

Pyrohydrolytic combustion ion chromatography

Determination of total chlorine and sulfur in cleanroom gloves

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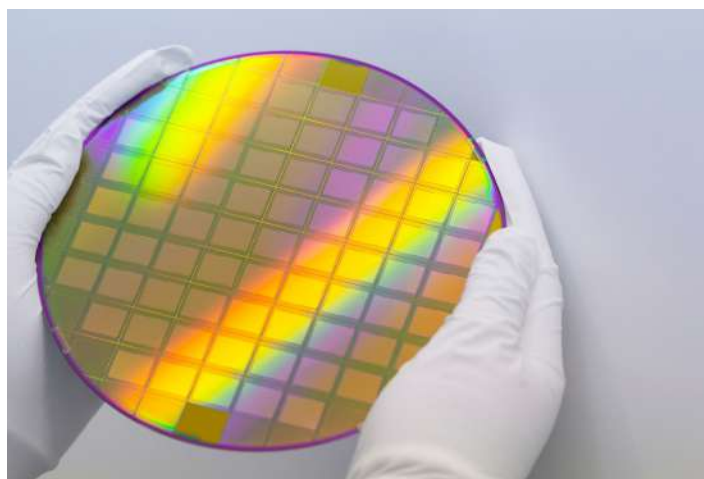
Goal

To demonstrate fast sample preparation using combustion IC

Introduction

In the electronics industries, product, process, and material cleanliness are important as ionic and organic contamination, as well as low levels of particulates, can cause damage to semiconductor devices and other electronic devices, such as printed circuit boards, cables, and disk drive assemblies. Anionic contamination, even at very low concentrations, is a major concern as anions can cause corrosion, deposition defects, electromigration, and electronic shorts in electronic devices. Ion chromatography (IC) with suppressed conductivity detection is the preferred and well-established method for determining anions, especially at $\mu\text{g/L}$ and ng/L concentrations.

The cleanliness of indirect materials, such as solvents, reagents, etching and plating chemicals, wipers, gloves,¹ cotton swabs, and wafer or device carriers, is also important to minimize cross-contamination caused by contact of the product with personnel and indirect materials. It is especially important that disposable gloves have low anionic contamination because gloves worn during the work period typically contact product or other



surfaces in the process, and therefore can easily transfer anionic and particulate contamination to the final product. The Institute of Environmental Sciences and Technology Recommended Practice, IEST-RP-CC005,² describes the determination of water-extractable halides and sulfate. The interior surface of an inverted glove (originally the outside surface) is extracted with hot deionized (DI) water for a set time, and then the solution is analyzed using IC. This widely used method has some disadvantages, such as the extraction process results in a highly diluted sample, the extraction time is not representative of the length of time the user wears the glove, and the method does not account for contamination leaching out over time. Additionally, the process is manual, time-consuming, and labor-intensive. However, these materials are solids that cannot be analyzed directly, requiring extraction or rinsing for IC analysis. Pyrohydrolytic combustion with IC

(CIC) has the advantages of eliminating complex sample matrices, such as polymers^{3–5} and printed circuit boards,⁶ and provides increased automation needed for sample preparation processes.

In this method, total chlorine and total sulfur are determined in three types of gloves—latex, cleanroom nitrile, and laboratory nitrile—using an automated combustion system for sample preparation. The sample is combusted and collected in a small volume (8 mL), and small aliquots (10 µL) are analyzed by the IC instrument. The anions are separated by an electrolytically generated KOH gradient from 0.5 to 40 mM on the Thermo Scientific™ Dionex™ IonPac™ AS17-C anion-exchange column and detected by suppressed conductivity detection. The method has good linear responses to concentration with $r^2 > 0.999$ for total chlorine and total sulfur, good recovery >90%, and acceptable reproducibility, RSD <9. The gloves contained chlorine and sulfur ranging from 100 to 1000 µg per area (in²).

Experimental

Equipment

- Nittoseiko Analytech, previously Mitsubishi Chemical Analytech, Automatic Combustion Unit
 - Model AQF-2100H system (Ion Chromatography Pretreatment unit), including:
 - Automatic Boat Controller Model ABC-210
 - Sample Changer Model Liquid/Solid ASC-260LS, using the tray for solid samples
 - Horizontal Furnace Model HF-210 with combustion tube and ceramic insert
 - Gas Absorption Unit GA-211
 - External Solution Selector ES-211
- Thermo Scientific™ 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 22153-62034

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

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

Product name	Description	P/N
Consumables for Dionex Integrion system		
Thermo Scientific™ Dionex™ IC PEEK Viper™ fitting tubing assembly kit	Dionex IC Viper fitting assembly kit for the Dionex Integrion HPIC system with CD	302965
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™ AG17-C Guard Column	Anion guard column, 2 × 50 mm	066297
Thermo Scientific™ Dionex™ IonPac™ AS17-C Analytical Column	Anion analytical column, 2 × 250 mm	066296
Eluent bottle	4 L eluent bottle	066019
Consumables for combustion system		
Quartz wool	Quartz wool for the combustion boats and the combustion tube	*
Extra combustion tube	AQF-2100H pyrolysis tube set	*
Extra absorption tube	Absorption tube, 10 mL	*
Extra ceramic inserts	Ceramic insert for combustion tube	*

*Available from the local distributor

For leachable extractions of the gloves (from Fisher Scientific™, unless otherwise specified)

- Hot plate, [P/N HP88854200](#)
- 1000 mL heavy-duty Griffin beaker, [P/N 02-555-25F](#)
- 250 mL Class B graduated cylinder, [P/N 08-550F](#)
- Ring stand and rings, [P/N S24240](#)
- Binder clips, stationary store, to hold gloves during liquid extraction
- Beaker tongs to handle the hot beaker, [P/N 02-620](#)

For handling glove samples (from Fisher Scientific, unless otherwise specified)

- Stainless steel tweezers, [P/N 16-100-107](#) or [P/N 17-467-201](#)

Sample preparation conditions	
Sample boats	Ceramic boat with quartz wool
Samples	15–30 mg of glove
AQF-2100H	
Mode	Constant volume
Sample mode	Absorbance, solid
Pyrolysis tube	Double quartz, inner ceramic tube
Calculated final volume (absorption tube)	9.75 mL
Absorption solution	300 mg/L hydrogen peroxide in ASTM Type I deionized water
Gas	
Argon and oxygen gas tank regulator, secondary setting	40 psi
Argon flow on HF-210	200 mL/min
Argon flow (humidification)	100 mL/min
Oxygen flow on HF-210	400 mL/min
Temperatures	
HF-210	Inlet: 800 °C; Outlet: 900 °C
Automatic boat controller, ABC program	
Pos 1 (mm)	130
Time (s)	480
Speed (mm/s)	20
Pos 2 (mm)	160
Time (s)	360
Speed (mm/s)	0.12
End time (s)	120
Cool time (s)	120
Home time (s)	120
Ar time (s)	30
O ₂ time (s)	600

- Polyester cleanroom wipes, [P/N 17-444-000](#)
- Clean scissors (stationary store, cleaned with isopropyl alcohol, DI)
- Ansell™ Nitrilite™ (Ansell LTD) cleanroom gloves, [P/N 19-014-687](#), or similar nitrile-based, powder-free, cleanroom gloves

Software

- Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) software, Chromeleon 7.2, version 10
- Mitsubishi NSX-2100 version 10.2.3

Detailed GA-211 Gas Absorption Unit conditions	
Absorption solution injection parameter	
Absorption solution volume (mL)	8
Water supply parameter	
Water supply scale	2
Ar flow for humidification (mL/min)	100
Washing parameter	
Water injection time (s)	17
Drain time (s)	17
Washing times	2
Gas line washing time (s)	0.5
Gas line washing interval (s)	3
Gas washing times	3
Washing time of a sample absorption line (s)	5
Syringe washing times	3
Gas line collection parameter	
Collection time (s)	0.5
Interval (s)	3
Times	3
Constant volume parameter	
Waiting time for stable liquid surface (s)	10
Mixing time (s)	10
Injection parameter	
Waiting time for injection start (s)	0
Sample purge time (s)	5
Sample absorption time (s)	10

Ion chromatography conditions

Columns	Dionex IonPac AG17-C, Dionex IonPac AS17-C anion-exchange columns, 2 mm i.d.
KOH gradient	0.5 mM (-3 to 1 min), 0.5–15 mM (1–20 min), 15–40 mM (20–24 min), 40 mM (24–27 min), 0.5 mM (27.1–30 min)
Eluent source	Dionex EGC-500 KOH eluent generator cartridge, Dionex CR-ATC 600 trap column, Dionex HP EG degas module
Injection volume	10 µL from GA-211 Gas Absorption unit valve, triggered by TTL_Input 3
Flow rate	0.25 mL/min
Column temperature	30 °C
Detection temperature	20 °C
Detection	Suppressed conductivity, 2 mm, ADRS 600 suppressor, constant current and recycle modes, 25 mA
Conductance background	<1 µS/cm
Conductance noise	<1 nS/cm
System backpressure	~2200 psi (~15.2 MPa)
Run time	IC: 30 min, total run time: 35 min

Reagents

- ASTM Type 1 deionized water (DI water) with 18 MΩ·cm resistivity⁷
- Argon (gas), UHP grade, 99.999%
- Oxygen (gas), UHP grade, 99.999%
- 30% Hydrogen peroxide 30%, Suprapur™, MilliporeSigma™ (Fisher Scientific P/N M1072980250)

Thermo Scientific™ Dionex™ Retention Time Standard, Routine Anion Determinations, [P/N 088957](#)

Thermo Scientific™ Dionex™ reagents for external calibration

- Dionex IC Standard, Chloride Standard (1000 mg/L), 100 mL, [P/N 037159](#)
- Dionex IC Standard, Sulfate Standard (1000 mg/L), 100 mL, [P/N 037160](#)
- Dionex Seven Anion Standard II, [P/N 057590](#)

Fisher Scientific reagents for recovery experiments, Certified ACS Grade

- Ammonium chloride, [P/N A661-500](#)
- Ammonium sulfate, [P/N A702-500](#), or benzenesulfonic acid, [P/N B34085G](#)

Standard and sample preparation

Use only ASTM Type I DI water for preparations.

Standards

Tip: Use only volatile salts, such as ammonium salts or benzenesulfonic acid, for combustion experiments. Sodium and potassium salts are not volatile and therefore not suitable for combustion experiments.

Prepare the individual 2500 mg/L chloride and sulfate stock standards by dissolving 297 mg of ammonium chloride and 754 mg of ammonium sulfate (824 mg of benzenesulfonic acid) in separate 100 mL of ASTM Type I DI water in a 125 mL HDPE or HDPP bottle. The 5,000 mg/L stock standards will also be used as spiking solutions. Prepare a combined 1,000 mg/L chloride and sulfate intermediate standard by pipetting 10 mL of 5,000 mg/L sulfate and 20 mL of 2,500 mg/L chloride stock standards into a 50 mL HDPE or HDPP bottle. Dilute to 50 g total volume with DI water. Create working standards (0.5, 1, 5, 25, 50, 100, 250 mg/L) in the same manner by diluting the 1,000 mg/L with DI water. Use the ES-210 external sampler to introduce the standards to the IC instrument.

Disposable glove samples

- Cleanroom Class 10 nitrile gloves (0.004 in, 0.102 mm thick)
- Nitrile exam laboratory gloves (0.006 in, 0.152 mm thick)
- Latex exam laboratory gloves (0.005 in, 0.127 mm thick)

Sample preparation for pyrohydrolytic combustion

The autosampler ceramic boats, containing a small amount of quartz wool to cover the bottom of the boat, were prepared by baking twice in the combustion oven using the default prebake program followed by the combustion method. After combustion, the boats were handled only with a pair of stainless-steel tweezers. To prepare the glove sample, a 1 × 1 cm piece of the glove was cut into 1–2 mm wide strips. Record the weight on an analytical balance (± 0.1 mg) after adding the strips to the previously tared boats, which had been subjected to prebake conditions twice. To determine recovery, prior to combustion, pipette 50 µL of 1,000 mg/L chloride and 50 µL of 5,000 mg/L

sulfate stock standards to autosampler boats containing glove samples. Alternatively, prepare four samples of approximately the same weight and add the standard to three of the four samples.

Sample preparation for liquid extraction

Turn the sample glove inside out. Using a graduated cylinder, add 200 mL of 85 °C DI water to the inside of the inverted glove. Hang the glove for 1 h. Mark the area filled with DI water to use for area calculations. Pour the extraction water into a clean polystyrene container. Shake to mix. Use the ES-210 external sampler to introduce the sample to the IC.

Hydrogen peroxide absorption solution

To prepare the 300 mg/L peroxide solution, dilute 1,000 µL of 30% hydrogen peroxide into 1 L total of ASTM Type I DI water.

Note: It is important that only high purity hydrogen peroxide is used for the absorption solution, as lower purity reagents have anionic contaminants.

Instrument setup and installation

Setup and install the pyrohydrolytic combustion-ion chromatography system as shown in Figures 1 and 2 and Thermo Scientific Technical Note 72211 – Combustion ion chromatography with a Dionex Integrion HPIC system.⁸ Configure the combustion system including the TTL connection, as described as “direct injection using the injection valve in the Mitsubishi GA-211 Module”.⁸

Conditioning the IC consumables

Condition the Dionex EGC-500 KOH cartridge and Dionex CR-ATC 600 trap column as described in the conditioning consumables on the Chromeleon Instrument Console or their product manuals.^{10–11} Condition the columns

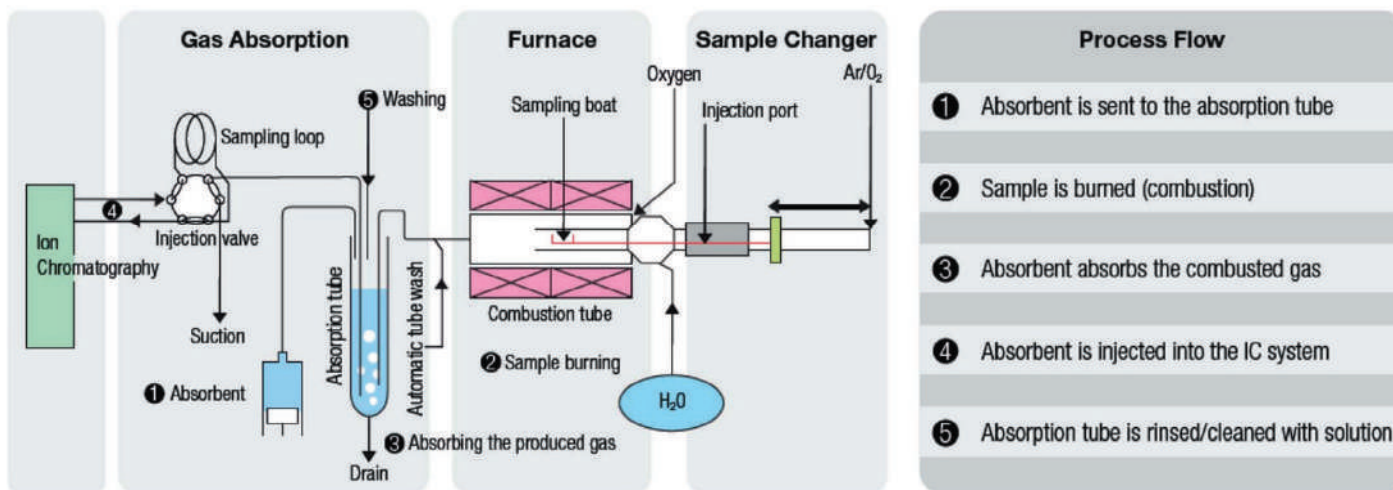


Figure 1. Diagram of a combustion IC system^{8,9}

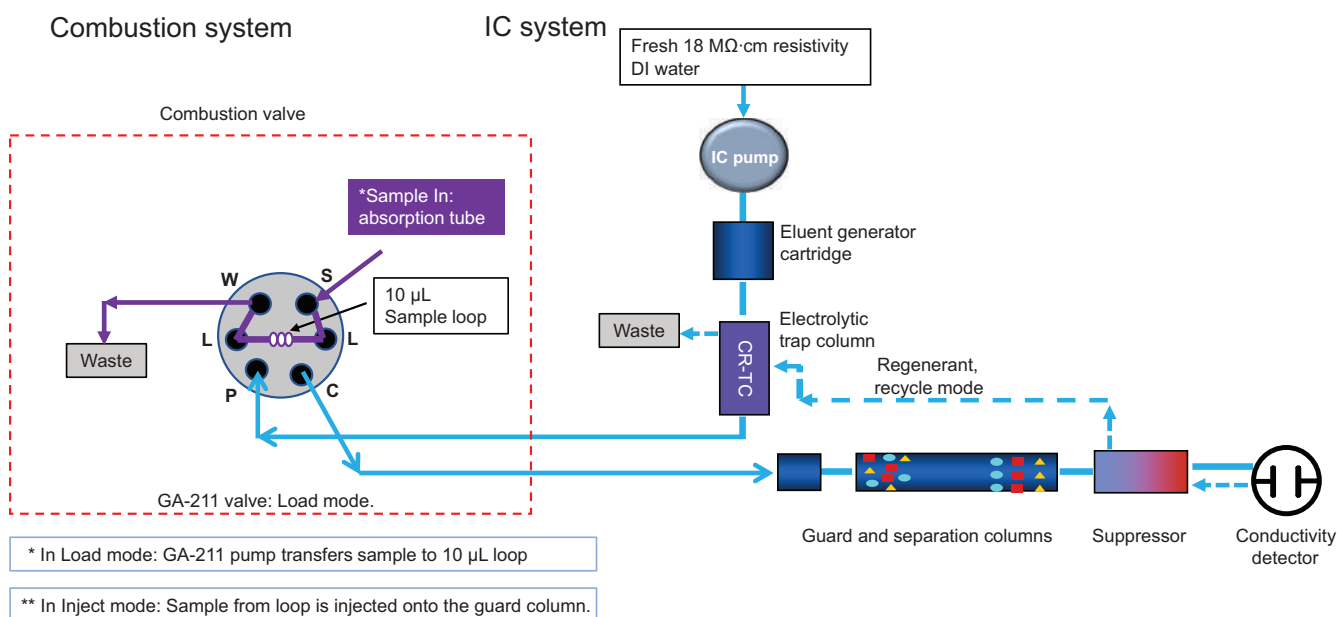


Figure 2. Flow diagram for the Dionex Integrion HPIC system

for 30 min using the column Quality Assurance Report (QAR) conditions with the column effluent directed to waste.¹² Hydrate and install the suppressor according to the instructions included in the suppressor box.¹³ Complete the installation according to Figure 2.

Equilibrate the IC system with the column QAR conditions until the total conductivity is <1 µS/cm. Run the column QAR conditions with the QAR standard to verify that the IC system is operating correctly. The sample introduction can be done manually or by convenience, through the ES-210 External Solution Selector module. For more information on creating instrument methods and sequences, refer to TN72211 and Thermo Scientific Application Note 73105 – Determination of total fluorine, chlorine, bromine, and sulfur in liquefied petroleum gas by pyrohydrolytic combustion ion chromatography.^{8,14}

Constant volume determination

The combusted sample and standards have an approximately 10-fold dilution because they are aerated into an absorption tube containing ~10 mL of 300 mg/L absorption solution. It is important to determine this correction factor, named constant volume factor, to account for the dilution when using the ES-210 External Sampler to introduce the standard or when converting to contaminant concentration per weight of sample. Phosphate is not detected by combustion IC, so it is an ideal peak to use for this calculation. To determine the constant volume factor, prepare 200 mL solution of ~100 mg/L phosphate. It is not important to prepare the exact concentration. Measure the IC response of phosphate when 1) using the ES-210 External Sampler and 2) using the 100 mg/L phosphate solution as the absorption solution (set at 8 mL).

Constant volume factor = 8 × phosphate peak areas of (external sampler/absorption solution)

For example: Phosphate peak area using the external sampler is 16.5403 µS·min; using the absorption solution it is 13.1674 µS·min. Therefore, the constant volume factor = 8 * (16.5403/13.1674) = 10.06

The resultant calculated ratio or constant volume factor for these experiments, as shown in the calculations above, is 10.06. This measurement is also thoroughly discussed in the AQH-2100 combustion system manual.⁹

Results and discussion

This application uses inline sample preparation by pyrohydrolytic combustion with oxidative reaction followed by sample absorption. After processing, the combustion

system triggers the IC to analyze the generated liquid samples. The sample boat containing quartz wool and sample are introduced by the Automatic Sample Changer model ASC-260S/L into the Automatic Boat Controller model ABC-210, followed by pyrohydrolytic combustion in the Horizontal Furnace model HF-210. The total halogen and total sulfur gases are absorbed into the 300 mg/L peroxide absorption solution in the Gas Absorption model GA-211. The 300 mg/L peroxide solution was selected as the absorption solution because using lower peroxide concentrations, such as 100 mg/L, resulted in incomplete conversion of sulfur species to sulfate. After mixing and dilution, a TTL connection triggers injection of the sample into the Dionex Integrion HPIC system. The total halogens and total sulfur are separated as anions on the Dionex IonPac AS17-C anion-exchange column and detected by suppressed conductivity.

Selected column

The Dionex IonPac AS17-C, a 7.5 µEquivalent capacity column, was selected for this application because this column with hydroxide-selective resin is optimized for fast gradient separations of low anion concentrations.¹⁵ Fluoride and other early eluting organic acids are well resolved from the void volume dip. The Dionex IonPac AS17-C column resin has nearly no sulfate bleed compared to other columns and is therefore ideal for determining low concentrations of sulfate.

Figure 3 shows the separation of seven anions on the Dionex IonPac AS17-C column using a KOH gradient from 0.5 to 40 mM over 27 min using the IC conditions setup in this application note.

Method evaluation

Reproducibility

This method was evaluated by measuring retention time and peak area reproducibilities, the anion response to concentration relationship (calibration), and sensitivity (method detection limits). Retention times and peak areas were determined in seven replicate injections of a 12.5 mg/L chloride and sulfate standard. The results were excellent with RSDs <0.06% for retention time and <0.13% for peak area (Table 2).

Table 2. Retention time and peak area reproducibility

	Average retention time (min)	RSD	Average peak area (µS·min)	RSD
Chloride	9.959	0.06	4.559	0.13
Sulfate	23.67	0.03	3.897	0.09

n=7

Columns: Dionex IonPac AG17-C, Dionex IonPac AS17-C, 2 mm i.d.
 KOH gradient: 0.5 mM KOH (-3–1 min), 0.5–15 mM (1.0–20 min), 15–40 mM (20–24 min), 40 mM (24–27 min), 40–0.5 mM (27–27.0 min), 0.5 mM (27.1–30 min)
 Eluent source: Dionex EGC-500 KOH cartridge, Dionex CR-ATC 600 trap column, Dionex high pressure degasser
 Flow rate: 0.25 mL/min
 Injection vol.: 10 µL
 Column temp.: 30 °C
 Detector oven temp.: 20 °C
 Detection: Suppressed conductivity, Dionex ADRS 600, 2 mm, constant current and recycle modes, 25 mA
 Autosampler: External sampler, ES-210 module

Columns: Dionex IonPac AG17-C, Dionex IonPac AS17-C, 2 mm i.d.
 KOH gradient: 0.5 mM KOH (-3–1 min), 0.5–15 mM (1.0–20 min), 15–40 mM (20–24 min), 40 mM (24–27 min), 40–0.5 mM (27–27.0 min), 0.5 mM (27.1–30 min)
 Eluent source: Dionex EGC-500 KOH cartridge, Dionex CR-ATC 600 trap column, Dionex high pressure degasser
 Flow rate: 0.25 mL/min
 Injection vol.: 10 µL
 Column temp.: 30 °C
 Detector oven temp.: 20 °C
 Detection: Suppressed conductivity, Dionex ADRS 600, 2 mm, constant current and recycle modes, 25 mA
 Sample prep.: Pyrolytic combustion
 75/25 isopropyl alcohol/DI water, 85 °C, 1 h
 800 °C inlet, 900 °C outlet
 Gas: 200 mL/min Ar, 400 mL/min O₂, 100 mL/min Ar + DI water
 Absorption sol.: 10 mL, 300 mg/L hydrogen peroxide
 Samples: Strips of cleanroom nitrile disposable glove, finger region, 15.4 mg, 1 × 1 cm
 A: Empty boat, B: First, C: Second combustion

Graph offset: 15%

Peaks:	A (mg/L)	B (mg/L)	C (mg/L)	First combustion efficiency (%)
1. Total fluorine	—	—	—	—
2. Total chlorine	0.19	3.30	0.16	~100
3. Chlorite	—	—	—	—
4. Nitrite	—	—	—	—
5. Nitrate	—	—	—	—
6. Carbonate	—	—	—	—
7. Total sulfur	0.57	17.3	0.50	~100

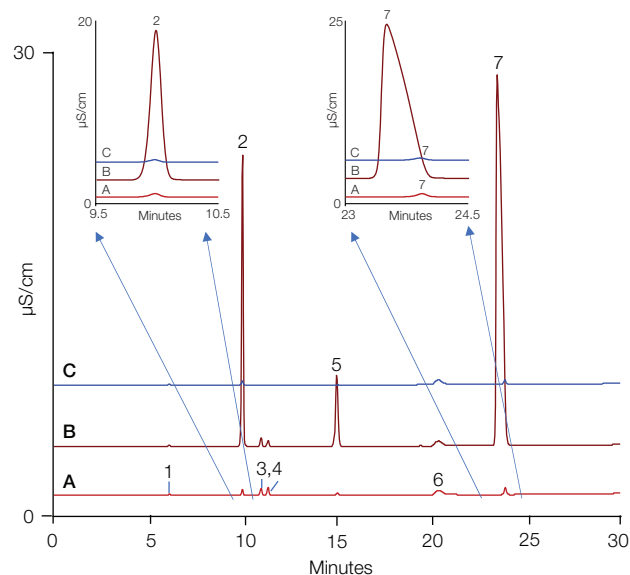


Figure 4. Approximately 100% combustion efficiency of cleanroom nitrile gloves

Samples and method characterization

The method was applied to nitrile cleanroom, nitrile laboratory, and latex laboratory gloves. To determine that the pyrohydrolytic combustion was complete, the total chlorine and total sulfur were measured from three sequential combustions of a 21 mg sample of a cleanroom glove. The efficiency was determined by comparing the first combustion results with the total results from the three combustions. The results showed very low total chlorine and sulfur in the second and third combustions indicating quantitative recovery with the first combustion, and 96.8% and 98% of the total chlorine and total sulfur of the three combustions combined. The results shown in Figure 4 demonstrate the findings, confirming that this method is acceptable for glove samples.

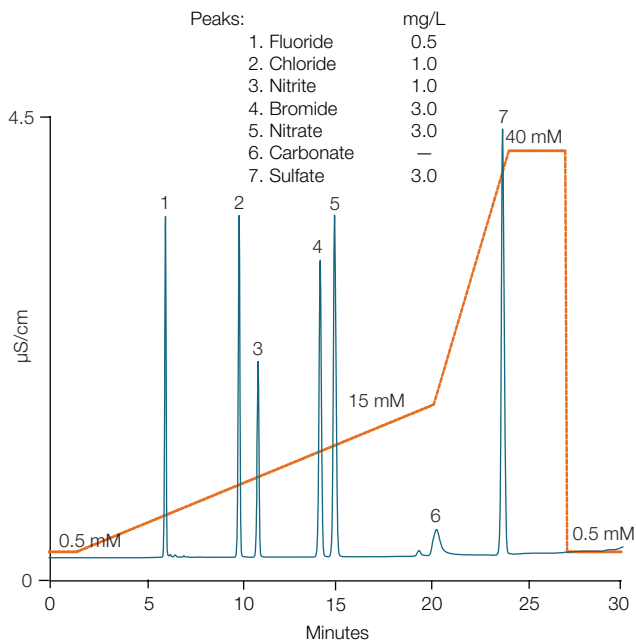


Figure 3. Seven anion standard using External Sampler mode

Calibration and limit of detection

Sodium and potassium salts are suitable for calibration using the ES-210 External Sampler (i.e., these are not combusted). Calibration curves were established using triplicate injections of nine standards (0.5, 1.0, 2.5, 5, 12.5, 25, 50, 100, 231 mg/L). The results (Table 3) show linear calibration responses for chloride and sulfate, as indicated by the coefficient of determination ($r^2 > 0.999$). Limit of detection (LOD) was used to determine method sensitivity. LOD was defined as 3x S/N of triplicate injections of 2.5 and 5 µg/L standards, and estimated to be 1.5 and 5.9 µg/L for chloride and sulfate, respectively.

Table 3. Summary of calibration and LOD results using external sampler mode

	Range (mg/L)	Type	Coefficient of determination (r^2)	LOD (µg/L)
Chloride	0.5 to 230	Linear with offset	0.9995	1.5
Sulfate			0.9993	5.9

*n=3 for nine standards (0.5, 1.0, 2.5, 5, 12.5, 25, 50, 100, 231 mg/L)

The total chlorine (measured as chloride) and total sulfur (measured as sulfate) in the glove samples were determined in 15 mg samples. To determine reproducibility, samples were analyzed in triplicate. Table 4 shows the results with total chlorine results ranging from 2.5 to 4.1 mg/L and total sulfur results ranging from 17 to 42 mg/L. As expected, the nitrile cleanroom gloves had the lowest total chlorine and total sulfur (3.3 mg/L and 17.3 mg/L, respectively). The latex exam glove had the highest results (6.8 mg/L total chlorine and 42 mg/L total sulfur). The method showed good reproducibility for the glove samples as indicated by the RSDs, 2.2–4.1 for total chlorine and 3.4–8.3 for total sulfur. This analysis confirmed cleanroom nitrile gloves are the best choice for minimizing contamination.

Accuracy

To evaluate accuracy, recoveries were determined. Four ~15 mg glove samples were prepared for each type. Ammonium salt standards (50 μ L of 940 mg/L chloride, 5,160 mg/L sulfate standard) were added to three of the four replicate samples. Table 5 summarizes the results, showing good recovery >90% for all samples, suggesting the method is accurate. Figures 5–7 also show that the chromatography results of the combusted samples are good, as indicated by well resolved peaks and narrow peak widths. The results are also expressed in contamination per total surface area, μ g/in² and μ g/cm².

Table 4. Summary of reproducibility results using pyrohydrolytic combustion IC

Glove	Weight (mg)	Total chlorine (measured as mg/L chloride)			Total sulfur (measured as mg/L sulfate)		
		Measured (mg/L)	Average (mg/L)	RSD (%)	Measured (mg/L)	Average (mg/L)	RSD (%)
Cleanroom nitrile glove	15.87	3.39	3.30	2.5	17.0	17.3	3.4
	15.62	3.25			17.0		
	14.48	3.25			18.0		
Nitrile exam glove	16.01	4.88	4.66	2.6	23.3	25.1	8.3
	15.55	4.55			27.4		
	15.43	4.55			24.8		
Latex exam glove	16.66	6.96	6.80	4.1	44.2	41.6	5.6
	16.91	6.82			41.2		
	15.43	6.62			39.5		

Table 5. Summary of recovery experiments

Glove	Weight (mg)	Total chlorine (measured as chloride)					Total sulfur (measured as mg/L sulfate)				
		Measured (mg/L)	Added (mg/L)	Measured with standard (mg/L)	Recovered (%)	Average recovery (%)	Measured (mg/L)	Added (mg/L)	Measured with standard (mg/L)	Recovered (%)	Average recovery (%)
Cleanroom nitrile glove	15.59	3.30	—	—	—	—	17.1	—	—	—	—
	15.23	—	4.7	7.50	93.8	94.5	—	25.8	40.8	95.1	96.3
	15.73	—	4.7	7.33	91.6		—	25.8	42.0	97.9	
	14.82	—	4.7	7.82	97.8		—	25.8	41.1	95.8	
Nitrile exam glove	15.25	4.66	—	—	—	—	25.1	—	—	—	—
	15.23	—	4.7	9.24	98.7	95.7	—	25.8	54.0	106	98.1
	15.72	—	4.7	9.06	96.8		—	25.8	49.6	97.4	
	14.82	—	4.7	8.58	91.7		—	25.8	46.3	91.0	
Latex exam glove	15.38	6.80	—	—	—	—	41.6	—	—	—	—
	15.20	—	4.7	10.2	87.5	91.8	—	25.8	63.7	94.5	94.6
	15.68	—	4.7	11.0	96.0		—	25.8	63.7	94.5	
	15.35	—	4.7	10.8	93.8		—	25.8	63.8	94.7	

Conditions: See Figure 4
 Samples: Strips of cleanroom nitrile disposable glove, finger region, 1 × 1 cm
 A: 15 mg of glove
 B: Sample A plus 4.7 mg chloride, 25.8 mg sulfate
 Graph offset: 10%

Peaks:	A (mg/L)	B (mg/L)	A: Total (µg/in ²)
1. Total fluorine	—	—	—
2. Acetate	—	—	—
3. Total chlorine	3.3	7.6	107
4. Unknown	—	—	—
5. Nitrite	—	—	—
6. Nitrate	—	—	—
7. Carbonate	—	—	—
8. Unknown	—	—	—
9. Total sulfur	17.1	41.3	554

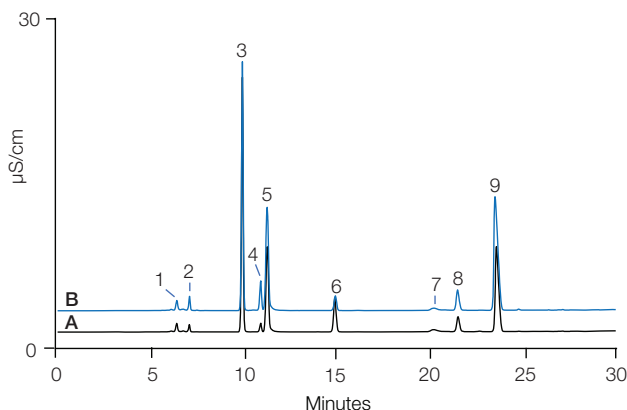


Figure 5. Total halide and total sulfur in cleanroom nitrile disposable gloves A) without and B) with added standard

Conditions: See Figure 4
 Samples: Strips of latex exam laboratory disposable glove, finger region, 1 × 1 cm
 A: 15 mg of glove
 B: 15 mg plus 4.7 mg chloride, 25.8 mg sulfate
 Graph offset: 10%

Peaks:	A (mg/L)	B (mg/L)	A: Total (µg/in ²)
1. Total fluorine	—	—	—
2. Acetate	—	—	—
3. Total chlorine	4.7	9.0	152
4. Nitrite	—	—	—
5. Nitrate	—	—	—
6. Carbonate	—	—	—
7. Unknown	—	—	—
8. Total sulfur	25.1	50.0	813

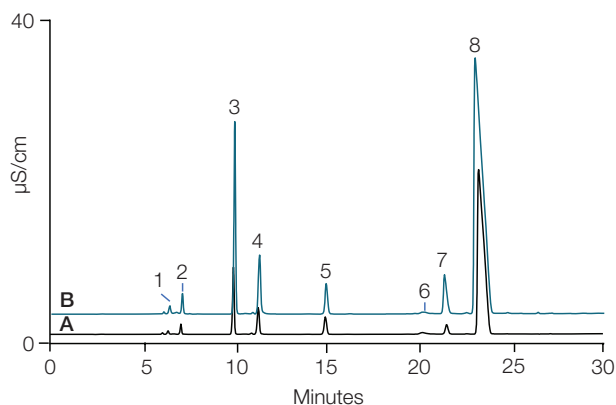


Figure 6. Total chlorine and total sulfur in nitrile exam gloves A) without and B) with added standard

Conditions: See Figure 4
 Samples: Strips of latex exam laboratory disposable glove, finger region, 1 × 1 cm
 A: 16 mg of glove
 B: 16 mg plus 4.7 mg chloride, 25.8 mg sulfate
 Graph offset: 10%

Peaks:	A (mg/L)	B (mg/L)	A: Total (µg/in ²)
1. Total fluorine	—	—	—
2. Acetate	—	—	—
3. Total chlorine	6.8	10.7	220
4. Nitrite	—	—	—
5. Carbonate	—	—	—
6. Total sulfur	41.6	63.7	1350

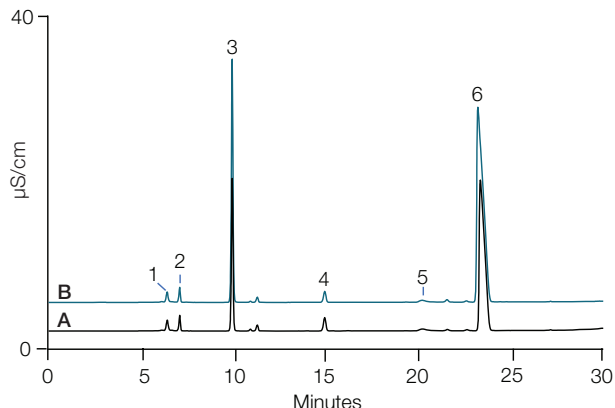


Figure 7. Total chlorine and total sulfur in latex exam disposable gloves A) without and B) with added standard

Results as compared to extraction of gloves

Determining contamination in gloves is traditionally done according to the Institute of Environmental Sciences and Technology recommended practices, IEST-RP CC005.² The ionic contamination is extracted from the outside of the glove by turning the glove inside-out and extracting the original outside surface with 85 °C DI water for 1 h. To compare the combustion IC method with the IEST-RP-C005 method, one nitrile cleanroom glove and one nitrile exam glove were extracted with the IEST method. Figures 8 shows the chromatography of the extracted samples. Table 6 shows that the combustion method has considerably higher results, >100x, those of the extraction method. The CIC method determines the total possible contamination while the liquid extraction method determines an arbitrary contamination value. The CIC results suggest that higher contamination from gloves can occur over longer use or more strenuous work conditions.

Table 6. Comparison of extraction and combustion results

Extraction results			Total chloride		Total sulfate	
	Surface area (in ²)	Dilution factor (mL)	Measured (µg/mL)*	Total chloride (µg/in ²)	Measured (µg/mL)*	Total sulfate (µg/in ²)
Cleanroom nitrile glove	19.34 (124.8 cm ²)	200	0.37	3.3 (0.59 µg/cm ²)	0.14	1.4 (0.22 µg/cm ²)
Nitrile exam glove	22.13 (142.8 cm ²)	200	2.21	22.8 (3.10 µg/cm ²)	0.25	2.2 (0.36 µg/cm ²)

Combustion Results			Total chlorine		Total sulfur	
	Surface area (in ²)	Dilution factor (mL)	Measured (µg/mL)*	Total chloride (µg/in ²)	Measured (µg/mL)*	Total sulfur as sulfate (µg/in ²)
Cleanroom nitrile glove	0.31 (2 cm ²)	10.06	3.30	107 (16.6 µg/cm ²)	17.1	550 (86 µg/cm ²)
Nitrile exam glove	0.31 (2 cm ²)	10.06	4.70	152 (23.6 µg/cm ²)	25.1	810 (26 µg/cm ²)

*mg/L=µg/mL

IC conditions: See Figure 4
 Autosampler: External sampler, ES-210 module
 Extraction sol.: 200 mL, DI water, 85 °C
 Sample prep.: Extract inside of reversed glove for 1 h
 Samples: Extraction solutions

A: Control
 B: Nitrile cleanroom disposable glove
 C: Nitrile exam disposable glove

Graph offset: 10%

Peaks:	A (mg/L)	B (mg/L)	C (mg/L)
1. Fluoride	—	0.006	0.006
2. Acetate	—	—	—
3. Organic acid	—	—	—
4. Formate	—	—	—
5. Chloride	0.088	0.369	2.21
6. Nitrate	—	—	—
7. Unknown	—	—	—
8. Carbonate	—	—	—
9. Unknown	—	—	—
10. Sulfate	0.024	0.136	0.246

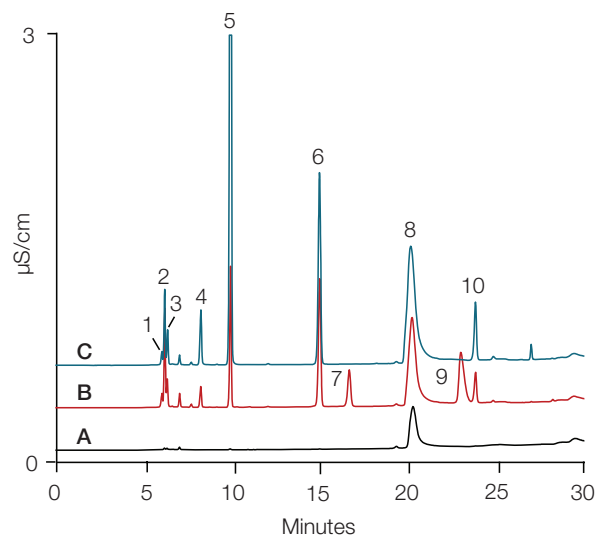


Figure 8. Comparison of A) extraction solution, B) extraction of nitrile cleanroom, and C) extraction of nitrile exam gloves

Conclusion

This application note demonstrated the determinations of total chlorine as chloride and total sulfur as sulfate in glove samples using CIC. The combustion system provided a fast, automated sample preparation of glove samples using the Nittoseiko AQF-2100 combustion system. The method was sensitive with LODs of single digit µg/L, accurate with >90% recoveries of added standard, and good reproducibilities with RSDs <9%. As expected, the CIC results did not correlate to the results using the IEST liquid extraction method, the method is an indication of the maximum contamination possible with extended wear. Both methods demonstrated that the nitrile cleanroom gloves had lower ionic contamination and total sulfur and total chlorine levels than latex and nitrile gloves intended for applications other than cleanrooms. More information on trace-level ion applications can be found in the Thermo Scientific AppsLab Library¹⁷ and in applications cited in References 18–33.

References

- Camden, Eric. Contamination risks related to ESD gloves and finger cots. Proceedings of SMTA International, Sep. 25-29, 2016, Rosemont, IL, USA pp 790-798. [Online] http://www.circuitinsight.com/pdf/Contamination_Risks_Related_ESD_Gloves_Finger_Cots_smta.pdf (Accessed October 2020.)
1. IEST-RP-CC005: Recommended practices for gloves and finger costs used in cleanrooms and other controlled environments. Institute of Environmental Sciences and Technology. Schaumburg, IL, USA. [Online] <https://www.iest.org/Standards-RPs/Recommended-Practices/1EST-RP-CC005> (Accessed October 2020.)
3. Thermo Scientific Application AN72349: Determination of chlorine, bromine, and sulfur in polyethylene materials using combustion ion chromatography, 2017. [Online] <https://assets.thermofisher.com/TFS-Assets/CMD/Application-Notes/AN-72349-IC-Chlorine-Bromine-Sulfur-Polyethylene-AN72349-EN.pdf> (Accessed October 2020.)
4. Thermo Scientific Application Note AN72573: Determination of halogens in polymers and electronics using a combustion ion chromatography system, 2017. Sunnyvale, CA, USA. [Online] <https://assets.thermofisher.com/TFS-Assets/CMD/Application-Notes/an-72573-combustion-ic-halogens-polymers-electronics-an72573-en.pdf> (Accessed October 2020.)
5. Thermo Scientific Application Update AU72588: Determination of chlorine, bromine, and sulfur in polyethylene materials using combustion IC with a carbonate/bicarbonate eluent, Sunnyvale, CA, USA, 2018. [Online] <https://assets.thermofisher.com/TFS-Assets/CMD/Application-Notes/au-72588-ic-combustion-cl-br-s-polyethylene-au72588-en.pdf> (Accessed October 2020.)
6. Thermo Scientific Application Note AN1163 Determination of anions on the surface of printed circuit boards by IPC-TM-650 Method 2.3.28 using HPIC, 2016. Sunnyvale, CA, USA. [Online] <https://assets.thermofisher.com/TFS-Assets/CMD/Application-Notes/AN-1163-IC-Anions-Printed-Circuit-Boards-AN72195-EN.pdf> (Accessed October 2020.)
7. ASTM International, ASTM D1193 - 99e1 Standard Specification for Reagent Water. [Online] <https://www.astm.org/DATABASE.CART/HISTORICAL/D1193-99E1.htm>
8. Thermo Scientific Technical Note TN72211: Combustion ion chromatography with a Dionex Integrion HPIC System, Sunnyvale, CA, USA, 2017 [Online] <http://tools.thermofisher.com/content/sfs/brochures/TN-72211-IC-Integrion-TN72211-EN.pdf> (Accessed October 2020.)
9. Nittoseiko Analytech, previously Mitsubishi Chemical Analytech. Operation Manual For NSX-2100 Series Automatic Combustion Unit Model AQF-2100H.
10. 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 October 2020.)
11. Thermo Scientific Product Manual: Continuously Regenerated Trap columns (CR-TC 500, CR-TC 600, Capillary), 2018, Sunnyvale, CA, USA. [Online] <https://assets.thermofisher.com/TFS-Assets/CMD/manuals/Man-032697-09-IonPac-Anion-Trap-Columns.pdf> (Accessed October 2020.)
12. Thermo Scientific Product Manual: Dionex IonPac AS17-C Column, Sunnyvale, CA, USA, 2012. [Online] <http://tools.thermofisher.com/content/sfs/manuals/Man-031529-AS17-AG17-Columns-Man031529-EN.pdf> (Accessed October 2020.)
13. 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 October 2020.)
14. Thermo Scientific Application Note AN73105: Determination of total fluorine, chlorine, bromine, and sulfur in liquefied petroleum gas by pyrohydrolytic combustion ion chromatography, Sunnyvale, CA, USA, 2019. [Online] <https://assets.thermofisher.com/TFS-Assets/CMD/Application-Notes/an-73105-ic-halides-sulfur-lpg-an73105-en.pdf> (Accessed October 2020.)
15. Thermo Scientific IonPac AS17-C Anion Exchange Column specification sheet, 2007. [Online] https://assets.thermofisher.com/TFS-Assets/CMD/Specification-Sheets/48831-DS_IonPac_AS17_C_released021307.pdf
16. 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 October 2020.)
17. Thermo Scientific Digital AppsLab Library. <https://apps.thermofisher.com/> (Accessed October 2020.)
18. Thermo Scientific Technical Note TN48: Determination of trace anions in high-purity water by high-volume direct injection with the EG40, 2000. Sunnyvale, CA, USA. [Online] <https://apps.thermofisher.com/App/2316/determination-trace-anions-highpurity-water> (Accessed October 2020.)
19. Thermo Scientific Technical Note AN85: Determination of trace anions in organic solvents, 2000. Sunnyvale, CA, USA. [Online] https://assets.thermofisher.com/TFS-Assets/CMD/Application-Notes/4173-AN85_LPN0482-03.pdf (Accessed October 2020.)
20. Thermo Scientific Application Update AU142: Improved determination of trace anions in high purity waters by high-volume direct injection with the Dionex EG40 eluent generator, 2001, 2017. Sunnyvale, CA, USA. [Online] <https://apps.thermofisher.com/App/2160/determination-trace-anions-high-purity-water> (Accessed October 2020.)
21. Thermo Scientific Technical Note TN44: The determination of trace anions in concentrated phosphoric acid, Sunnyvale, CA, USA, 2002, 2017. [Online] <https://assets.thermofisher.com/TFS-Assets/CMD/Technical-Notes/tn-44-ic-trace-anions-phosphoric-acid-tn72547-en.pdf> (Accessed October 2020.)
22. Thermo Scientific Application Update AU163: Determination of trace anions in organic solvents using matrix elimination and preconcentration, 2007. Sunnyvale, CA, USA. [Online] <https://assets.thermofisher.com/TFS-Assets/CMD/Application-Notes/au-163-ic-trace-anions-organic-solvents-au72543-en.pdf> (Accessed October 2020.)
23. Thermo Scientific Technical Note TN45: Determination of Trace anions in hydrofluoric acid, ammonium fluoride, and a buffered oxide etchant, Sunnyvale, CA, USA, 2010, 2017. [Online] <https://assets.thermofisher.com/TFS-Assets/CMD/Technical-Notes/tn-45-ic-strong-acid-anions-hf-tn72548-en.pdf> (Accessed October 2020.)
24. Thermo Scientific Application Note AN94: Determination of trace cations in concentrated acids (sulfuric acid) using autoneutralization pretreatment and ion chromatography, 2014. Sunnyvale, CA, USA. [Online] <https://assets.thermofisher.com/TFS-Assets/CMD/Application-Notes/an-94-ic-trace-cations-concentrated-acids-an72536-en.pdf> (Accessed October 2020.)
25. Thermo Scientific Customer Application Note CAN118: Determination of trace sodium in diesel and biodiesel fuel, 2014. Sunnyvale, CA, USA. [Online] <https://apps.thermofisher.com/SearchTag/SearchTag?tagName=biodiesel> (Accessed October 2020.)
26. Thermo Scientific Application Note AN153: Monitoring for trace anion contamination in the extracts of electronic components, 2015, 2017. Sunnyvale, CA, USA. [Online] <https://apps.thermofisher.com/App/1536/trace-anion-contamination-electronic-components> (Accessed October 2020.)
27. Thermo Scientific Application Note AN146: Determination of trace anions in high-purity waters by ion chromatography with the Dionex IonPac AS17 column using high-volume direct injection, 2016, 2017. Sunnyvale, CA, USA. [Online] <https://assets.thermofisher.com/TFS-Assets/CMD/Application-Notes/an-146-ic-trace-anions-high-purity-waters-an71550-en.pdf> (Accessed October 2020.)
28. Thermo Scientific Application Note AN152: Determination of sodium at the parts-per-trillion level in the presence of high concentrations of ethanolamine in power plant waters, 2016. Sunnyvale, CA, USA. [Online] <https://assets.thermofisher.com/TFS-Assets/CMD/Application-Notes/AN-152-IC-Sodium-Ethanolamine-Power-Plant-Waters-LPN1526-EN.pdf> (Accessed September 2020.)
29. Thermo Scientific Technical Note TN112: Determination of trace anions in ultrapure water using capillary ion chromatography, 2016, 2017. Sunnyvale, CA, USA. [Online] <https://assets.thermofisher.com/TFS-Assets/CMD/Technical-Notes/tn-112-ic-trace-anions-ultrapure-water-tn72560-en.pdf> (Accessed October 2020.)
30. Thermo Scientific Application Brief AB106: Trace anion analysis using an ICS-2100 System with RFIC-ESP and an Electrolytic Water Purifier, 2009, 2016. Sunnyvale, CA, USA. [Online] <https://assets.thermofisher.com/TFS-Assets/CMD/Application-Notes/AB-106-IC-Trace-Anion-Analysis-RFIC-ESP-Electrolytic-Water-Purifier-AB71939-EN.pdf> (Accessed October 2020.)
31. Thermo Scientific Technical Note TN177, Configuring the Dionex Integrion HPIC System for trace anion determinations in ultrapure water, 2016. Sunnyvale, CA, USA. [Online] <https://apps.thermofisher.com/App/2890/trace-anion-analysis-ultrapure-water-using-an-electrolytic-water-purifier-with-a-compact-ion-chromatography-system-50-ppt-standard> (Accessed October 2020.)

32. Thermo Scientific Technical Note TN72206: Configuring the Dionex Modular HPIC System with an inline water purifier and inline calibration for trace anion determinations in ultrapure water, 2016. Sunnyvale, CA, USA. [Online] <https://appslab.thermofisher.com/App/3625/trace-anions-using-ewp-autoprep-module> (Accessed October 2020.)
33. Thermo Scientific Application Update AU159: Determination of volcanic gases as anions in caustic solutions using autoneutralization, automated dilutions, and a Reagent-Free Ion Chromatography System, 2016. [Online] <https://assets.thermofisher.com/TFS-Assets/CMD/Application-Notes/AU-159-IC-Volvanic-Gases-Anions-Caustic-Solutions-LPN1892-EN.pdf> (Accessed October 2020.)

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