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

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Goal

Demonstrate fast determinations of total halides and total sulfur in *n*-butane liquefied petroleum gas using pyrohydrolytic combustion with sample preconcentration prior to ion chromatography analysis.

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. It is used primarily as a fuel to generate electricity, and as feed stock for plastic materials. For more convenient storage and transportation, natural gas is often pressurized to a liquid state, known as liquefied petroleum gas (LPG).[2] Determinations of halide- and sulfur-containing compounds in LPG is needed because these contaminants can foul the catalysts during processing and as the final product. Analysis of LPG can be challenging for ion chromatography (IC) because of its non-polar characteristics and because it rapidly expands from its liquid form to gaseous form. As with other challenging matrices, pyrohydrolytic 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 fuel matrices, including crude oil, aromatic hydrocarbons, and liquefied petroleum gas samples (LPG).[3-9] Determination of halogens and sulfur by CIC is described in ASTM method D 7994[10] and recently in Thermo Scientific™ Application Note AN73105 Determination of total fluorine, chlorine, bromine, and sulfur in liquefied petroleum gas by pyrohydrolytic combustion ion chromatography[11]. These combustion IC applications directly injected an aliquot of the absorption solution containing the combusted, absorbed sample. Preconcentration methods for pyrohydrolytic combustion IC require additional instrumental connections. These connections have been made using relay functions for analysis of solid samples[12], and generically using TTL connections in Thermo Scientific Technical Note TN72211 Combustion ion chromatography with a Thermo Scientific™ Dionex™ Integrion™ HPIC™ System.[13]

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This Application Update updates Application Note AN73105[11] by using preconcentration via TTL connections to increase sensitivity to µg/kg concentrations. Preconcentration provides improved response and quantitation needed for LPG samples with lower halogen and sulfur contamination levels than previously demonstrated and increases quantitation accuracy for lower concentration ions such as bromide and iodide. The method had good accuracy with sample recoveries within 85–116% and good reproducibility with <3% RSDs.

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
- Dionex Integrion HPIC system, RFIC model, including:
  - Dionex Integrion HPIC System Pump
  - Detector Compartment Temperature Control
  - Eluent generation
  - Thermo Scientific™ Dionex™ Integrion IC Conductivity Detector (P/N 079829)
  - Thermo Scientific™ Dionex™ AXP auxiliary pump (P/N 063973)

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

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

Table 1. Consumables List for the Dionex Integrion HPIC System.*

Product name	Description	P/N
Thermo Scientific™ Dionex™ IC PEEK Viper™ fitting tubing assembly kit	Dionex IC Viper fitting assembly kit for the Dionex Integrion HPIC system with CD	088798
Thermo Scientific™ Dionex™ EGC 500 KOH Eluent Generator cartridge	Anion eluent generator cartridge for HPIC high pressure systems	075778
Thermo Scientific™ Dionex™ CR-ATC 600 Electrolytic trap column	Continuously regenerated anion trap column used with the Dionex Integrion system	088662
Thermo Scientific™ Dionex™ HP EG Degasser Module	Degasser installed after Dionex CR-TC 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
Thermo Scientific™ Dionex™ IonPac™ UTAC-ULP2 concentrator column	Anion preconcentration column, 5 × 23 mm	079918
Thermo Scientific™ Dionex™ IonPac™ ATC-HC 500 trap column	Anion trap column, 9 × 75 mm, attached to the outlet of the AXP auxiliary pump. Used to purify DI water rinse solution.	075978
4L eluent bottle	One 4 L eluent bottle is 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. In North America, the distributor is COSA Xentaur. COSA Xentaur reorder P/N.[14]

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 + 9s) Multiple combustions: 100 s × # combustions + 5 s + 9 s
Calculated final volume	9.75 mL
Absorption solution	50 mg/L hydrogen peroxide, 1000 mg/L hydrazine in ASTM Type I deionized water**
Gas parameters	
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
GA-211 Module	Sample Injection+
Sample purge time	5 s
Sample absorption time	50 s

** The detailed conditions are the same as those in AN73105 with the exceptions of sample purge and sample absorption times.

Ion chromatography conditions	
Columns	Dionex IonPac AG20 guard (2 × 50 mm) and IonPac AS20 separation (2 × 250 mm)
KOH eluent	KOH
Eluent source	Dionex EGC 500 KOH eluent cartridge, Dionex CR-ATC 600 trap column and high pressure degas module
KOH gradient	10 mM KOH (0–0.1 min), 10–24.9 mM (0.1–7 min), 24.9–26 mM (7–9 min), 26–40 mM (9–14 min), 10 mM (14.1–20 min)
Flow rate	0.375 mL/min
Concentration volume	200 µL from GA-210 Gas Absorption Unit
Concentrator	Dionex UTAC-LP2, 5 × 23 mm. Timing is described in the Setup section
Concentrator wash	1 min at 1.0 mL/min by AXP Auxiliary pump, dispensed through Dionex IonPac ATC-HC 500 trap column
Column temperature	35 °C
Detection/suppressor compartment	20 °C
Detection	Suppressed conductivity, Dionex DRS 600 suppressor, 2 mm, 38 mA, constant current and recycle modes
Background	<1 µS/cm
Noise	<1 nS/cm
System backpressure	~2800 psi
Run time	IC: 21 min; total run time: 23 min

Reagents

ASTM Type 1 deionized water (DI water) with 18 MΩ-cm resistivity[15]

- Thermo Scientific™ Dionex™ Stock Standards for external calibration
  - Dionex 1000 mg/L Chloride Standard
  - Dionex 1000 mg/L Fluoride Standard
  - Dionex 1000 mg/L Sulfate Standard
- 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.

Vendor: Red Ball Technical Gas Services, a division of Red Ball Oxygen[16]

- *n*-butane LPG tanks (density: 0.5788 mg/kg) are pressurized to 200 psi with helium and has dip tube valve. The tank valve outlets are CGA 510 P SS (note: reverse thread).

Tanks 1–4 described in Table 2 and Application Note AN73105 were used in this application update:

Table 2. *n*-butane LPG tanks used as standards and samples.

n-butane LPG	Manufacture date	Additives
1	2019	none
2	2019	2.1 mg/kg of total fluorine (F) as fluorobenzene, 2.0 mg/kg total chlorine (Cl) as chlorobenzene, 2.0 mg/kg total bromine (Br) as bromobenzene, 2.1 mg/kg total iodine as iodobenzene and 2.0 mg/kg total sulfur (S) as dimethylsulfide
3	2019	15.1 mg/kg of total fluorine (F) as fluorobenzene, 16.4 mg/kg total chlorine (Cl) as chlorobenzene, 15.4 mg/kg total bromine (Br) as bromobenzene, 16.5 mg/kg total iodine as iodobenzene, and 15.1 mg/kg total sulfur (S) as dimethylsulfide
4	2018	15.0 mg/kg of total fluorine (F) as fluorobenzene, 15.1 mg/kg total chlorine (Cl) as chlorobenzene, 15.0 mg/kg total sulfur (S) as dimethylsulfide

Preparation of absorption solutions, standards, and samples

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

This absorption solution was needed for iodide determinations, and therefore used for this application. To prepare the 1 L of the absorption solution, 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.

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 to the HF-210 furnace.

- Sample introduction
  - The same as described in AN73105
- Pyrohydrolysis and combustion
  - The same as described in AN73105
- Sample absorption
  - The argon gas carries and aerates the sample into a 50 mg/L peroxide 1000 mg/L hydrazine absorption solution (recommended for total iodine)
  - The aeration continues which provides mixing while the sample is diluted to 10 mL total volume
- Sample analysis
  - The GA-211 unit loads a 200-µL aliquot of the sample to a 200-µL sample loop
  - The GA-211 unit triggers the IC sample loading via the 6-port GA-211 high pressure injection valve, TTL_Input_3 cable, and programming instructions created in Chromeleon configuration
  - The Integrion injection valve is rotated to the load position, the AXP auxiliary pump turns on and transfers the sample solution from the sample loop to the concentrator column and rinses the matrix from the concentrator column. The anions are retained on the concentrator column and the DI water and matrix are flushed to waste.

- The Chromeleon program triggers the Integrion valve to rotate to the injection position thus starting the chromatography of the concentrated anions

Physical configuration

To install the CIC system, follow the installation instructions as described in Thermo Scientific Technical Note TN72211 Combustion ion chromatography with a Dionex Integrion HPIC System[13] 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.

Installing AXP pump drivers and identifying the COM port for the AXP pumps:

1. Connect the power cord of the AXP. Connect a micro-USB cable from the AXP pump to the computer. The micro-USB drivers will automatically download.
2. Connect a USB serial cable or USB serial adapter to the computer and turn on the AXP pump
3. Device Manager: Open Device Manager to identify the USB serial ports being used by the AXP pump

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. Assign control of the Integrion injection valve to Integrion. Close and save configuration. This application is configured as described under the "Preconcentration" section in TN72211. Additional information on the combustion system can be found in the product manual.[18]

Adding the AXP pump to the configuration:

1. Open configuration. To add the AXP pump: Add a module, IC: Dionex Modules, AXP Pump, and click the OK button.
2. Select the correct COM channel (as described in Installing AXP drivers and Identifying the COM channel) and click the OK button
3. After clicking OK, the connection will try to initiate the AXP driver and messages will appear in the Instrument Controller panel
4. Wait approximately 30 s. If the initiation is correct, no messages will appear after Initiating Driver AXP Pump.
5. If the initiation is incorrect, an error message will occur. Return to steps described in Installing AXP drivers and identifying COM port.
6. Select the other COM channel. Click OK. Wait about 30 s to ensure that no error messages occur.
7. Close and save configuration

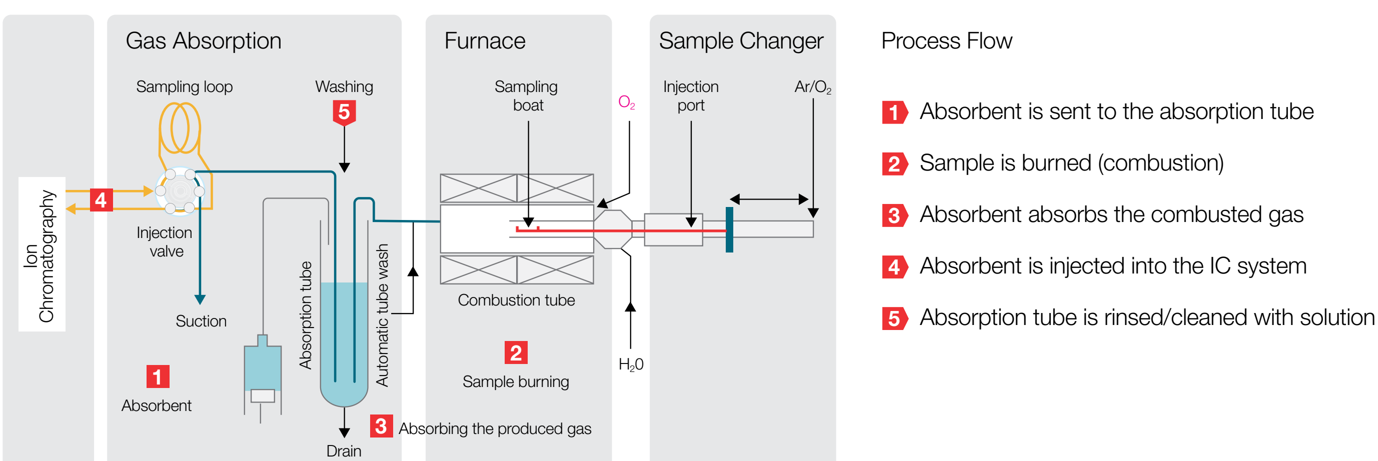


Figure 1. Diagram of combustion IC system.[17,18]

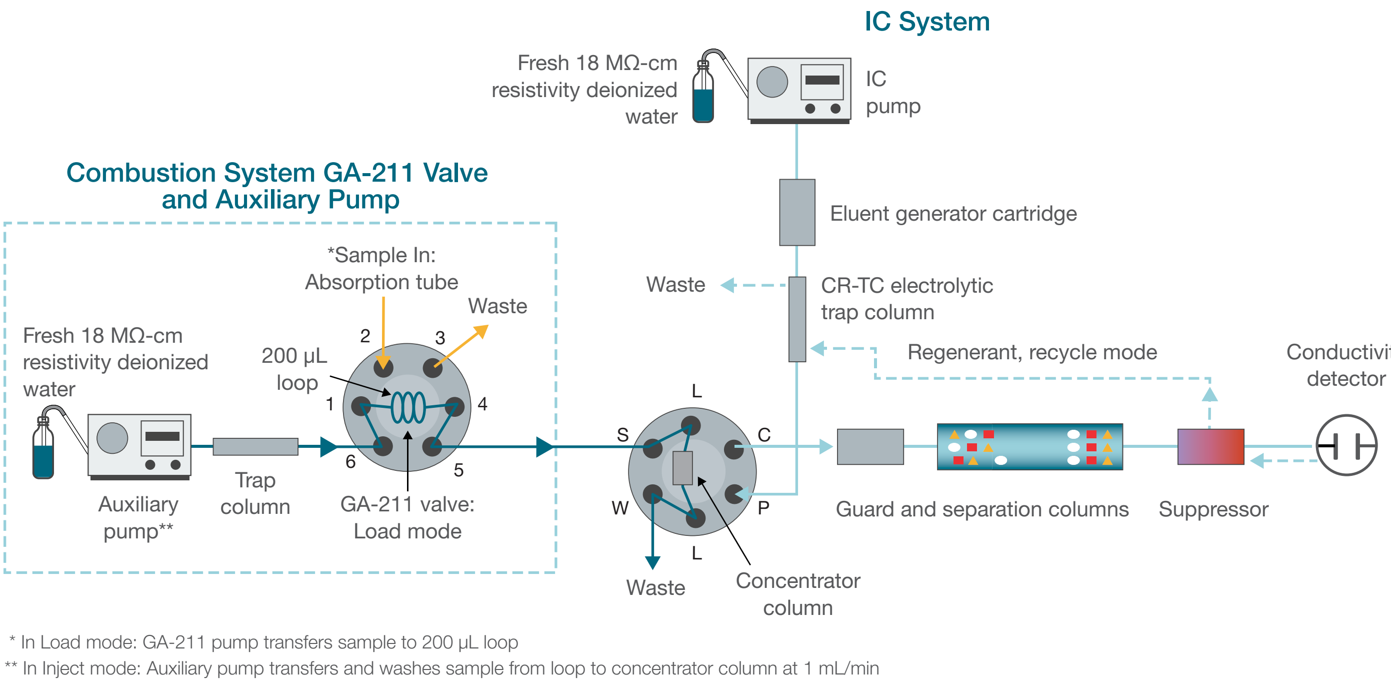


Figure 2. Flow diagram for Integrion HPIC system using preconcentration.[19]

Plumbing the Integrion IC

Plumb the Dionex Integrion IC as a standard Thermo Scientific™ Dionex™ Reagent-Free™ IC (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. Install the concentrator column. The flow path arrow on the concentrator column should point in the same direction as the flow path of the eluent pump. To achieve the best chromatography, use a shorter length of tubing in Port L next to Port S (load direction) than in Port L next to Port P. The sample will load on to the concentrator column in the opposite flow direction of the eluent.

Conditioning electrolytic devices and columns

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

Follow the conditioning and hydrating instructions described in AN73105.

Equilibrating the 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, and a new processing method. Approve the consumables in the Consumables Tracking panel located on the Chromeleon console (Thermo Scientific Technical Note TN175 Configuring the Dionex Integrion HPIC for High-Pressure Reagent-Free Ion Chromatography[20]). Start the Chromeleon sequence. Compare the results against QAP. Do not proceed if the results are not equivalent of the QAR.

Combustion system

Install the LPG transfer lines and pyrolysis tubes as described in AN73105. Start 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: HF-210 furnace module (140 mL/min Ar, 400 mL/min O2); GI-260 Gas Injection module (60 mL/min argon carrier); humidification (100 mL/min Ar). To heat the furnace, select the second flame icon. The heat up time to the set temperatures will be ~1 h. Create an AQF-2100 schedule as described in the Conditions section and in AN73105.

Creating a Chromeleon software 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 and Table 3. Save the sequence.

Table 3. Chromeleon script editor commands for preconcentration mode.

Time			
–1.1	Equilibration stage		
	Command	Value	Results
	InjectValve_CIC2.Inject	–	GA-211 valve to inject.
	Pump_ECD.InjectValve.LoadPosition	–	Integrion valve to load.
–1.0	Pump.State	On	AXP pump turns on.
	Pump.flow	1.0	AXP pump transfers sample from GA-211 injection loop to concentrator and washes concentrator column.
0.0	Inject stage		
	Command	Value	Results
	InjectValve_CIC2.Inject	–	Integrion valve to inject. Sample injects.
	Pump.State	Off	AXP pump turns off.

Starting the Chromeleon software sequence and AQF-2100 schedule

Start the Chromeleon software sequence before the AQF-2100 schedule. To start the Chromeleon software sequence, approve the consumables in the Consumables Tracking panel located on the Chromeleon console (See TN175)[19]. Add the Chromeleon sequence into the Instrument queue, select Check sequence, correct any errors, and select Start.

Select the AQF-2100 schedule, 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 Dionex Integrion to start the Chromeleon software sequence. The data will be stored in Chromeleon software.

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 4×. Complete the cool-down of Horizontal Furnace HF-211 module to room temperature, and then turn-off gas flows.

Results and discussion

This Application Update updates Application Note AN73105 by using preconcentration to increase sensitivity of total bromine and total iodine µg/kg.[13] A 30-µL aliquot of the LPG sample is treated with pyrohydrolytic combustion using the conditions described in AN73105 and absorbed in 10 mL of 50 mg/L hydrogen peroxide, 1000 mg/L hydrazine solution. The combustion system GA-211 module delivers a 200-µL aliquot of the absorbed, combusted sample to the sample loop which is transferred by an AXP pump delivering DI water at 1 mL/min to the Dionex IonPac UTAC-LP2 concentrator column on the Dionex Integrion injection valve in the load position. The anions are collected and concentrated on the Dionex IonPac UTAC-LP2 column as the liquid flows to waste. The resultant concentrated anion sample is eluted from the concentrator column to the Dionex IonPac AS20 column set and separated using an electrolytically generated multi-step KOH gradient from 10 to 40 mM KOH at 35 °C at 0.30 mL/min. 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 a total run time of 22 min in overlap mode.

Method development

Most of the method development, including the anion-exchange conditions, was previously completed in AN73105. In addition, preconcentration with pyrolytic combustion IC was demonstrated in TN72211[13], and in Agustin, et al.[12] poster and therefore minimal optimization was needed. However, the following timings were adjusted to achieve the highest responses:

1. Sample loading by the GA-211

2. Sample transfer and sample concentration by AXP pump. In the previous application, Agustin et al. demonstrated preconcentration of 1 mL of combusted, absorbed sample in hydrogen peroxide. However, in these experiments, the peroxide-hydrazine absorption solution, needed for total iodine (I) determinations, generated additional ionic compounds which impacted the capacity of the concentrator column. Preconcentration of 200 µL of sample was found to be an acceptable compromise to achieve increased peak responses without overloading the concentrator column capacity.

Figure 3 compares the responses of direct injection and concentration of the same sample, a year-old tank of *n*-butane with 15 mg/kg of total fluorine (F), total chlorine (Cl), and total sulfur (S), collected in the peroxide-hydrazine absorption solution. Peaks 1, 4, and 8 show expected higher responses in preconcentration mode (200 µL) as compared to 50% of the sample injected directly (100 µL), demonstrating that the preconcentration was working as expected. The reproducibilities of n=3 standards had similar results as in AN73105, ~3% RSDs.

LPG blanks

Characterizing the blank is important to assess the background contamination and as part of a sensitivity determination. Figure 4 shows a chromatogram of pyrohydrolytic combustions of *n*-butane without additives and with 2 mg/kg additives. Figure 5 shows the same LPG blank (i.e., the standard without additives).

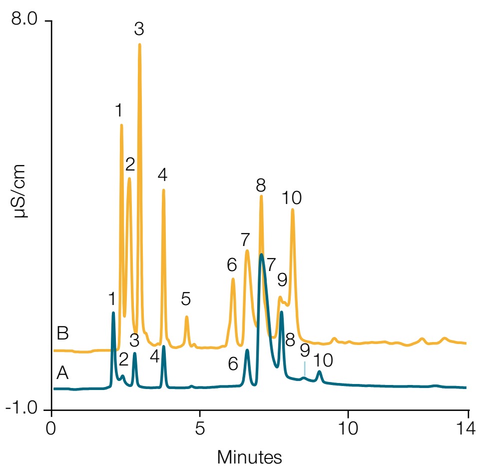


Figure 3. Comparison of direct injection (100 µL) and concentration (200 µL) of one-year old *n*-butane LPG with 15 mg/kg additives.

Columns:	Dionex IonPac AG20, Dionex IonPac AS20, 2 mm i.d.
Gradient:	10 mM KOH (0–0.1 min), 10–24.9 mM (0.1–7 min), 24.9–26 mM (7–9 min), 26–40 mM (9–14 min), 10 mM (14.1–20 min)
Eluent source:	Dionex EGC 500 KOH cartridge, Dionex CR-ATC 600 trap column, Dionex high pressure degasser device
Flow rate:	0.375 mL/min
Column temp.:	Column: 35 °C, Detector: 20 °C
Detection:	Suppressed conductivity, Dionex ADRS 600, 2 mm, constant current and recycle modes, 38 mA
Concentration:	A: None, 100 µL loop injection B: 200 µL, Dionex IonPac UTAC-ULP2 concentrator column, 5 × 23 mm
Sample prep. mode:	Combustion, Absorption, and Injections
Sample mode:	Liquefied 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 hydrazine
Sample:	*n*-butane LPG with 15 mg/kg additives (Fluorine (F) as fluorobenzene, chlorine (Cl) as chlorobenzene, sulfur (S) as dimethylsulfide)
Peak alignment:	Aligned at the chloride peak

Peaks:	**mg/kg**
1. Total Fluorine (F)	12.8
2. Acetate	–
3. Formate	–
4. Total Chlorine (Cl)	12.7
5. Nitrite	–
6. Nitrate	–
7. Carbonate	–
8. Total Sulfur (S)	14.9
9-10. System peaks	–

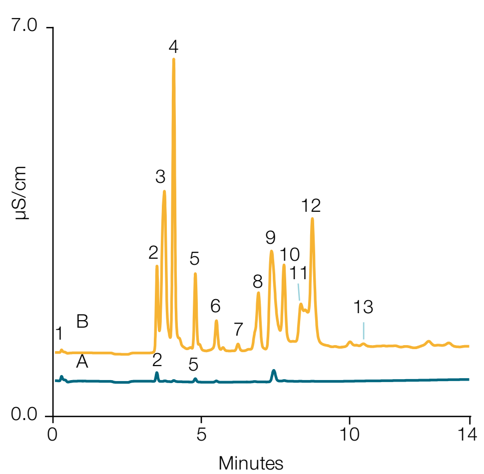
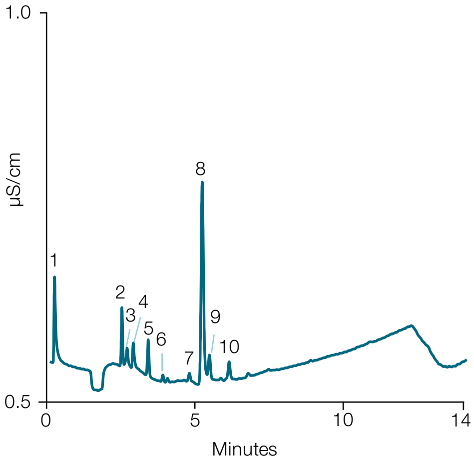


Figure 4. Preconcentration of 200 µL of combusted and absorbed *n*-butane LPG A) without additives and B) with 2 mg/kg additives.

Columns:	Dionex IonPac AG20, Dionex IonPac AS20, 2 mm i.d.
Gradient:	10 mM KOH (0–0.1 min), 10–24.9 mM (0.1–7 min), 24.9–26 mM (7–9 min), 26–40 mM (9–14 min), 10 mM (14.1–20 min)
Eluent source:	Dionex EGC 500 KOH cartridge, Dionex CR-ATC 600 trap column, Dionex high pressure degasser device
Flow rate:	0.375 mL/min
Column temp.:	Column: 35 °C, Detector: 20 °C
Detection:	Suppressed conductivity, Dionex ADRS 600, 2 mm, constant current and recycle modes, 38 mA
Concentration:	200 µL, Dionex IonPac UTAC-ULP2 concentrator column, 5 × 23 mm
Sample prep. mode:	Combustion, Absorption, and Injections
Sample mode:	Liquefied 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
Sample:	*n*-butane LPG. A: without additives, B: with 2 mg/kg additives (Fluorine (F) as fluorobenzene, bromine (Br) as bromobenzene, chlorine (Cl) as chlorobenzene, sulfur (S) as dimethylsulfide, iodine (I) as iodobenzene)
Offset:	5% offset

Peaks:	**A mg/kg**	**B mg/kg**
1. System peak	–	–
2. Total Fluorine (F)	0.12	2.10
3. Acetate	–	–
4. Formate	–	–
5. Total Chlorine (Cl)	0.28	2.10
6. Nitrite	–	–
7. Total Bromide (Br)	–	2.00
8. Nitrate	–	–
9. Carbonate	–	–
10. Total Sulfur (S)	0.05	2.10
11. System peaks	–	–
12. System peaks	–	–
13. Total Iodine (I)	–	1.80



Columns:	Dionex IonPac AG20, Dionex IonPac AS20, 2 mm i.d.
Gradient:	10 mM KOH (0–0.1 min), 10–24.9 mM (0.1–7 min), 24.9–26 mM (7–9 min), 26–40 mM (9–14 min), 10 mM (14.1–20 min)
Eluent source:	Dionex EGC 500 KOH cartridge, Dionex CR-ATC 600 trap column, Dionex high pressure degasser device
Flow rate:	0.375 mL/min
Temperatures:	Column: 35 °C, Detector: 20 °C
Detection:	Suppressed conductivity, Dionex ADRS 600, 2 mm, constant current and recycle modes, 38 mA
Concentration:	200 µL, Dionex IonPac UTAC-ULP2 concentrator column, 5 × 23 mm
Sample prep. mode:	Combustion, Absorption, and Injections
Sample mode:	Liquefied 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
Sample:	*n*-butane LPG without additives

Peaks:	**mg/kg**
1. System peak	–
2. Total Fluorine (F)	0.12
3. Acetate	–
4. Formate	–
5. Total Chlorine (Cl)	0.28
6. Nitrite	–
7. Nitrate	–
8. Carbonate	–
9. Total Sulfur (S)	0.05
10. Unknown	–

Figure 5. Expanded scale of Figure 4A, preconcentration of combusted, absorbed *n*-butane LPG without additives.

Method qualification

To qualify the method, the calibration ranges, and method detection limits (MDLs), were determined. A calibration curve from 2 to 16 mg/kg was developed by combusting one, two, four, and eight 30-µL aliquots of the 2 mg/kg additive LPG standard to generate a 2.0, 4.0, 8.0, and, 16.0 mg/kg additives in LPG. The results, summarized in Table 4, demonstrate the effectiveness of generating calibration curves by combusting multiple amounts of one standard.

Table 4 shows that the fluoride calibration results were best fit with a quadratic equation, whereas chloride, bromide, iodide, and sulfate had more linear responses. The coefficients of determination (r^2) >0.999.

MDLs were calculated using 3 × S/N (n=3) and determined using 1/10th the concentration volume used in 2 mg/kg calibration plot and blanks, (20 µL full loop versus 200 µL). The small volume preconcentration was used to imitate low concentration standards. The results in Table 4 show estimated MDLs from µg/kg for total fluorine (F), total bromine (Br), total chlorine (Cl), and total sulfur (S) to mg/kg for total iodine (I). The LODs using preconcentration versus direct injection (AN73105) resulted in increased and quantifiable responses for total chlorine, total bromine, and total iodine. However, the sensitivities were not enhanced for preconcentration as direct injection of total fluorine (F), and total sulfur (S), suggesting that the baseline contamination (measured in the blank LPG sample) is the limiting factor. That is, the trace contaminants in the blank LPG tank or contamination from handling the tank may limit lower detection limits for these ions.

Table 4: Summary of calibration and MDL results.

	Calibration range (mg/kg)	Calibration fit (with offset)	Coefficient of determination (r^2)	LOD† above LPG blank (ug/kg)	Without LPG blank (ug/kg)
Total Fluorine (F)	2–16	Quadratic	0.9991	200	81
Total Chlorine (Cl)	2–16	Linear	0.9994	290	8
Total Bromine (Br)	2–16	Linear	0.9989	300	300
Total Sulfur (S)	2–16	Linear	0.9996	125	75
Total Iodine (I)	2–16	Linear	0.9996	1070	1070

† Concentration of 1/10 volume as the standard.

Sample analysis

The application method was applied to standards as samples: a new *n*-butane tank with 2 mg/kg and ~15 mg/kg of total fluorine (F), chlorine (Cl), bromine (Br), sulfur (S), and iodine (I) additives, and a one-year old *n*-butane LPG tank with the similar concentrations of total fluorine (F), chlorine (Cl), and sulfur (S) additives. Smaller volumes of the combusted absorbed solution were pre-concentrated as shown in Table 5. Recoveries were estimated by comparing the measured results against the expected results as defined as the fraction of volume preconcentrated versus the calibration standard multiplied by the manufacturer's reported concentrations. Table 6 shows acceptable estimated recoveries of 88–116%, indicating that the method is accurate. The lowest recoveries, 88–93%, were with the one-year 15 mg/kg standard as a sample.

Table 5: Using a smaller concentration volumes than the calibration standard (200 µL) to simulate low concentrations.

n-LPG sample	Concentration vol. (µL)	Fluorine (F) (mg/kg)	Chlorine (Cl) (mg/kg)	Bromine (Br) (mg/kg)	Sulfur (S) (mg/kg)	Iodine (I) (mg/kg)
2 mg/kg standard	50	0.48	0.51	—	0.53	—
15 mg/kg standard	20	1.76	1.69	1.68	1.74	—
1-year old 15 mg/kg standard	50	3.35	3.34	—	3.52	—

The calibration standards preconcentrated 200 µL.

Table 6: Estimated recoveries of expected results.

n-LPG sample	Sample vol./ calibration vol.	Fluorine (F) (%)	Chlorine (Cl) (%)	Bromine (Br) (%)	Sulfur (S) (%)	Iodine (I) (%)
2 mg/kg standard	0.25	91.4	102.0	< LOQ	106.0	< LOD
15 mg/kg standard	0.10	116.0	103.0	109	115.0	< LOQ
1-year old 15 mg/kg standard	0.25	89.9	88.4	—	93.1	—

Estimated recovery is (fraction of sample preconcentrated) × (expected results reported by the manufacturer) × 100.

Conclusion

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

Preconcentration improves sensitivity for bromine and iodine as compared with direct injection in AN73105 but it is limited by the baseline contamination levels in the LPG blank that interfere with total fluorine (F), chlorine (Cl), and sulfur (S) determinations.

The method was applied to three LPG standards as samples and was found to be accurate for total sulfur and total halides, 88–116% recovery.

More information on CIC and CIC applications can be found on Thermo Scientific website and on the Thermo Fisher Scientific AppsLab Digital Library.[20,21]

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