied gas samples (e.g. LPG). Determination of halogens and sulfur by CIC is described in ASTM method D-7994.[20]

This application note demonstrates the determinations of total halo-benzene compounds and total dimethylsulfide in *n*-butane LPG as fluoride, chloride, bromide, iodide, and sulfate using pyrohydrolytic combustion coupled with IC. A single 30 µL aliquot or multiple 30 µL aliquots of LPG were combusted under argon and oxygen gas aerated with water at 800 °C to 900 °C. The resultant reduced compounds were absorbed into 50 mg/L hydrogen peroxide absorption solution (except for iodide), of which a 100 µL aliquot was injected into the IC. The resultant anions were separated on a Thermo Scientific™ Dionex™ IonPac™ AS20 (2 × 250 mm) anion-exchange column using an electrolytically generated gradient from 10 to 38 mM KOH at 30 °C and 0.3 mL/min, eluted, and detected within 20 min by suppressed conductivity detection. The results show that reliable and accurate calibration curves can be generated by incrementally combusting multiple aliquots of the standard into the absorption solution. The reproducibility, RSDs <2%, and recoveries were good, 85–107%. However, a hydrazine absorption solution was required to improve iodide recovery.

Experimental

Equipment

- Mitsubishi Chemical Analytech™ Automatic Combustion Unit Model AQF-2100H system, including:
  - Automatic Boat Controller Model ABC-210
  - Automatic LPG Gas Injector Model GI-260 with inner pyrolysis tube
  - Horizontal Furnace Model HF-210
  - Gas Absorption Unit GA-211
  - External Solution Selector ES-210/211
- Thermo Scientific™ Dionex™ Integrion™ HPIC™ system with reagent-free ion chromatography (RFIC™) capabilities, including:
  - Dionex Integrion HPIC System Pump
  - Detector Compartment Temperature Control
  - Eluent generation
  - Integrion IC Conductivity Detector, P/N 079829

Table 1 lists the consumable products needed for the CIC system.

Software

- Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) 7.2 Software, version SR9
- Mitsubishi NSX-2100 version 10.2.3.0

Table 1. Consumables list for the Mitsubishi combustion system coupled to the Dionex Integrion HPIC system

Product Name	Description	Thermo Scientific P/N
Thermo Scientific™ Dionex™ IC PEEK Viper™ fitting tubing assembly kit	Dionex IC Viper fitting assembly kit for the Dionex Integrion RFIC system with CD: Includes one each of P/Ns: 088805–088811	088798
Thermo Scientific™ Dionex™ EGC 500 KOH Eluent Generator cartridge	Eluent generator cartridge for the Dionex Integrion system	075778
Thermo Scientific™ Dionex™ CR-ATC 600 Electrolytic trap column	Continuously regenerated anion trap column used with the Dionex Integrion system	088662
HP EG Degasser Module	Degasser installed after Dionex CR-ATC trap column and before the injection valve, used with eluent generation, included with installation	075522
Thermo Scientific™ Dionex™ ADRS 600 suppressor	Suppressor for 2 mm anion columns	088667
Thermo Scientific™ Dionex™ IonPac AG20 Guard Column	Anion guard column, 2 × 50 mm	063066
Thermo Scientific™ Dionex™ IonPac AS20 Analytical Column	Anion analytical column, 2 × 250 mm	063065
4 L eluent bottle	Two 4 L eluent bottles are needed for the CIC system	066019
Quartz wool	Quartz wool for the combustion boats and the combustion tube	MC06175*
Extra combustion tube	AQF-2100H pyrolysis tube set	MC28002*
Extra inner pyrolysis tube	Inner pyrolysis tube for GI 260 module for the AQF-2100H combustion system	MC28035*
Extra absorption tube	Absorption tube, 10 mL	MC25000*
Swagelok Snoop® solution	Leak testing the LPG sample transfer line	Fisher Scientific NC0971675

*The distributors provide sales support and replacement parts. The U.S. distributor is COSA Xentaur. COSA Xentaur reorder P/N[21]

Conditions

Pyrohydrolytic combustion conditions

AQF-2100H	
Mode:	Constant volume
Sample mode:	Liquefied gas sampling
LPG loop volume:	30 µL
Pyrolysis tube:	Double quartz, inner tube for LPG analysis
Combustion run time	
Single combustion:	114 s (100 s + 5 s + 9 s)
Multiple combustion:	100 s x # combustions + 5 s + 9 s
Calculated final volume	9.75 mL
Absorption solution:	50 mg/L hydrogen peroxide in ASTM Type I deionized water*
Gas	
Argon and oxygen gas tank regulator, secondary gauge setting:	40 psi
Argon flow on HF-210:	140 mL/min
Argon flow (carrier) on GI-260:	60 mL/min
Argon flow (humidification):	100 mL/min
Oxygen flow on HF-210:	400 mL/min
Temperatures	
GI-260 expansion chamber:	85 °C
HF-210 Furnace:	Inlet: 800 °C Outlet: 900 °C
Iodine (I) absorption solution	
Absorption solution:	50 mg/L hydrogen peroxide, 1000 mg/L hydrazine in ASTM Type I deionized water*

*ASTM Type I deionized water can be used as an absorbing solution for fluoride and chloride determinations (ASTM 7994)[20]

Detailed pyrohydrolytic combustion conditions (part 1)

GI-260	
LPG loop volume:	30 µL
Argon gas flow (carrier):	60 mL/min
Expansion chamber setting temperature:	85 °C
Liquefied gas sampling	
Purge time:	5 s
Wait time:	9 s
Time of liquefied gas sample injection:	100 s
HF-210 module	
HF-210 heater temperatures	
Inlet:	800 °C
Outlet:	900 °C
Standby:	300 °C
HF-210 gas flow	
Ar:	140 mL/min
O_2:	400 mL/min
Standby:	50 mL/min
HF-210 timing	
Ar:	150 s
O_2:	0 s
Ar replace time:	30 s
HF-210 valve timing	
Valve selection:	On
Ar to O_2:	10 s
O_2 to Ar:	10 s
GA-211 module	
Absorption tube:	10 mL
Sample loop:	100 µL
Final absorption volume:	10 mL

Detailed pyrohydrolytic combustion conditions (part 2)

GA-211 washing conditions	
Absorption solution volume:	3.5 mL
Water supply scale:	2
Ar flow for humidification:	100 mL/min
Water injection time:	15 s
Drain time:	12 s
Washing time:	2
Gas line washing time:	0.5 s
Gas line washing interval:	3 s
Gas line washing times:	3
Washing time of sample absorption line:	5 s
Syringe washing times:	3
GA-211 gas line collection parameters	
Collection time:	0.5 s
Collection interval:	3 s
Times:	3
Constant volume function parameter	
Waiting time for stable liquid surface:	10 s
Mixing time:	10 s
GA-211 injection parameters	
Washing time for injection start:	0 s
Sample purge time:	5 s
Sample absorption time:	10 s

Ion chromatography conditions (part 1)

Columns:	Dionex IonPac AG20 guard (2 x 50 mm) and IonPac AS20 analytical (2 × 250 mm)
Eluent:	KOH
Eluen source:	Dionex EGC 500 KOH eluent generator cartridge, Dionex CR-ATC 600 trap column, and high pressure degas module
KOH gradient:	10–38 mM KOH from 0 to 14 min, 10 mM KOH from 14.1 to 20 min
Flow rate:	0.375 mL/min
Injection or conc. volume:	100 µL from GA-210 Gas Absorption Unit

Ion chromatography conditions (part 2)

Column temperature:	35 °C
Detection/Suppressor compartment:	20 °C
Detection:	Suppressed conductivity, Dionex ADRS 600 suppressor, 2 mm, 36 mA, constant current and recycle modes
Background:	<1 µS/cm
Noise:	<1 nS/cm
System backpressure:	~2800 psi
Run time:	IC: 20 min, Total run time: ~22 min

Iodine (I) gradient

KOH gradient:	10–24.9 mM KOH from 0 to 7 min, 24.9–26 mM KOH from 7 to 9 min, 26–40 mM KOH from 9 to 14 min, 10 mM KOH from 14.1 to 20 min

Reagents

- ASTM Type 1 deionized water (DI water) with 18 MΩ·cm resistivity[21]
- Thermo Scientific™ Dionex™ Stock Standards for external calibration
  - Dionex 1000 mg/L Chloride Standard (P/N 037159)
  - Dionex 1000 mg/L Fluoride Standard (P/N 037158)
  - Dionex 1000 mg/L Sulfate Standard (P/N 037160)
- Bromide, 1000 mg/L for Ion Chromatography, Fisher Scientific P/N ASBR9-2Y
- Hydrazine, monohydrate, 99%, Fisher Scientific P/N AA1665122
- 30 wt% hydrogen peroxide, stabilized, Suprapur™, EMD Millipore P/N M1072980250, Fisher Scientific P/N M1072980250 (density: 1.1 g/mL), used to prepare the 100 mg/kg peroxide absorption solution.
- UHP grade gas for pyrohydrolytic combustion
  - Argon gas
  - Oxygen gas
  - Nitrogen gas, also used to pressurize the LPG cylinders with 300-400 psi headspace

Liquefied petroleum gas (LPG) standards and samples

Caution: Electrically ground and secure the LPG tanks according to local safety and fire regulations.

Red Ball Technical Gas Services, a division of Red Ball Oxygen[22] *n*-butane LPG tanks (density: 0.5788 mg/kg) are pressurized to 200 psi with helium and have a dip tube valve. The tank valve outlets are CGA 510 P SS (note: reverse thread).

Tanks 1-3 were prepared March 2019 from the same lot of *n*-butane LPG:

1. LPG butane blank (CAS 106-97-8).

2. LPG butane with 2 mg/kg additives containing 2.1 mg/kg total fluorine (F) as fluorobenzene (CAS 462-06-6), 2.0 mg/kg total chlorine (Cl) as chlorobenzene (CAS 108-90-7), 2.0 mg/kg total bromine (Br) as bromobenzene (CAS108-86-1), 2.1 mg/kg total iodine (I) as iodobenzene (CAS 59150-4), and 2.0 mg/kg total sulfur (S) as dimethylsulfide (CAS 75-18-1).

3. LPG butane with 15 mg/kg additives containing 15.1 mg/kg total fluorine (F) as fluorobenzene, 16.4 mg/kg total chlorine (Cl) as chlorobenzene, 15.4 mg/kg total bromine (Br) as bromobenzene (CAS 108-86-1), 16.5 mg/kg total iodine (I) as iodobenzene, and 15.1 mg/kg total sulfur (S) as dimethylsulfide.

Tank 4 was a 1-year-old tank prepared May 2018 from a different lot of *n*-butane LPG than Tanks 1–3.

4. LPG butane with 15 mg/kg additives containing 15.0 mg/kg total fluorine (F) as fluorobenzene, 15.1 mg/kg total chlorine (Cl) as chlorobenzene, and 15.1 mg/kg total sulfur (S) as dimethylsulfide.

Preparation of absorption solutions, standards, and samples

50 mg/L hydrogen peroxide absorption solution

The 50 mg/L hydrogen peroxide solution was used for sample absorption of total sulfur and the halides, except iodide. Typically, fluoride, chloride, and bromide can be absorbed in ASTM Type I DI water, whereas a solution of 50 mg/L peroxide is used to absorb sulfur species for total sulfur determinations. To prepare the 50 mg/L hydrogen peroxide, dilute 166 µL of the 30 wt% Suprapur hydrogen peroxide into 999.8 mL of ASTM Type I DI water.

Preparation of 50 mg/L hydrogen peroxide, 1000 mg/L hydrazine absorption solution

This absorption solution was used for iodide determinations. To prepare the 50 mg/L hydrogen peroxide 1000 mg/L hydrazine, pipette 166 µL of the 30 wt% Suprapur hydrogen peroxide and 1000 µL of hydrazine into 998.8 mL of ASTM Type I DI water.

Standard and sample preparation

No preparation is needed for the LPG standards.

Aqueous standards for external calibration

Dilute the 1000 mg/L individual aqueous standards with ASTM Type I DI water to make a 1 mg/L mixed intermediate standard. Use the intermediate standard and ASTM Type I DI water as needed to generate 0.01, 0.015, 0.020, 0.040, 0.06, 0.08, and 0.1 mg/L mixed anion working standards.

Instrument setup and installation

This application uses inline sample preparation by pyrohydrolytic combustion with oxidative reaction followed by sample absorption, mixing, and dilution. The combustion system triggers the IC to analyze the samples. The combustion tube is connected to the ABC-210 Automatic Boat Controller module and in the HF-210 furnace.

- Sample introduction:
  - To obtain sampling consistency and uniformity, pressurize the LPG tanks (300–400 psi, 2000–2760 kPa) with inert gas per Section 8.8 of ASTM D7994.[20]
  - Check the LPG tank prior to analysis and re-pressurize as needed.
  - The LPG liquid sample is transferred from the bottom of the pressurized LPG tank to the Mitsubishi Gas Injection GI-260 module. Argon carrier gas at 60 mL/min transfers a 30 µL aliquot of the LPG sample from the 30 µL sample loop, through a heated expansion chamber, and into the combustion tube.

- The injection time is 114 s for a single combustion, which includes 14 s to purge the gas from the system.

- Pyrohydrolysis and combustion:
  - Initially, the LPG sample is pyrolyzed under argon inert atmosphere (burned without oxygen) at 800 °C and then hydrolyzed in the presence of oxygen and water vapor to hydrogen halide and sulfur gases at 900 °C.
- Sample absorption:
  - The argon gas carries and aerates the sample into a 50 mg/L peroxide absorption solution (recommended for total fluorine, chlorine, bromine and total sulfur) in the GA-211 Gas Absorption unit.
  - The aeration continues, which provides mixing while the sample is diluted to 10 mL total volume.
- Sample analysis:
  - The GA-211 unit loads a 100 µL aliquot of the sample directly into the 100 µL sample loop and triggers the IC injection via the 6-port GA-211 high pressure injection valve, a TTL_Input_3 cable, and programmed commands stored in the Chromeleon CDS configuration.

Physical configuration

To install the CIC system, follow the installation instructions described in Thermo Scientific Technical Note TN72211 - Combustion ion chromatography with a Dionex Integrion HPIC System[24] and Figures 1 and 2. Connect the RS232 cable from the HF-210 module and the USB cable from the Dionex Integrion IC to the computer. Connect the RS232 cables from the ES-210, ABC-210 and GI-260 modules to the HF-210 module. Install the power cords and power-up the modules. Install the twisted pair cable from the Integrion IC to the Mitsubishi GA-211 module according to the instructions in TN72211.

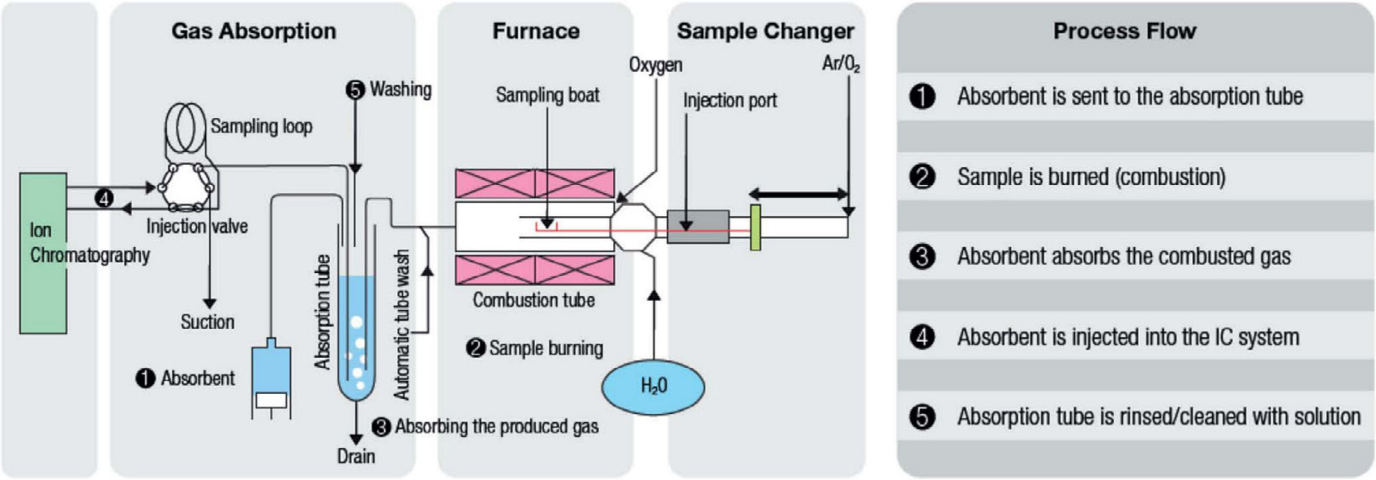


Figure 1. Diagram of a combustion IC system[24,25]

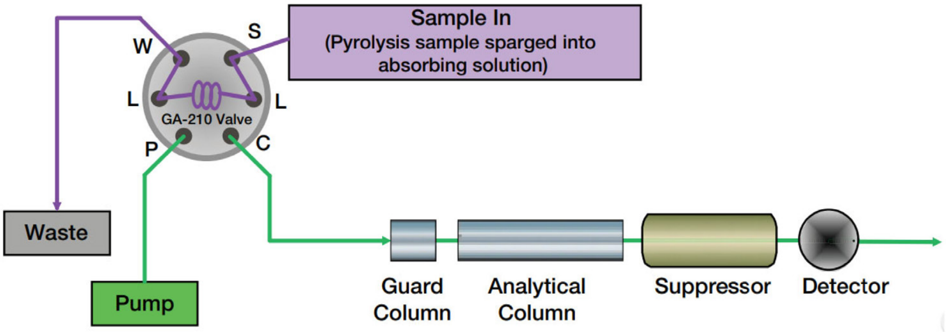


Figure 2. IC schematic[24,25]

Electronic configuration

Configure the IC modules in the Chromeleon CDS software as described in TN72211, including the instructions for TTL_Input_3 and the Device Name as InjectValve_CIC. Add the AGF-2100H combustion system as the Remote Inject Device module according to the instructions. This application is configured as described under “Direct injection using the injection valve in the Mitsubishi GA-210 Module” in TN72211. Additional information on the combustion system can be found in the product manual.[24]

Plumbing the Dionex Integrion IC

Plumb the Dionex Integrion IC as a standard RFIC system shown in Figure 2 and shown on the schematics on the inside doors of the Dionex Integrion IC system. Yellow (0.003 in i.d., 0.0762 mm i.d.) PEEK tubing was added after the degas module and before the IC injection valve to bring the IC system pressure to ~2200 psi.

Conditioning electrolytic devices and columns

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

Hydrate and condition the Dionex EGC 500 KOH eluent generator cartridge and Dionex CR-ATC 600 Continuously Regenerated Trap column according to TN175, product manuals, or the instructions in the drop-down menu (Chromeleon Console, under Consumables drop-down menu).[27-29] Condition the columns as described in the Dionex IonPac AS20 product manual or Consumables Conditioning instructions (Chromeleon Console, under Consumables drop-down menu), 35 mM KOH, 30 °C at 0.35 mL/min for 30 min while directing the effluent to waste.[30] Install the conditioned columns according to Figure 2.

To hydrate the Thermo Scientific™ Dionex™ ADRS™ 600 suppressor, follow the instructions in the Suppressor Installation Checklist that is included with the suppressor. Install the suppressor according to Figure 2. To ensure that the suppressor is within backpressure specifications, follow the instructions in the Suppressor Installation Checklist. The backpressure resulting from the suppressor (1) should be <50 psi, whereas the backpressure applied after the suppressor (2) should be <100 psi. The operations of the Dionex ADRS 600 suppressor are thoroughly discussed in the Dionex DRS 600 suppressor manual.[31]

Equilibrating IC system and Consumables Device Tracking

Equilibrate the IC using the Quality Assurance Report (QAR) conditions for the Dionex IonPac AS20 column until the total conductivity is <2 µS/cm. Using the Chromeleon Wizard program, create a new instrument method using the QAR conditions, a new processing method, and a new sequence. Approve the consumables in the Consumables Tracking panel located on the Chromeleon console (TN175). Start the Chromeleon sequence. Compare the results against QAR report.

Combustion system

LPG transfer line

To connect the LPG tank to the GI-260 module, use a 1/16 inch o.d. transfer line to minimize void volume, and stainless-steel Swagelok™ fittings to connect to the 1/8 inch stainless steel Swagelok fittings on the GI-260 LPG inlet port. The LPG tanks should be stored, secured, and electrically grounded in accordance with local safety and fire regulations.

Installing the pyrolysis tubes

Insert a small piece of quartz wool into the outlet of the outer pyrolysis tube. Assemble the inner and outer pyrolysis tubes using the ground glass joints and install and secure the assembled pyrolysis tubes inside the HF-210 furnace.

Starting the CIC system

Power up each module. Open the Ar and O_2 gas tank regulators and set the secondary gauges of the gas regulators to 40 psi. Open the gas flow to the tubes feeding the CIC system.

Open the AQF-2100H software program. Turn on the gas by selecting the first flame icon. Wait a few seconds for the gas flows to reach the set points (Ar: 140, O_2: 400, WS Ar: 100, GI Ar: 60 mL/min for argon carrier, oxygen, argon hydration, and argon carrier, respectively). To heat up the furnace, select the second flame icon. The heat up time to the set temperatures will be ~1 h.

Creating an AQF-2100 schedule

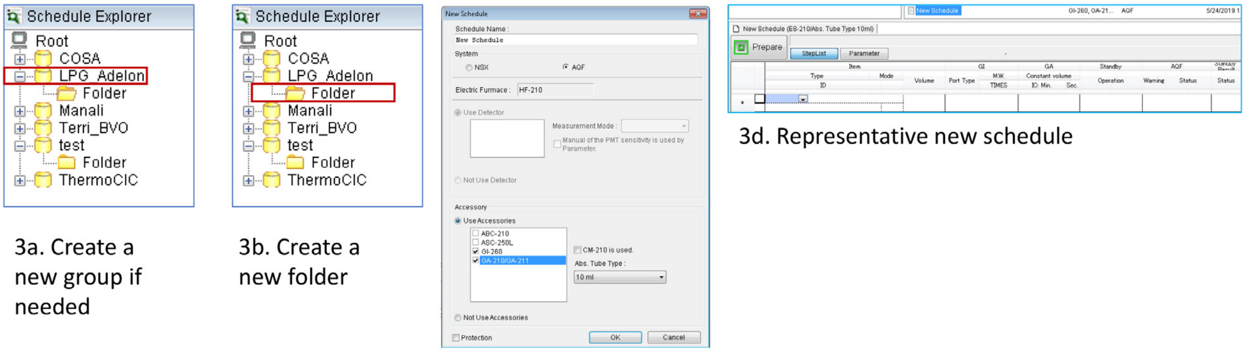
1. If necessary, create a new Group by right-clicking the “Root” icon in the system explorer and select New > Group (Figure 3A).
2. In the desired Group, right-click the desired folder for the location of the schedule and select New > Schedule (Figure 3B).
3. Name the schedule and select the appropriate accessories (Figure 3C). Check the “Protection” option if you want to prevent future deletion of the schedule.
4. Click OK and the new schedule will open (Figure 3D).

To generate a schedule method, select the Step Editor icon (Figure 4), which will open a Step Editor window.

Enter the parameters from Table 2. Click on the “Add” button to add the sample to the schedule. Repeat for all samples. Select the shutdown programs by selecting Standby, and selecting these commands, one for each step in the following order:

1. End GA-210/211 processing
2. Heater off
3. Wait for 60 min
4. Gas Valve off

Click on the “Close” button to end Step Editor.



Schedule Name : New Schedule

System

○ NSX ● AQF

Electric Furmace : HF-210

○ Use Detector

Measurement Mode :

☐ Manual of the PMT sensitivity is used by Parameter.

○ Not Use Detector

Accessory

● Use Accessories

☐ ABC-210
☐ ASC-250L
☑ GI-260
☑ GA-210/GA-211

☐ CM-210 is used.

Abs. Tube Type : 10 ml

○ Not Use Accessories

☐ Protection

New Schedule GI-260, GA-21... AQF 5/24/2019 1

New Schedule (ES-210/Abs. Tube Type 10ml)

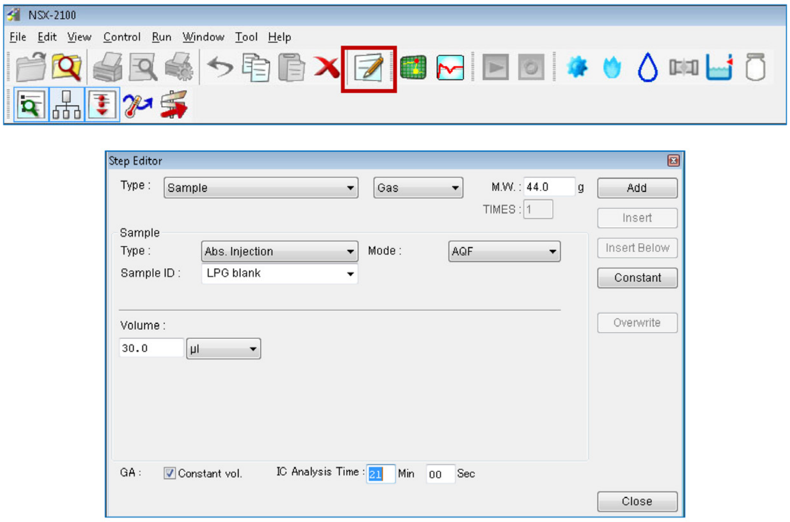
3a. Create a new group if needed

3b. Create a new folder

3c. Create a new schedule

3d. Representative new schedule

Figure 3. Creating a new schedule



Type : Sample

Gas

M.W. : 44.0 g

TIMES : 1

Sample

Type : Abs. Injection

Mode : AQF

Sample ID : LPG blank

Volume : 30.0 µl

GA : ☑ Constant vol.

IC Analysis Time : 21 Min 00 Sec

4a. Select the Step Editor icon

4b. Select parameters for an LPG method

Figure 4. Using the Step Editor to create a schedule method

Table 2. Step Editor parameters

Parameter	Action	Description
Type	Select Sample	To run samples
	Select Standby	Creates shutdown or start-up functions
Gas or Liquefied gas	Select Liquefied gas	LPG is a liquefied gas
MW	Enter 44	
Times	Enter 1	Programs the number of combustions combined into one sample injection. For example, enter "1" for one combustion.
	Enter another number from 2 to 9	Programs multiple aliquots of 30 µL combusted and collected as one sample injection. Useful for calibration plots
Sample	Select Abs. Injection	Inject into IC system
	Select AQF	
Sample ID	Enter sample name	
Volume (µL)	Enter LPG sample loop volume	
GA		
Constant volume	Check box	
IC analysis time	Enter IC run time plus 1 min	
Add, Insert or Insert below	Click on Add	Select Add to add a line to the sequence
	Click on Insert button	Select Insert to add a line above the current line

Create a Chromeleon sequence

Open the Chromeleon instrument console program and create a sequence duplicating the list of samples in the combustion sequence. Create an IC instrument method using the Chromeleon Wizard and the parameters listed in the Ion Chromatography Conditions section. Save the sequence.

Starting the Chromeleon sequence and AQF-2100 schedule

The Chromeleon sequence is started before the AQF-2100 schedule. To start the Chromeleon sequence, approve the consumables in the Consumables Tracking panel located on the Chromeleon console (See TN175). Add the Chromeleon sequence into the Instrument queue, select Check Sequence, correct any errors, and select Start.

Select the AQF-2100 schedule and double click to open. Verify that the furnace temperatures and gas flows of the combustion system are at the set points. Select the "Prepare" button to save and load the schedule and select start (blinking blue arrow). The AQF-2100 will trigger the IC to start the Chromeleon sequence. The data will be stored in Chromeleon.

Calculations

Calibration through the combustion furnace

The Gas Injector GI-260 module has an incremental combustion feature that allows single to multiple combustions of the sample loop volume to be absorbed in the 10 mL absorption solution. This feature results in a convenient and economic analysis using one LPG tank for calibration.

The CIC results are expressed in mg/kg of total fluorine, chlorine, bromine, sulfur, and iodine where their respective ions of fluoride, chloride, bromide, sulfate, and iodide are separated and detected. Using the processing method program, set the concentration units to mg/kg, and set up the calibration plot using the specifications on the LPG tank (mg/kg). The sample results will be expressed in mg/kg.

For example, if the LPG tank contains 2.1 mg/kg total fluorine as fluorobenzene, and 2.5 mg/kg sulfur as dimethylsulfide, then enter 2.1 mg/kg for total fluorine and 2.5 mg/kg for total sulfur in the component table as the first concentration level (a single 30 µL combustion). Enter 4.2 and 5.0 mg/kg of total fluorine and total sulfur, respectively for Standard 2 (two 30 µL combustions).

External calibration

To use a calibration independent of the combustion, such as the External Sampler ES-210/211 module, the LPG injection must be converted from volume to mass and the IC results (x in µg/mL) must be adjusted by the LPG mass (mg) and the absorption volume (mL).

The mass of the LPG combusted is the sample loop volume (µL) times the density in mg/µL (equivalent to g/mL)

$$\text{Conc of Analyte}\left[\frac{\mu g}{mg}\right] = x \text{ in } \mu g/mL \cdot \frac{\text{Absorption volume in mL}}{\text{LPG weight in mg}}$$

The calculated concentration in µg/mg must be converted to mg/kg by multiplying by 1000.

Shutdown

The Gas Injector GI-260 module has built-in purging features to provide easier and safer purging of flammable liquids such as LPG. To shut down the system at the end of the day and at the end of the sequence, close the LPG tank by turning the tank valve clockwise. Purge the LPG from GI-260 module and the transfer line by pressing the purge button on the GI-260 module for 30 s. Repeat four times. Complete the cool-down of the Horizontal Furnace HF-211 module to room temperature, and then turn off the gas flows.

Results and discussion

In this application, total sulfur as sulfate, total of each halogen as fluorine, chlorine, and bromine are determined in liquefied petroleum gas (LPG) standards as samples. A modified method was used for iodine determinations. The LPG sample, 30 µL aliquots, are treated with pyrohydrolytic combustion at 800 °C to 900 °C under inert and oxygen atmosphere. During the combustion process, the halo-benzene and dimethylsulfide additives in the LPG were converted to HX (gas) and SOx (gas) and absorbed in 10 mL of 50 mg/L hydrogen peroxide. Anions in the 100 µL aliquot of the absorbed, combusted sample are separated by anion-exchange chromatography using an electrolytically generated gradient from 10 to 38 mM KOH at 35 °C and 0.30 mL/min. The Dionex IonPac AS20 separation column (2 × 250 mm) and guard were selected for this application because it was optimized for the elution of highly retained anions, such as iodide. All anions eluted from the column within 20 min and were detected by suppressed conductivity. The LPG combustion time is 114 s for one combustion (plus 100 s for each additional aliquot of LPG), resulting in a total run time of 22 min in overlap mode. The method had good accuracy with recoveries within 85–110% and good reproducibility with <3% RSDs.

For iodine (I) determinations, a multi-step gradient was developed by reducing the gradient slope between 7 and 9 min to increase resolution of sulfate from carbonate. An absorption solution of 50 mg/L peroxide and 1000 mg/L hydrazine was used to increase collection of iodine compounds as iodide. The peroxide-hydrazine absorption solution improved the iodide reproducibility and response to generate a calibration curve, but the responses (<0.05 µS/cm) and recoveries remained low. The method development, qualification, and results are discussed here.

External calibration

It is useful to compare a calibration through the combustion system to a direct injection using the External Sampler ES-210/211 module. To evaluate external calibration mode, seven aqueous standards from 0.01 to 0.1 mg/L were used to generate the calibration curve.

Method development

To optimize this method, the effect of absorption solution, separation temperature, and KOH gradient were evaluated based on the ions' response and reproducibility. One method was developed for the determinations of total fluorine, chlorine, bromine, and total sulfur, and a second modified version of the method was used for iodine determinations. The absorption solution was found to be a critical parameter, as the reagent used to prepare the absorption solution impacts the IC blank and the collection of the ions. ASTM Type I DI water, 30 mg/L hydrogen peroxide, 50 mg/L hydrogen peroxide, and 50 mg/L hydrogen peroxide, 1000 mg/L hydrazine were evaluated. The experiments showed that DI water contributed the lowest background contamination, but peroxide was needed to fully oxidize the sulfur species to sulfate. The 30 mg/L and 50 mg/L solutions prepared from the high purity hydrogen peroxide resulted in acceptable contamination peaks (low acetate, formate, and carbonate), providing a good compromise for all anions. Iodine (I) determinations were the exception, requiring hydrazine in addition to the 50 mg/L peroxide to reduce iodine to iodide. The peroxide-hydrazine solution resulted in significantly higher contamination of acetate and formate, which impacted fluorine quantification and carbonate and resulted in poor sulfate resolution and quantification. The compromise was to use the peroxide-hydrazine absorption solution for iodine determinations and the 50 mg/L peroxide absorption solution for the other anions.

A simple gradient, from 10 to 38 mM KOH at 35 °C, was selected because it had good resolution for the anions, except when using the peroxide-hydrazine absorption solution. The separation conditions were optimized for iodide determinations by flattening the gradient to 0.05 mM KOH/min where carbonate-sulfate elute between 7 to 9 min.

The optimized method for total fluorine, chlorine, bromine, and sulfur is shown in Figure 5. The absorption solution is 50 mg/L hydrogen peroxide. The separation conditions are a simple gradient from 10 to 38 mM KOH at 35 °C over 14 min with 6 min for equilibration. Figure 5A shows the separation results of a single 30 µL combustion of *n*-butane LPG without additives (LPG blank). Figure 5B shows the lowest standard, LPG with 2 mg/kg additives. Iodine was not detected with this method.

LPG blanks

Characterizing the blank is important to assess the background contamination and as part of the sensitivity determination. Figure 6 shows the IC of pyrohydrolytic combustion of n-butane without additives (n = 3). The results show fluorine and bromine in the LPG blank are below the quantitation level, and sulfur and chlorine are present at sub-ppm concentrations.

Columns: Dionex IonPac AG20, Dionex IonPac AS20, 2 mm i.d.
Gradient: 10–38 mM KOH (0–14 min), 10 mM (14.1–20 min)
Eluent Source: Dionex EGC 500 KOH cartridge, Dionex CR-ATC 600 trap column, Dionex high pressure degasser
Flow Rate: 0.375 mL/min
Injection Vol.: 100 µL
Column Temp.: 35 °C
Detector Temp.: 20 °C
Detection: Suppressed conductivity, Dionex ADRS 600, 2 mm, constant current and recycle modes, 36 mA
Sample Prep. Mode: Combustion, Absorption, and Injections
Sample Mode: Liquified gas sampling
LPG Sample: 30 µL, 85 °C, 60 mL/min Ar carrier
Temperatures: 800 °C inlet, 900 °C outlet
Gas: 140 mL/min Ar, 400 mL/min O_2, 100 mL/min Ar + DI water
Absorption Sol.: 10 mL, 50 mg/L hydrogen peroxide
Samples: A: *n*-butane LPG without additives
B: *n*-butane LPG with 2 mg/kg additives
(Fluorine as fluorobenzene, bromine as bromobenzene, chlorine as chlorobenzene, sulfur as dimethylsulfide, iodine as iodobenzene)

Peaks:	A	B mg/kg
1. Total Fluorine (F)	Not quantified	2.21
2. Acetate	--	--
3. Formate	--	--
4. Total Chlorine (Cl)	MDL (~0.3)	1.81
5. Total Bromine (Br)	--	1.90
6. Carbonate	--	--
7. Total Sulfur (S)	0.106	1.75

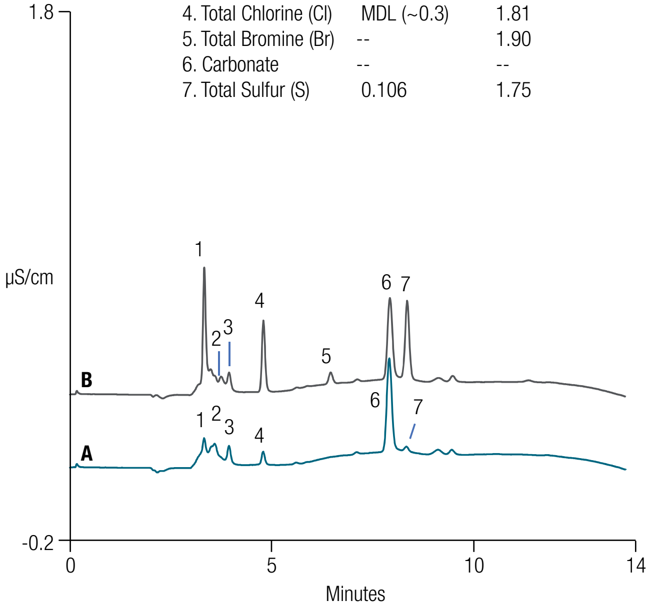


Figure 5. Comparison of *n*-butane A) LPG blank and B) LPG with 2 mg/kg additives

Columns:	Dionex IonPac AG20, Dionex IonPac AS20, 2 mm i.d.
Gradient:	10–38 mM KOH (0–14 min), 10 mM (14.1–20 min)
Eluent Source:	Dionex EGC 500 KOH cartridge, Dionex CR-ATC 600 trap column, Dionex high pressure degasser
Flow Rate:	0.375 mL/min
Injection Vol.:	100 µL
Column Temp.:	35 °C
Detector Temp.:	20 °C
Detection:	Suppressed conductivity, Dionex ADRS 600, 2 mm, constant current and recycle modes, 36 mA
Sample Prep. Mode:	Combustion, Absorption, and Injections
Sample Mode:	Liquified gas sampling
LPG Sample:	30 µL, 85 °C, 60 mL/min Ar carrier
Temperatures:	800 °C inlet, 900 °C outlet
Gas:	140 mL/min Ar, 400 mL/min O_2, 100 mL/min Ar + DI water
Absorption Sol.:	10 mL, 50 mg/L hydrogen peroxide
Sample:	*n*-butane LPG without additives

Peaks:		Average, mg/kg
	1. Total Fluorine (F)	Not quantified
	2. Acetate	---
	3. Formate	--
	4. Total Chlorine (Cl)	MDL (~0.3)
	5. Total Bromine (Br)	--
	6. Carbonate	--
	7. Total Sulfur (S)	0.106

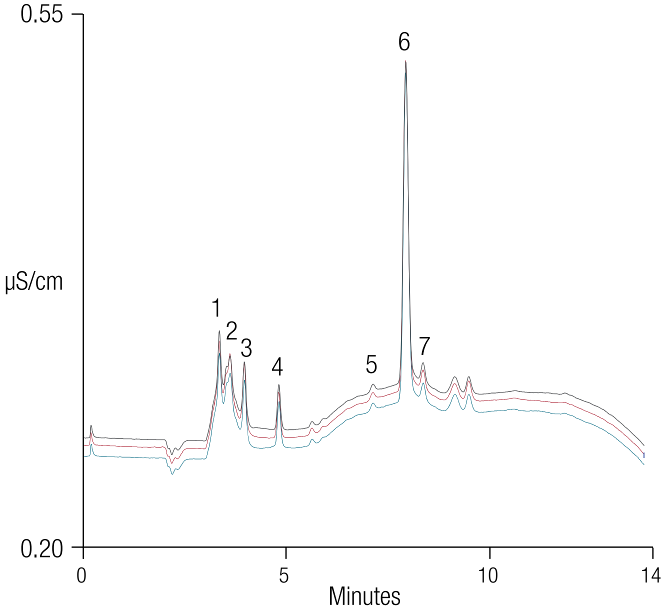


Figure 6. Triplicate injections of combusted *n*-butane LPG without additives with 5% offset applied

Method qualification

To qualify the method, the calibration ranges and method detection limits (MDLs) were determined. Two calibration ranges were evaluated: 2 to 18 mg/kg and 15 to 135 mg/kg of halogens (except iodine) and sulfate. Total iodine was evaluated from 15 to 135 mg/kg using a peroxide-hydrazine absorption solution to reduce the oxidized forms to iodide. Figures 7 and 8 show the calibration curves for fluorine, chlorine, bromine, and sulfur. The calibration curve for iodine is included in Figure 8. The low calibration curve, 2 to 18 mg/kg, was developed by combusting incremental 30 µL aliquots of the 2 mg/kg additive LPG standard to generate 2.0, 4.0, 6.0, 8.0, 10.0, 12.0, 14.0, 16.0, and 18.0 mg/kg additives in LPG. The highest calibration curve, 15 to 135 mg/kg, was developed similarly with the 15 mg/kg additives in LPG. The results, summarized in Table 3, demonstrate the effectiveness of generating calibration curves by combusting multiple amounts of one standard.

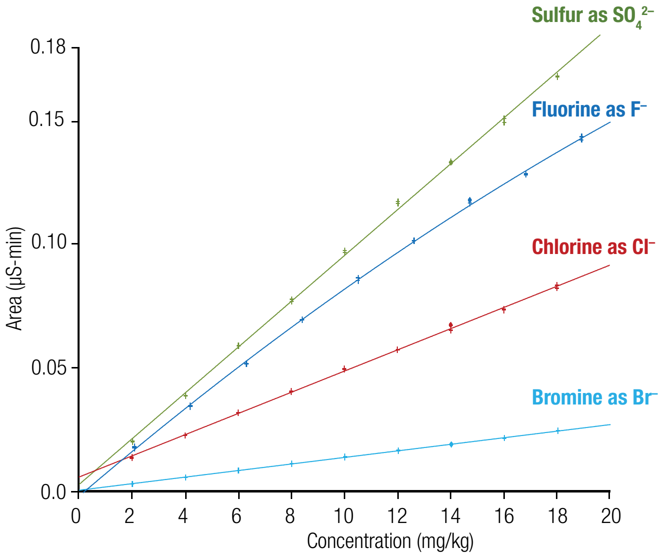
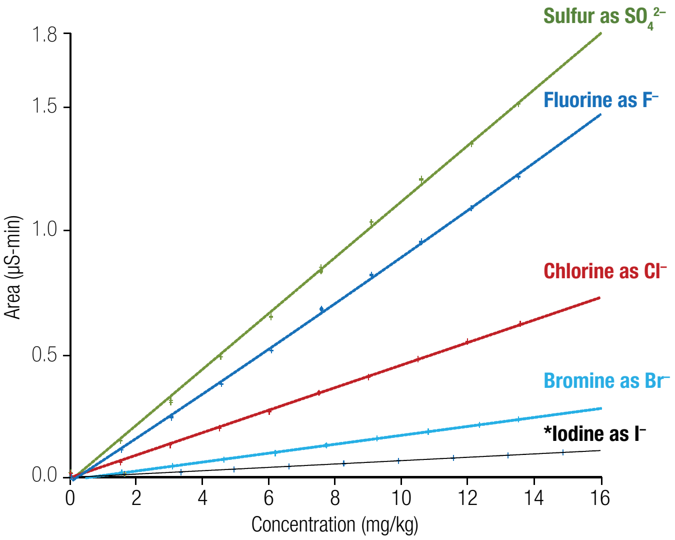


Figure 7. Calibration using incremental combustion of *n*-butane LPG with 2 mg/kg additives



*50 mg/L peroxide, 1000 mg/L hydrazine absorption solution

Figure 8. Calibration using incremental combustion of *n*-butane LPG with 15 mg/kg additives

Table 3. Method qualification results showing calibration ranges, linear response, and estimated MDL

Compound*	Calibration Range (mg/kg)	Type	Coefficient of Determination (r^2)	MDL using small loop injections (µg/kg)	Calibration Range (mg/kg)	Type	Coefficient of Determination (r^2)
Total Fluorine as Fluoride	2–18	Quadratic	0.9994	17	15–135	Quadratic	0.9992
Total Chlorine as Chloride	2–18	Linear	0.9990	280	15–135	linear	0.9988
Total Bromine as Bromide	2–18	Linear	0.9995	1000	15–135	linear	0.9996
Total Sulfur as Sulfate	2–18	Linear	0.9991	36	15–135	linear	0.9986
Total Iodine as Iodide*	--	--	--	4000	15–135	linear	0.9986*

*A calibration curve was obtained for total iodine using 50 mg/L peroxide, 1000 mg/L hydrazine absorption solution.

Table 3 shows that fluorine calibration results were best fit with quadratic equations, whereas chlorine, bromine, and sulfur had a more linear response. Iodine absorbed in the peroxide-hydrazine solution had a linear response with the coefficient of determination (r^2) >0.998.

MDLs were determined using small loop (5, 10 µL) injections rather than the 100 µL injection used for the 2 mg/kg calibration plot (Figure 7). Figure 9 shows a chromatogram of the small volume injection (5 µL) to imitate low concentration standards in a 100 µL injection. The results in Table 3 show estimated MDLs from µg/kg for fluorine, chlorine, and sulfur to mg/kg for bromine and iodine.

Sample analysis

The application method was applied to standards as samples:

Sample 1: *n*-butane LPG Tank 4, a one-year old tank with 15 mg/kg fluorine, chlorine, and sulfur additives

Sample 2: using nine combustions of *n*-butane Tank 2 as one injection. (Tank 2 has 2 mg/kg of fluorine, chlorine, bromine, iodine, and sulfur additives.)

Columns:	Dionex IonPac AG20, Dionex IonPac AS20, 2 mm i.d.
Gradient:	10–38 mM KOH (0–14 min), 10 mM (14.1–20 min)
Eluent Source:	Dionex EGC 500 KOH cartridge, Dionex CR-ATC 600 trap column, Dionex high pressure degasser
Flow Rate:	0.375 mL/min
Injection Vol.:	5 µL
Column Temp.:	35 °C
Detector Temp.:	20 °C
Detection:	Suppressed conductivity, Dionex ADRS 600, 2 mm, constant current and recycle modes, 36 mA
Sample Prep. Mode:	Combustion, Absorption, and Injections
Sample Mode:	Liquified gas sampling
LPG Sample:	30 µL, 85 °C, 60 mL/min Ar carrier
Temperatures:	800 °C inlet, 900 °C outlet
Gas:	140 mL/min Ar, 400 mL/min O_2, 100 mL/min Ar + DI water
Absorption Sol.:	10 mL, 50 mg/L hydrogen peroxide
Sample:	*n*-butane LPG with 2 mg/kg additives (Fluorine as fluorobenzene, bromine as bromobenzene, chlorine as chlorobenzene, sulfur as dimethylsulfide, iodine as iodobenzene)

Peaks:		mg/kg
	1. Total Fluorine (F)	0.105
	2. Total Chlorine (Cl)	0.100
	3. Carbonate	--
	4. Total Sulfur (S)	0.105

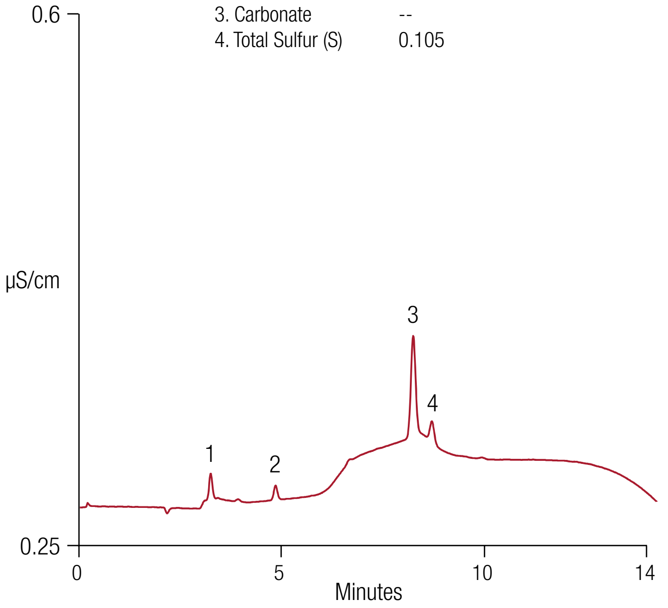


Figure 9. Using a small loop injection to determine MDL

Accuracy was determined by peak area reproducibility (n = 3), and recoveries (n = 3) by comparing the measured value versus the expected value. Figures 10 and 11 show that the LPG standards as samples have good peak shape and baseline resolution between all peaks of interest. Figure 12 shows the chromatography of the LPG standard using a modified gradient to increase resolution of sulfate (Peak 8) from a large carbonate peak and a peroxide-hydrazine absorption solution to obtain iodine results. Nitrate, acetate, and formate have a much higher response than shown in Figure 11, which is attributable to the hydrazine absorption solution. The iodine peak is small, with some asymmetry resulting in challenging quantification and low measured recovery.

Columns:	Dionex IonPac AG20, Dionex IonPac AS20, 2 mm i.d.
Gradient:	10–38 mM KOH (0–14 min), 10 mM (14.1–20 min)
Eluent Source:	Dionex EGC 500 KOH cartridge, Dionex CR-ATC 600 trap column, Dionex high pressure degasser
Flow Rate:	0.375 mL/min
Injection Vol.:	100 µL
Column Temp.:	35 °C
Detector Temp.:	20 °C
Detection:	Suppressed conductivity, Dionex ADRS 600, 2 mm, constant current and recycle modes, 36 mA
Sample Prep. Mode:	Combustion, Absorption, and Injections
Sample Mode:	Liquified gas sampling
LPG Sample:	30 µL, 85 °C, 60 mL/min Ar carrier
Temperatures:	800 °C inlet, 900 °C outlet
Gas:	140 mL/min Ar, 400 mL/min 0_2, 100 mL/min Ar + DI water
Absorption Sol.:	10 mL, 50 mg/L hydrogen peroxide
Sample:	*n*-butane LPG with 15 mg/kg additives, 1 year old (Fluorine as fluorobenzene, chlorine as chlorobenzene, sulfur as dimethylsulfide)

Peaks:		mg/kg
	1. Total Fluorine (F)	12.8
	2. Formate	--
	3. Total Chlorine (Cl)	12.7
	4. Carbonate	--
	5. Total Sulfur (S)	14.9
	6. Unknown	--

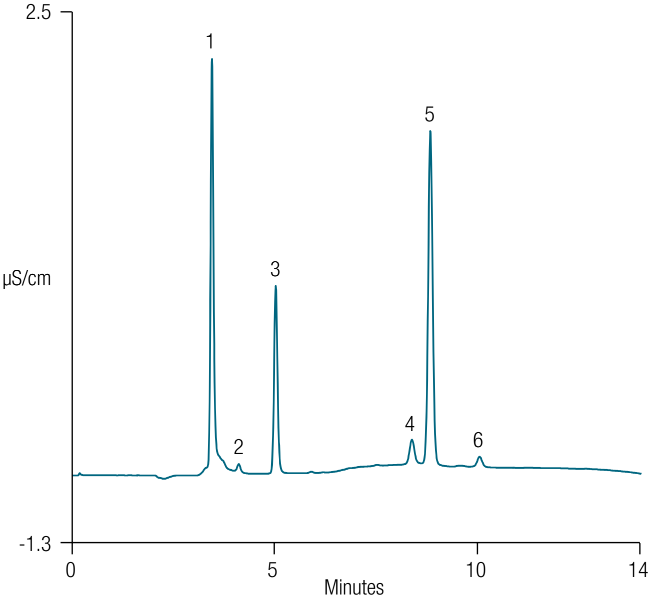


Figure 10. One combustion of one-year-old *n*-butane LPG Standard with ~15 mg/kg additives with results calculated using the 2–18 mg/kg calibration curve

Columns:	Dionex IonPac AG20, Dionex IonPac AS20, 2 mm i.d.
Gradient:	10–38 mM KOH (0–14 min), 10 mM (14.1–20 min)
Eluent Source:	Dionex EGC 500 KOH cartridge, Dionex CR-ATC 600 trap column, Dionex high pressure degasser
Flow Rate:	0.375 mL/min
Injection Vol.:	100 µL
Column Temp.:	35 °C
Detector Temp.:	20 °C
Detection:	Suppressed conductivity, Dionex ADRS 600, 2 mm, constant current and recycle modes, 36 mA
Sample Prep. Mode:	Combustion, Absorption, and Injections
Sample Mode:	Liquified gas sampling
LPG Sample:	30 µL, 85 °C, 60 mL/min Ar carrier
Temperatures:	800 °C inlet, 900 °C outlet
Gas:	140 mL/min Ar, 400 mL/min 0_2, 100 mL/min Ar + DI water
Absorption Sol.:	10 mL, 50 mg/L hydrogen peroxide
LPG tank Conc.:	*n*-butane LPG with 2 mg/kg additives (Fluorine as fluorobenzene, bromine as bromobenzene, chlorine as chlorobenzene, sulfur as dimethylsulfide, iodine as iodobenzene)

Peaks:		mg/kg
	1. Total Fluorine (F)	20.1
	2. Formate	--
	3. Total Chlorine (Cl)	17.3
	4. Total Bromine (Br)	19.7
	5. Carbonate	--
	6. Total Sulfur (S)	17.5
	7. Unknown	--
	8. Total Iodine (I)	--

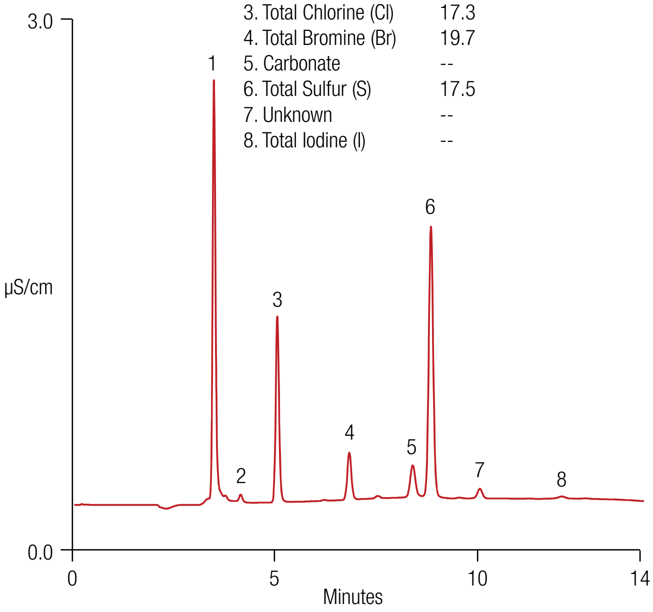
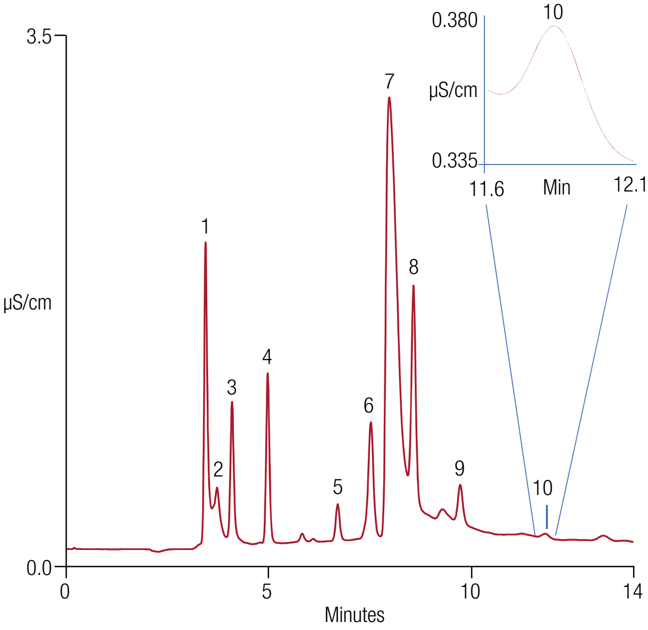


Figure 11. Nine incremental combustions of *n*-butane LPG standard with 2 mg/kg additives with results calculated using the 15–135 mg/kg calibration curve



Columns:	Dionex IonPac AG20, Dionex IonPac AS20, 2 mm i.d.
Gradient:	10–38 mM KOH (0–14 min), 10 mM (14.1–20 min)
Eluent Source:	Dionex EGC 500 KOH cartridge, Dionex CR-ATC 600 trap column, Dionex high pressure degasser
Flow Rate:	0.375 mL/min
Injection Vol.:	100 µL
Column Temp.:	35 °C
Detector Temp.:	20 °C
Detection:	Suppressed conductivity, Dionex ADRS 600, 2 mm, constant current and recycle modes, 36 mA
Sample Prep. Mode:	Combustion, Absorption, and Injections
Sample Mode:	Liquified gas sampling
LPG Sample:	30 µL, 85 °C, 60 mL/min Ar carrier
Temperatures:	800 °C inlet, 900 °C outlet
Gas:	140 mL/min Ar, 400 mL/min O_2, 100 mL/min Ar + DI water
Absorption Sol.:	10 mL, 50 mg/L hydrogen peroxide, 1000 mg/L hydrazine
LPG tank Conc.:	*n*-butane LPG with 2 mg/kg additives (Fluorine as fluorobenzene, bromine as bromobenzene, chlorine as chlorobenzene, sulfur as dimethylsulfide, iodine as iodobenzene)

Peaks:		mg/kg
1.	Total Fluorine (F)	20.1
2.	Acetate	--
3.	Formate	--
4.	Total Chlorine (Cl)	17.3
5.	Total Bromine (Br)	19.7
6.	Nitrate, system	--
7.	Carbonate, system	--
8.	Total Sulfur (S)	17.5
9.	Unknown	--
10.	Total Iodine (I)	14.7

Figure 12. Nine incremental combustions of *n*-butane LPG standard with 2 mg/kg additives with results calculated using the 15–135 mg/kg calibration curve and peroxide-hydrazine absorption solution

Table 4 summarizes the reproducibility results showing acceptable variation, RSD values of 0.7% to 2.0%. Table 5 shows good recovery results for fluorine, chlorine, bromine, and sulfur, from 85% to 107% of the expected value, indicating good accuracy. Iodine had 78.9% recovery of the expected value.

Table 4. Reproducibility results

n-butane LPG	Total Fluorine as Fluoride (mg/kg)	RSD	Total Chlorine as Chloride (mg/kg)	RSD	Total Bromine as Bromide (mg/kg)	RSD	Total Sulfur as Sulfate (mg/kg)	RSD	Total Iodine as Iodide (mg/kg)	RSD
Nine 30 µL combustions of 2 mg/kg additives	19.6	1.9	17.3	1.5	19.6	2.0	17.2	1.5	14.8	1.2
One-year-old tank, ~15 mg/kg additives	13.2	1.7	12.8	1.0	Not present	--	14.9	0.7		

*Nine 30 µL aliquots were combusted, and absorbed and injected as one sample

Table 5. Recovery results

n-butane LPG	Total Fluorine as Fluoride		Total Chlorine as Chloride		Total Bromine as Bromide		Total Sulfur as Sulfate		Total Iodine as Iodide	
	Predicted Conc. (mg/kg)	Recovery (%)	Predicted Conc. (mg/kg)	Recovery (%)	Predicted Conc. (mg/kg)	Recovery (%)	Predicted Conc. (mg/kg)	Recovery (%)	Predicted Conc. (mg/Kg)	Recovery (%)
Nine 30 µL combustions of 2 mg/kg additives	18.0	106	18.9	91.5	18.0	109	18.0	95.4	18.9	78.9
One-year-old tank, ~15 mg/kg additives	15.1	88.0	15	85.3	--	--	15	99.3	--	--

*Nine 30 µL aliquots were combusted, and absorbed and injected as one sample

Conclusion

Combustion IC using the AQF-2100H system with Gas Injection GI-260 module combined with IC provides an automated and fast method to determine total halides and total sulfur in complex and challenging samples, such as LPG, by eliminating the sample matrix and converting the organohalide compounds to halides and sulfate. The Gas Injector GI-260 module allows easy management of LPG with built-in safety venting features. The GI-260 module is also used to combust incremental aliquots of one LPG standard to generate calibration curves, which is more convenient and economical than using multiple LPG standards while achieving acceptable reproducibility and accuracy.

The method was applied to two LPG standards as samples and was found to be accurate for total sulfur and total fluorine, bromine, and chlorine with 85% to 107% recovery, and reproducible with RSDs <2. To determine iodine, the absorption solution was modified with 1000 mg/L hydrazine, which showed linear calibration plots, however the recovery was just below 80%.

More information on CIC and CIC applications can be found on Thermo Scientific website and on the Thermo Fisher Scientific AppsLab Digital Library.[33]

References

1. International Energy Agency. Key word statistics, IEA Publications, November 2018. [online] https://www.eia.gov/todayinenergy/detail.php?id=36292 (accessed May 2019.)
2. Sulfide-producing bacteria dominate hydraulically fractured oil and gas wells, Phys. org, July 5, 2017. https://phys.org/news/2017-07-sulfide-producing-bacteria-dominate-hydraulically-fractured.html (accessed May 2019.)
3. Rooney, P.C.; Bacon, T.R.; DuPart, M.S. Effect of Heat Stable Salts on MDEA Corrosivity, Parts 1 and 2. *Hydrocarbon Processing*, **1996,** Mar, 95–103; **1997,** Apr, 65–71
4. Thermo Fisher Scientific. Dionex Application Note 138: Determination of Thiosulfate in Refinery and Other Wastewaters. Sunnyvale, CA, USA. 2001. [Online] https://appslab.thermofisher.com/App/1415/an-138-determination-thiosulfate-refineryotherwastewaters. (accessed May 2019.).
5. Thermo Fisher Scientific. Dionex Technical Note 122: Separation of Heat Stable Amine Salts in Methyldiethanolamine (MDEA) Solutions. Sunnyvale, CA, USA. 2013. [Online] https://appslab.thermofisher.com/App/1664/tn122-separation-heatstableamine-salts-methyldiethanolamine-mdea-solutionsusing-highpressure-ic. (accessed May 2019.)
6. Thermo Scientific Application Note AN72622: Fast Separation of Heat Stable Salts, 2018, Sunnyvale, CA, USA. [Online] https://assets.thermofisher.com/TFS-Assets/CMD/Application-Notes/an-72622-ic-fast-separation-heat-stable-salts-an72622-en.pdf (accessed May 2019)
7. Thermo Scientific Application Update AU126 Determination of Diethanolamine and Triethanolamine in Surface Finishing, Wastewater and Scrubber Solutions, 2014, Sunnyvale, CA, USA. [Online] https://assets.thermofisher.com/TFS-Assets/CMD/Application-Notes/AU-126-IC-Diethanolamine-Triethanolamine-Wastewater-AU71356-EN.pdf (accessed May 2019.)
8. Thermo Scientific Application Update AU138: Determination of Ethanolamines in Industrial Waters by Cation-Exchange Chromatography, 1998, Sunnyvale, CA, USA. [Online] https://tools.thermofisher.com/content/sfs/brochures/4241-AU138_LPN0995-01.pdf (accessed May 2019.)
9. Thermo Scientific Application Note AN72609 Using ion chromatography with electrospray ionization mass spectrometry for the determination of cations and amines in alkanolamine scrubbing solutions, 2018, Sunnyvale, CA, USA. https://assets.thermofisher.com/TFS-Assets/CMD/Application-Notes/an-72609-ic-ms-alkanolamine-scrubbing-solutions-an72609-en.pdf (accessed May 2019.)
10. Thermo Scientific Application Note AN73030 Alkanolamine determinations in neutralizing amines samples with improved separation technology, 2019, Sunnyvale, CA, USA. [Online] https://assets.thermofisher.com/TFS-Assets/CMD/Application-Notes/an-73030-ic-alkanolamine-neutralizing-amines-an73030-en.pdf (accessed June 2019)
11. R. Nadkarni, ed., MNL44-2ND-EB Guide to ASTM Test Methods for the Analysis of Petroleum Products and Lubricants, 2nd ed. West Conshohocken, PA: ASTM International, 2007. doi: https://doi.org/10.1520/MNL44-2ND-EB
12. Thermo Scientific Application Note AN72333: Determination of Adsorbable Organic Halogen in Wastewater using a Combustion Ion Chromatography System, 2017. Sunnyvale, CA, USA. [Online] https://appslab.thermofisher.com/App/3857/determining-aox-by-combustion-ion-chromatography (Accessed June 2019)
13. Thermo Scientific Application Note AN72693: Determination of Total Fluorine, Chlorine, and Sulfur in Aromatic Hydrocarbons by Oxidative Pyrolytic Combustion Followed by Ion Chromatography, 2018. Sunnyvale, CA, USA. [Online] https://appslab.thermofisher.com/App/4125/halogens-sulfur-gasoline-by-cic (Accessed June 2019.)
14. Thermo Scientific Digital AppsLab Library record: Determination of Chloride in Algal Oil Using Combustion Ion Chromatography, 2015. Sunnyvale, CA, USA. [Online] https://appslab.thermofisher.com/App/2237/determination-chloride-algal-oil-using-combustion-ion-chromatography. (Accessed June 2019.)
15. Thermo Scientific Digital AppsLab Library record: Determination of Halogens and Sulfur in Refuse Derived Fuel by Combustion Ion Chromatography, 2015. Sunnyvale, CA, USA. [Online] https://appslab.thermofisher.com/App/2234/determination-halogens-sulfur-refuse-derived-fuel-by-combustion-ion-chromatography (Accessed June 2019.)
16. Thermo Scientific Digital AppsLab Library record: Determination of Chloride and Sulfate in Crude Oil by Combustion Ion Chromatography, 2017. Sunnyvale, CA, USA. [Online] https://appslab.thermofisher.com/App/3708/determination-chloride-sulfate-crude-oil-by-combustion-ion-chromatography (Accessed June 2019.)
17. Thermo Scientific Digital AppsLab Library record: Determination of Halogens and Sulfate in Liquid Petroleum Gas Using Combustion Ion Chromatography, 2016. Sunnyvale, CA, USA. [Online] https://appslab.thermofisher.com/App/3609/halogens-sulfate-lpg (Accessed June 2019.)
18. Thermo Scientific Application Note AN1145: Determination of Halogens in Coal Using Combustion Ion Chromatography. [Online] https://appslab.thermofisher.com/App/2252/an1145-determination-halogens-coal-using-combustion-ion-chromatography (Accessed June 2019.)
19. Thermo Scientific Digital AppsLab Library record: Determination of Chlorine and Sulfur in Wood Chips Using Combustion Ion Chromatography. [Online] https://appslab.thermofisher.com/App/2235/determination-chlorine-sulfur-wood-chips-using-combustion-ion-chromatography (Accessed June 2019.)
20. ASTM International, ASTM D7994 - Standard Test Method for Total Fluorine, Chlorine, and Sulfur in Liquid Petroleum Gas (LPG) by Oxidative Pyrohydrolytic Combustion Followed by Ion Chromatography Detection (Combustion Ion Chromatography-CIC)
21. Cosa Xentaur distributors. https://cosaxentaur.com/distributors

22. ASTM International, ASTM D1193 - 99e1 Standard Specification for Reagent Water. [Online] https://www.astm.org/DATABASE.CART/HISTORICAL/D1193-99E1.htm
23. Red Ball Technical Gas Services. https://www.redballoxygen.com/isgas
24. Thermo Scientific Technical Note TN72211 Combustion ion chromatography with a Dionex Integrion HPIC System, 2016. Sunnyvale, CA, USA. [Online] https://assets.thermofisher.com/TFS-Assets/CMD/Technical-Notes/tn-72211-integrion-hpic-combustion-ic-tn72211-en.pdf. (Accessed June 2019.)
25. Thermo Scientific Application Note AN72268: Figure 1 Diagram of a combustion ion chromatography (CIC) setup from Determination of Fluoride in Tea using a Combustion Ion Chromatography System, 2017. Sunnyvale, CA, USA. [Online] https://appslab.thermofisher.com/App/3789/fluoride-tea (Accessed June 2019.)
26. Mitsubishi Chemical Analytech. Operation Manual For NSX-2100 Series Automatic Combustion Unit Model AQF-2100H, "Instruction Manual of Absorption Unit GA-210" section.
27. Thermo Scientific Technical Note TN175 Configuring the Dionex Integrion HPIC System for High-Pressure Reagent-Free Ion Chromatography, 2016, Sunnyvale, CA, USA. https://assets.thermofisher.com/TFS-Assets/CMD/Technical-Notes/tn-175-hpic-high-pressure-rfic-tn71961-en.pdf (Accessed June 2019.)
28. Thermo Scientific Product Manual: Dionex Eluent Generator Cartridges, 2018, Sunnyvale, CA, USA. [online] https://assets.thermofisher.com/TFS-Assets/CMD/manuals/Man-065018-Eluent-Generator-Cartridge-MAN065018-EN.pdf (Accessed June 2019.)
29. Thermo Scientific Product Manual: Continuously Regenerated Trap columns (CR-TC 500, CR-TC 600, CR-TC Capillary), 2019, Sunnyvale, CA, USA. [online] https://assets.thermofisher.com/TFS-Assets/CMD/manuals/Man-079684-Continuously-Regenerated-Trap-CR-TC-Man079684-EN.pdf (Accessed June 2019.)
30. Thermo Scientific Product Manual: Dionex IonPac AS20 Column, 2012, Sunnyvale, CA, USA. [online] https://assets.thermofisher.com/TFS-Assets/CMD/manuals/man-065044-ionpac-as20-columns-man065044-en.pdf (Accessed June 2019.)
31. Thermo Scientific Product Manual: Dionex DRS 600 Suppressor, Dionex ERS 500e Suppressor, Dionex ERS 500 Carbonate Suppressor, 2018, Sunnyvale, CA, USA. [online] https://assets.thermofisher.com/TFS-Assets/CMD/manuals/man-031956-dionex-suppressors-man031956-en.pdf (Accessed June 2019.)
32. Thermo Scientific. Combustion IC System [Online] https://www.thermofisher.com/us/en/home/industrial/chromatography/ion-chromatography-ic/ion-chromatography-systems/combustion-ic-system.html (Accessed June 2019.)
33. Thermo Scientific Digital AppsLab Library. https://appslab.thermofisher.com (Accessed June 2019.)

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