



Trace Chloride, Fluoride, and Bromide in Liquid Organics by Combustion Ion Chromatography (CIC)

UOP Method 991-17

Scope

This method is for determining trace concentrations of chloride, fluoride, and bromide in liquid organics by Combustion Ion Chromatography (CIC). This method has a lower limit of quantitation of 0.1 mg/kg (mass-ppm) for fluoride and chloride, and 0.2 mg/kg for bromide.

References

- Instruction Manual for Automatic Quick Furnace, Model AQF-2100H, www.cosa-instrument.com
UOP Method 999, "Precision Statements in UOP Methods," www.astm.org

Outline of Method

A reproducible volume of sample is injected into a quartz boat. The boat is introduced into a multi-position horizontal furnace under controlled temperature and moisture. The sample is then combusted in a pyrohydrolytic, oxygen enriched environment. The halogens in the sample are converted to hydrogen halides and halogen gas. These gases are then absorbed into an aqueous solution of constant volume. An aliquot of the solution is injected into an ion chromatograph (IC) where chloride, fluoride, and bromide are separated by anion exchange and measured by a conductivity detector with ion suppression. External standards are used for quantitation.

Apparatus

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used.

Balance, semi-micro, capacity 220 g, readable to 0.00001 g at 81 g

Chromatographic column, IonPac AS11-HC Analytical, 250-mm length by 4-mm ID, Dionex, Thermo Fisher, Cat. No. 052960

Combustion system, equipped with AQF-2100H furnace (HF-210 horizontal furnace), GA-210 gas adsorption unit, ABC-210 automatic boat controller, ASC-250L liquid autosampler, and AQF Software, COSA Instrument Corp. Newer models from the same manufacturer are also suitable.

Deionized water system, Barnstead GenPure xCAD Plus UV – TOC (bench version), Thermo Scientific, ThermoFisher Cat. No. 50136153

Dry block heater, digital, 2 block capacity, 120V, 50/60Hz, 210W, VWR, Cat. No. 12621-088, and heating blocks with 15- and 28-mm diameter vial wells, Cat. Nos. 12621-126 and -138, respectively

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Flask, volumetric, 1-L, borosilicate glass, Class A, VWR, Cat No. 89000-412

Ion chromatograph, equipped with a pump, injection valve/autosampler, eluent generator, continuously regenerated trap column, suppressor, conductivity detector, computer, and Chromeleon software, Dionex, Thermo Fisher, Model ICS-2100

Muffle furnace, capable of operation at 800°C, Barnstead/Thermolyne compact benchtop muffle furnace, Thermo Scientific, VWR Cat. No. 30631-230

Pipettor, Eppendorf Reference single-channel, variable volume, 100-1000 mL, VWR, Cat. No. 10032-682

Refrigerator, laboratory, explosion proof or flammable storage, Fisher Scientific, Cat. No. 05EREETSA

Regulator, argon, two-stage, high purity, delivery pressure range 30-700 kPa (4-100 psi), Matheson Tri-Gas, Model 3122-590

Regulator, oxygen, two-stage, high purity, delivery pressure range 30-700 kPa (4-100 psi), cleaned for oxygen service, Matheson Tri-Gas, Model 3810-540

Ultrasonic bath, Electron Microscopy Sciences Model 3510-MT, VWR, Cat. No. 100493-068

Vortex mixer, digital, 120V, 30W, VWR, Cat. No. 97043-564

Reagents and Materials

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used. References to water mean deionized and distilled water that is subsequently treated to produce ionically pure, 18.2 megaohm-cm, organic-free (<1 ppm), water.

Acetone, B&J Brand, >99.9%, VWR, Cat. No. BJ010

Adsorption tube, 10-mL, COSA Instrument Corp., Cat. No. MC25000 (replacement)

Argon, 99.999% pure

Ball joint with U-shaped tube, COSA Instrument Corp., Cat. No. MC28017 (replacement)

4'-Bromoacetanilide, 98% pure, Sigma-Aldrich, Cat No. 161659

4-Fluorobenzoic acid, 99+% pure, Sigma-Aldrich, Cat. No. 418846

Methanol, B&J Brand, >99.9%, VWR, Cat. No. BJ230

Oxygen, 99.999% pure

Pipet, Pasteur, disposable, borosilicate glass, 146-mm length, Fisher Scientific, Cat. No. 13-678-20A

Pipet bulb, 1-mL, Fisher Scientific, Cat. No. S34793

Pipet tips, Eppendorf epTIPS, 50-1000-μL, VWR, Cat. No. 47745-108

Potassium hydroxide cartridge, RFIC EluGen, EGC III KOH, Dionex, Thermo Fisher, Cat. No. 074532

Pyrolysis tube, inner and outer, COSA Instrument Corp., Cat. Nos. AQ3QPN (inner w/ flange joint), FN2QPG (outer), set MC28002 (replacement)

Septum, sample injection, for use with Automatic Boat Controller, COSA Instrument Corp., Cat. No. MC15652

Syringe, microsyringe, Gastight, 100- μ L, SGE, COSA Instrument Corp., Cat. No. MC18530, two required

Toluene, B&J Brand, >99.8%, VWR, Cat. No. BJ347

2,4,6-Trichlorophenol, 98% pure, Sigma-Aldrich, Cat. No. 156515

Quartz boat, samples, COSA Instrument Corp., Cat. No. MC06280

Quartz wool, fine grade, 10 g, COSA Instrument Corp., Cat. No. MC06175

Vials, autosampler, 4-mL, for use with COSA ALS Liquid Autosampler, Thermo Scientific, Cat. No. C4015-2

Caps, autosampler, for 4-mL autosampler vials, Thermo Scientific, Cat. No. C4015-45W

Vials, sample prep, 40-mL, Thermo Scientific Certified 300 Series, ThermoFisher, Cat. No. C336-0040

Water, deionized, subsequently treated with a Thermo Scientific Nanopure Water Purification System with Total Organic Carbon Analyzer to produce ionically pure, 18.2 megaohm-cm, organic-free (<1 ppm), water

Procedure

The analyst is expected to be familiar with general laboratory practices, oxygen safety, handling of flammable organics, the technique of CIC, and the equipment being used. Dispose of used reagents, materials, and samples in an environmentally safe manner according to local regulations.

Preparation of Instrument

The specifics of this procedure are written for the COSA AQF-2100H combustion system. The procedure using another model from COSA Instrument or alternative instrumentation would be similar. Follow the instructions provided with the instrumentation being used.

Combustion Preparation

1. Assemble and test all combustion system components as per the manufacturer's specifications.
2. Insert quartz wool in the end of the pyrolysis tube before inserting into the furnace. Do not connect ball joint of the GA-210 to the AQF-2100H.
 - Never touch the pyrolysis tube or quartz wool using bare hands, as skin oils can promote devitrification. Use gloves or tweezers.
 - The quartz wool should fill 3-4 mm from the ball joint end of the pyrolysis tube.
 - The quartz wool is used as a filter to prevent coke from entering the adsorption unit.
 - The quartz wool in the pyrolysis tube will devitrify over time. Replace the quartz wool if this occurs.
 - Inspect the pyrolysis tube every few months for devitrification. White discoloration would be signs of devitrification on the pyrolysis tube. These areas will become brittle, crack and cause mechanical failure. If devitrification has occurred, look for cracks in the devitrified area. Replace the tube if there are any signs of cracks in the inspected area.
 - Refer to section 6-1-2 of the HF-210 section of the Instruction Manual for a list of periodic maintenance checks.
3. Fill the quartz boat with quartz wool, packing it tightly, flush with the top of the boat.
 - The quartz wool will devitrify over time. Replace the quartz wool in the quartz boat if this occurs.
 - Inspect the quartz boat for devitrification. Replace the boat if there are any devitrified areas.

4. Turn on all modules and gases. Turn on the furnace heater. Use the operating conditions listed in Table 1.

Table 1
HF-210 Parameters

Inlet temperature	730°C
Outlet temperature	1050°C
Argon flow rate	200 mL/min
Oxygen flow rate	400 mL/min
Argon replace time	30 seconds
Valve sel. ON time	1 second
Ar→O₂ valve selection time	10 seconds
O₂→Ar valve selection time	10 seconds

5. Log into AQF software and connect to the modules needed for operation. Options are listed below (**ABC-210** will always be active):

- a. **ASC-250L, GA-210, HF-210, PC**

These modules are used for analysis of samples and standards using the *Liquid Injection* procedure.

- b. **ASC-250L, HF-210, PC**

These modules are used for testing combustion programs for using the *Liquid Injection* procedure.

- c. **GA-210, HF-210, PC**

These modules are used for analysis of samples and standards using the *Heated Sample Injection* procedure.

- d. **HF-210, PC**

This module is used for testing combustion programs for using the *Heated Sample Injection* procedure.

6. When the set temperature is reached, a pop-up window on the AQF software will notify the analyst to turn on the water pump. Set the water flow rate to 2 for analysis of samples between concentration ranges of 0.1 to 10 mg/kg.

- For higher concentration samples it may be necessary to change to the 20 mL capacity adsorption tube, raise the liquid level sensor and increase the adsorption solution volume to an appropriate level per Table 4-4 of the GA-210 section of the Instruction Manual.
 - Table 4-4 displays the volume of each position of the laser level as well as the maximum absorption solution volume.
 - Standards and samples must be analyzed under the same absorption solution conditions.
 - An increased volume of absorption solution will decrease the response of each analyte.

7. Identify the correct combustion program for each sample (see *Appendix*).

8. Pre-bake the quartz boat before analysis. (see *Appendix*)

- It is recommended to run at least 5 boat-prebakes before proceeding to Step 9.

9. Connect the ball joint from GA-210 to AQF-2100H.

Chromatography Preparation

1. Assemble and test all ion chromatographic system (IC) components per the manufacturer's specifications.

2. Install the analytical column and suppressor (configured in recycle mode).
3. Turn on the IC and set the IC to the recommended chromatographic conditions as listed in Table 2.

Table 2	
Recommended Chromatographic Conditions	
Analytical column	Dionex IonPac AS11-HC
Suppressor	Dionex ASRS 300 (4-mm)
Suppressor current	81 mA
Mobile phase	27mM KOH
Mobile phase flow rate	1.2 mL/min
Column temperature	30°C
Background	<1μS
Analysis time	12 minutes
Injection loop	25μL

4. Allow the IC to equilibrate. Typical background conductivity should be at or below 1 μ S.
 - Change the source of deionized water or check the functionality of the suppressor if the background conductivity is above 1 μ S.

Communication Between IC and AQF Software

The AQF and Chromeleon softwares do not directly communicate with each other. The AQF software initiates the injection into the IC by timed events. Set the time equal to or greater than the IC analysis time in the analysis parameters tab in the AQF software. This will ensure that there will not be an injection into the IC while the instrument is running a sample. A contact closure is set up to relay the signal to the IC to start each sample run once the combustion apparatus fills the sample loop. These connections are made during installation.

Operating Conditions

Table 1 summarizes the AQF parameters for analysis. These conditions should not be changed. See the *Appendix* for method editing for combustion programs and autosampler programs.

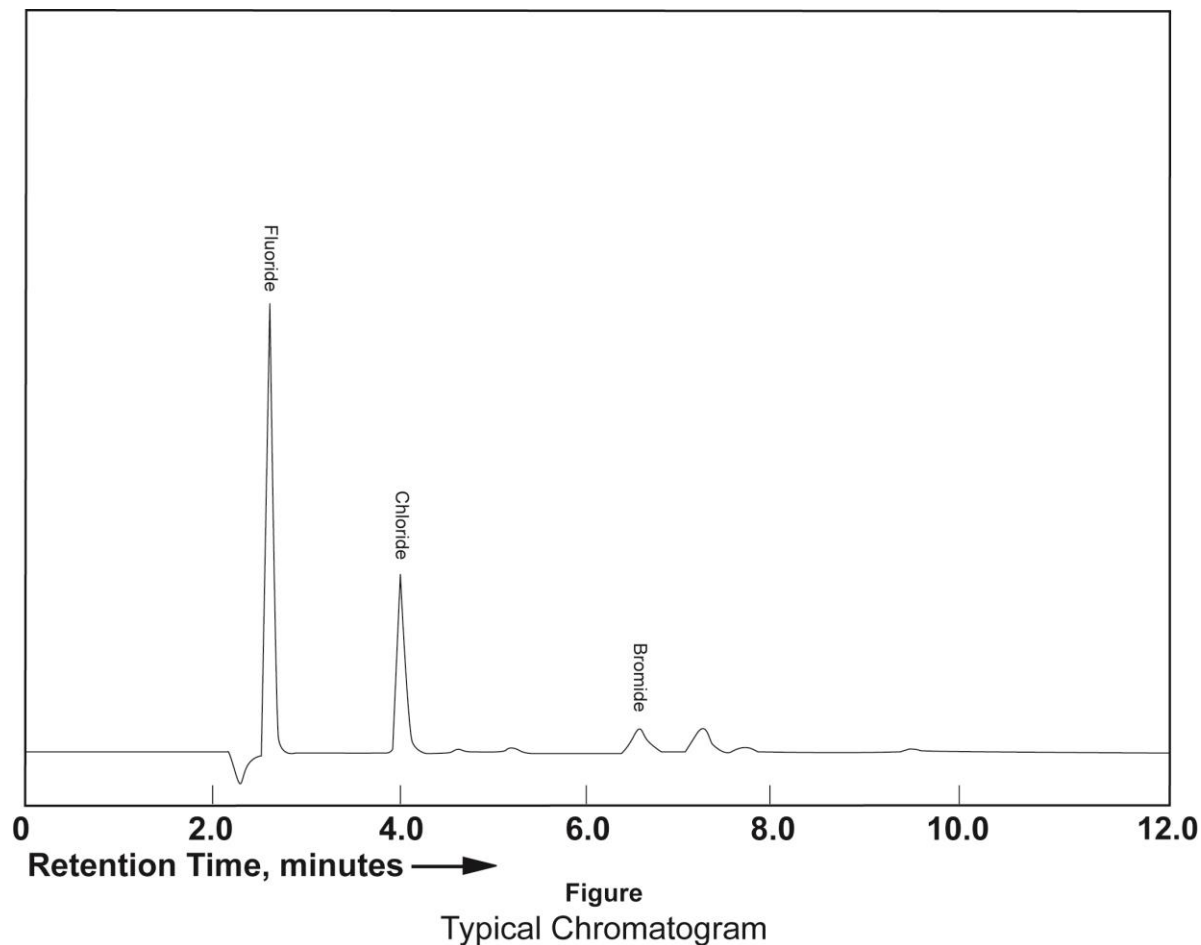
Table 2 summarizes the recommended chromatographic operating conditions for the convenience of the method user. Other conditions may be used, provided they produce the required sensitivity and chromatographic separations equivalent to those shown in the Typical Chromatogram. (See Figure).

The GA-210 uses a liquid level sensor in order to provide an adsorption solution of constant volume. For 0.1 to 100 mg/kg samples in a 10 mL capacity adsorption tube, set the liquid volume sensor to low and the adsorption solution volume to 5 mL.

- For higher concentration samples it may be necessary to change to a 20-mL adsorption tube, raise the liquid level sensor and increase the adsorption solution volume.

Calibration

Calibration factors are required that relate to the instrument response for each analyte. Detector response is measured in microsiemens (μ S) units of conductivity. It is proportional to the ionic concentration and the inherent mobility of each analyte type present when measured by the conductivity detector. External standard calibration is performed using blends and procedures described below. Calibrate the instrument with calibration standards each day samples are to be analyzed. Stock solutions, if stored in a refrigerator, are stable for six months. Calibration standards are stable for one month.



Toluene/Empty Boat Analysis

An analysis of the toluene used as diluent for the calibration solutions and samples is needed to check for chloride contamination.

1. Start the combustion and IC process with an empty sample boat under the same burn program as the standards and/or samples.
2. Identify and integrate peak areas of interest (see Figure).
 - Use the same number of accumulated injections in the empty boat as will be used with the analysis of the standard calibration solutions.
3. If background peak areas for analytes of interest are higher than 0.01 $\mu\text{S}/\text{min}$, run the default boat prebake method 5 times and re-analyze another empty sample boat blank injection. If background is still high, remove the old quartz boat. Replace it with a new quartz boat and quartz wool. Run 5 boat prebakes and then return to Step 1.
4. Fill an autosampler vial with the toluene that will be used for the calibration solutions and/or diluted samples.
5. Inject 80 μL of toluene and start the combustion and IC process under the same burn program that will be used for the standards.
 - Use the same number of accumulated injections in the toluene blank as will be used with the analysis of the standard calibration solutions.

- Identify and integrate peak areas of interest.
- The toluene background should be similar to the empty boat background. A fresh bottle from the recommended supplier will typically show this low background. If the toluene background is more than 25% higher than the empty boat background, the toluene may have become contaminated. If the background for the toluene injections is high, select a fresh bottle of toluene and repeat Steps 4-6 with the new toluene.

Preparation of Standards

Prepare individual stock solutions for each component. Alternatively, pre-made individual stock solutions may be purchased from AccuStandard or other appropriate suppliers. Standards must bracket the sample concentration range. The analyst may need to prepare higher concentration standards if needed.

- Weigh, to the nearest 0.00001 g, 0.1 ± 0.001 g of 4'-bromoacetanilide into a 40 ml sample prep vial. Add 36 ± 1 g of toluene and reweigh to the nearest 0.0001 g. Record the weights. Cap the solution and sonicate until dissolved. Label the jar: Standard Stock Solution Bromide.
- Weigh, to the nearest 0.00001 g, 0.1 ± 0.001 g of 2,4,6-trichlorophenol into a 40 ml sample prep vial. Add 52 ± 1 g of toluene and reweigh to the nearest 0.0001 g. Cap the solution and sonicate until dissolved. Record the weights. Label the jar: Standard Stock Solution Chloride.
- Weigh, to the nearest 0.00001 g, 0.2 ± 0.001 g of 4-fluorobenzoic acid into a 40 ml sample prep vial. Add 13 ± 1 g of methanol and reweigh to the nearest 0.0001 g. Cap the solution and sonicate until dissolved. Add 13 g of toluene to the jar and reweigh to the nearest 0.0001 g. Shake to mix. Record the weights. Label the jar: Standard Stock Solution Fluoride.
- Calculate the concentration of each analyte in each Standard Stock Solution to three significant figures using Equation 1.

$$A = \frac{10^6 BCD}{E} \quad (1)$$

where:

- A** = concentration of analyte in Standard Stock Solution, mg/kg
- B** = mass of compound in Standard Stock Solution, g
- C** = fraction of analyte in pure compound, decimal form, see Table 3
- D** = fraction purity of compound, decimal form, see Table 3
- E** = total mass of Stock Solution, g
- 10^6** = factor to convert to mg/kg

Table 3
Concentration of Analyte in Blend Component

<u>Component</u>	<u>Analyte</u>	<u>Fraction of Analyte in Compound</u>	<u>Purity of Compound*</u>
4-Fluorobenzoic Acid	Fluoride	0.136	0.990
2,4,6-Trichlorophenol	Chloride	0.539	0.980
4'-Bromoacetanilide	Bromide	0.373	0.980

*Check certificate of analysis for lot used

- Weigh, to the nearest 0.00001 g, 0.2 ± 0.001 g of each Standard Stock Solution in a 40 mL sample vial. Add 20 ± 1 g of toluene and reweigh to the nearest 0.0001 g. Cap the solution and vortex mix approximately 30 seconds. Label the vial: Standard Calibration Mix.

6. Calculate the concentration of each analyte in the Standard Calibration Mix to three significant figures using Equation 2.

$$F = \frac{AG}{H} \quad (2)$$

where:

- A** = concentration of each analyte in the Standard Stock Solution, from Equation 1
- F** = concentration of each analyte in each level of Standard Calibration Mix, mg/kg
- G** = mass of aliquot of Standard Stock Solution, g
- H** = total mass of Standard Calibration Mix, g

7. Prepare the 1st level standard from Standard Calibration Mix. Weigh, to the nearest 0.00001 g, 0.2 ± 0.001 g of Standard Calibration Mix in a 40 ml sample prep vial. Add 20 ± 1 g of toluene and reweigh to the nearest 0.0001 g. Cap the solution and vortex mix approximately 30 seconds. Label the vial: Standard Calibration Solution 0.1 ppm. This standard contains nominally 0.1 mg/kg of each analyte.
8. Prepare the 2nd level standard from Standard Calibration Mix. Weigh, to the nearest 0.00001 g, 0.5 ± 0.001 g of Standard Calibration Mix in a 40 ml sample prep vial. Add 20 ± 1 g of toluene and reweigh to the nearest 0.0001 g. Cap the solution and vortex mix approximately 30 seconds. Label the vial: Standard Calibration Solution 0.25 ppm. This standard contains nominally 0.2 mg/kg of each analyte.
9. Prepare the 3rd level standard from Standard Calibration Mix. Weigh, to the nearest 0.00001 g, 1.0 ± 0.001 g of Standard Calibration Mix in a 40 ml sample prep vial. Add 20 ± 1 g of toluene and reweigh to the nearest 0.0001 g. Cap the solution and vortex mix approximately 30 seconds. Label the vial: Standard Calibration Solution 0.5 ppm. This standard contains nominally 0.5 mg/kg of each analyte.
10. Prepare the 4th level standard from Standard Calibration Mix. Weigh, to the nearest 0.00001 g, 2.0 ± 0.001 g of Standard Calibration Mix in a 40 ml sample prep vial. Add 20 ± 1 g of toluene and reweigh to the nearest 0.0001 g. Cap the solution and vortex mix approximately 30 seconds. Label the vial: Standard Calibration Solution 1.0 ppm. This standard contains nominally 1.0 mg/kg of each analyte.
 - If the analytes in the samples are expected to be above 5 mg/kg, prepare standards approximating the concentrations in the samples in a manner similar to those above. If the analytes in the samples are expected to be above 100 mg/kg, quantitatively dilute the samples before analysis.
11. Calculate the concentration of each analyte in each level of Standard Calibration Solution to three significant figures using Equation 3.

$$L = \frac{FJ}{K} \quad (3)$$

where:

- F** = concentration of each analyte in the Standard Solution Mix, from Equation 2
- J** = mass of aliquot of Standard Calibration Mix, g
- K** = total mass of Standard Calibration Solution, g
- L** = concentration of each analyte in each level of Standard Calibration Solution, mg/kg

Density Correction

Calculations are performed based upon the mass of sample and calibration standard injected. Follow the steps below to determine the mass of the sample and calibration standard injected. The

measurements are added to the sequence file and the chromatography software will automatically compensate the difference of standard injection weight to sample injection weight. If the sample is viscous or waxy, heat the sample and syringe as described in *Heated Sample Injection* before proceeding.

1. Remove sample syringe from autosampler and tare syringe on the balance used for the method.
2. Rinse the syringe with material to be weighed with three syringe volumes.
3. Draw approximately 5 μL of air into the tared syringe; then draw 80 μL of sample/standard into the syringe.
4. Place syringe on balance and weigh syringe. Record the weight to nearest 0.00001 g.
 - For a sample that must be heated, weigh the heated syringe with sample and immediately dispense the contents.
5. Enter the weight in the chromatography software under the weight column for the associated sample/standard.
6. Dispense weighed liquid into the waste bottle of the autosampler.
7. Rinse syringe with 3 syringe volumes of toluene.
 - a. Repeat Steps 2-6 for all samples and standards.
 - b. Proceed to Step 8 when all standards and samples have been weighed.
8. Return the clean syringe to the autosampler and proceed to Step 3 of *Liquid Injection* for liquid samples or Step 5 of *Heated Sample Injection* for viscous or waxy samples to start the analysis.

Analysis of Standard Calibration Solutions

1. Fill sample vials with all four Standard Calibration Solutions and load them onto the liquid autosampler.
2. Inject 80 μL of Standard Calibration Solution 1 into the quartz boat of the automatic boat controller (ABC) and start the combustion and IC sequences. Identify and integrate each peak for the calibration standards. Identification can be aided by comparing to the typical standard chromatogram (see Figure).
 - Individual standards may need to be prepared to identify retention times.
 - Cumulative multiple injections in the absorption solution increase the effective concentration of the analytes of interest. For low concentrations, from 0.1-10 mg/kg, it is required to run 3 cumulative injections to increase the response of fluoride, chloride, and bromide. For concentrations from 10-1000 mg/kg, a single injection is sufficient.
3. Calculate the response factor for each analyte using the chromatography software or Equation 3 in *Calculations*.
4. Repeat Steps 3 and 4 with Standard Calibration Solutions 2, 3, and 4.

Analysis of Blank

Blank runs may be needed to check for interference or carryover from a previous analysis.

1. Start the combustion and IC process with an empty sample boat under the same burn program as the standards and/or samples.
2. Identify and integrate peak areas of interest.
3. If background peaks are higher than the lowest standard, run the default boat prebake method

five times and re-analyze another empty sample boat blank injection. If background is still high, remove the old quartz boat. Replace with a new quartz boat and quartz wool. Run five boat prebakes and then return to Step 1.

Sample Analysis

There are two types of injections listed below. Use *Liquid Injection* for samples that do not need to be heated prior to analysis. Use *Heated Sample Injection* for samples that are viscous or waxy at room temperature. Samples that are still viscous after heating must be diluted with toluene.

Liquid Injection

1. Proceed to Step 3 if the sample is not to be diluted. If the sample is to be diluted, weigh approximately 1 g of the sample into a 40 ml sample prep vial and record the weight to the nearest 0.00001 g.
2. Add approximately 9 g of toluene to the solution and record the total diluted weight to the nearest 0.0001 g. Cap the vial and vortex the sample solution for approximately 30 seconds so that the sample is thoroughly mixed.
3. Fill an autosampler vial with the sample or the diluted sample.
4. Inject 80 μL of the sample into the quartz boat and start the combustion and IC sequences.
 - If accumulated injections were run on the standards, the exact same number of accumulated injections must be run on the samples, for example if three 80- μL injections were made for the calibration standards, then three 80- μL injections are required for the samples.
5. Identify each analyte by retention time (see Figure). Integrate the analyte peaks of interest to calculate the area response.
6. If the areas obtained for any of the analytes are above the highest standard, prepare quantitative serial dilution(s) of the sample. This is done by diluting the sample or sample solution in toluene on a mass/mass basis until the resulting chromatographic analyte peak areas fit within the calibration standards. Record the weights of each serial dilution to the nearest 0.00001 g. Label as Serial Diluted Sample (X). Repeat Steps 3 and 4 of *Liquid Injection* for the serially diluted sample(s).

Heated Sample Injection

1. Turn on the digital block heater. The heater should not exceed 70-80°C.
2. Place sample vial in heater block until sample is liquefied.
3. Remove the sample vial from heater block, uncap, and pour an aliquot into an autosampler vial.
4. Place the autosampler vial into the vial heater to keep warm.
5. Slide the autosampler away from the injection port of the automatic boat controller and inject 80 μL of sample directly into the quartz boat. Start the combustion and IC sequences.
 - If accumulated injections were run on the standards, the exact same number of accumulated injections must be run on the samples, for example, if three 80- μL injections were made for the calibration standards, then three 80- μL injections are required for the samples.
 - Place the syringe on the heater block to warm up to the same temperature as the sample. This will prevent the sample from solidifying in the syringe when trying to inject into the quartz boat in the automatic boat controller.
6. Identify each analyte by retention time (see Figure). Integrate the analyte peaks of interest to calculate the area response.

7. If the areas obtained for any of the analytes are above the highest standard, prepare quantitative serial dilution(s) of the sample. This is done by diluting the samples in toluene on a mass/mass basis until the resulting chromatographic analyte peak areas fit within the calibration standards. Record the weights of each serial dilution to the nearest 0.00001 g. Label as Serial Diluted Heated Sample (X). The vials may need to be heated to ensure the sample is completely dissolved. Weigh the syringe as described in *Density Correction*, and repeat Steps 4 and 5 in *Heated Sample Injection* for the serially diluted and heated samples.

Calculations

All calculations are performed by the instrument software and results are displayed and printed in mass-ppm (mg/kg). If the sample and standard vary in density, the masses of an 80-μL liquid injection of the samples and standards are entered during sample data entry to compensate for the difference. The calculations below are included for information and for single point manual calculation, if desired.

Calculate the response factor for each analyte in the standard calibration solutions to three significant figures using Equation 4.

$$M = \frac{L}{N} \quad (4)$$

where:

L = concentration of each analyte in each level of Standard Calibration Solution, mg/kg, as defined in Equation 3

M = response factor for each analyte

N = analyte response area

Calculate the dilution factor for each sample to three significant figures using Equation 5. Proceed to Equation 6 if the sample was not diluted. The dilution factor = 1 if no dilution was made.

$$R = \frac{P}{Q} \quad (5)$$

where:

P = total mass of sample and diluent (*Liquid Injection*, Step 2), g

Q = total mass of sample weighed (*Liquid Injection*, Step 1), g

R = dilution factor for diluted sample solution

Calculate the ratio of standard weight injected to sample weight injected to three significant figures using Equation 6.

$$U = \frac{S}{T} \quad (6)$$

where:

S = weight of standard injected

T = weight of sample injected

U = ratio of standard weight injected to sample weight injected

Calculate each analyte concentration in the original sample to the nearest 0.1 mg/kg, not to exceed two significant figures, using Equation 7.

$$\text{Concentration of analyte in sample or sample solution, mg/kg} = (MRUV) \left(\frac{W}{Z} \right) \quad (7)$$

where:

M = response factor for each analyte, from Equation 4

R = dilution factor for diluted sample solution, from Equation 5

U = ratio of standard weight injected to sample weight injected, from Equation 6

V = Area of peak of each analyte in sample

W = final diluted sample mass (if serial dilution is needed), g
Z = mass of IC sample stock solution aliquot (if serial dilution is needed), g
 If no serial dilution is required, **W/Z = 1**

Precision

Precision statements were determined using UOP Method 999, "Precision Statements in UOP Methods."

Repeatability and Site Precision

A nested design was carried out for determining halogens in liquid organics by two analysts, with each analyst performing analyses on four samples on two separate days, performing two analyses each day for a total of 32 analyses. Using a stepwise analysis of variance procedure, the within-day and within-lab estimated standard deviations (esd) were calculated at the concentration means listed in Table 4. Two analyses performed in one laboratory by the same analyst on the same day should not differ by more than the repeatability allowable differences shown in Table 4 with 95% confidence. Two analyses performed in one laboratory by different analysts on different days should not differ by more than the site precision allowable differences shown in Table 4 with 95% confidence.

Table 4
Repeatability and Site Precision, mg/kg

Component	Mean	Repeatability		Site Precision	
		Within-Day esd	Allowable Difference	Within-Lab esd	Allowable Difference
Chloride	0.1	0.01	0.1	0.01	0.1
Chloride	1.4	0.08	0.3	0.09	0.3
Chloride	10.7	0.25	1.0	0.35	1.4
Chloride	16.7	0.34	1.4	0.36	1.4
Fluoride	0.1	0.01	0.1	0.01	0.1
Fluoride	0.6	0.11	0.4	0.21	0.9
Fluoride	8.8	0.12	0.5	0.41	1.9
Fluoride	13.8	0.49	1.9	0.49	2.5
Bromide	0.1	0.02	0.1	0.02	0.1
Bromide	1.3	0.14	0.6	0.14	0.6
Bromide	12.2	0.32	1.3	0.38	1.5
Bromide	17.8	0.36	1.4	0.52	2.0

The data in Table 4 represent short-term estimates of the repeatability of the method. When the test is run routinely, use of a control standard and a control chart is recommended to generate an estimate of long-term repeatability.

Reproducibility

There is insufficient data to calculate the reproducibility of the test at this time.

Time for Analysis

The elapsed time for the preparation and analysis of one sample, including the analysis of a blank and calibration, is 2 hours. The labor requirement is 1 hour.

Suggested Suppliers

AccuStandard, 125 Market St., New Haven, CT 06513, USA (203-786-5290)
www.accustandard.com

COSA Instrument Corp., 55 Oak St., Norwood, NJ 07648, USA (201-767-6600), distributor for Mitsubishi Chemical Analytech 370 Enzo, Chigasaki, Kanagawa Pref., 253-0084, Japan (+81-467-86-3864) www.cosa-instrument.com

Thermo Fisher Scientific Company LLC, 4500 Turnberry Dr., Hanover Park, IL 60133, USA www.thermoscientific.com

Fisher Scientific, 711 Forbes Ave., Pittsburgh, PA 15219-4785, USA (412-490-8300) www.fishersci.com

Grace Davison Discovery Sciences, 2051 Waukegan Rd., Deerfield, IL 60015, USA (847-948-8600) www.discoverysciences.com

Matheson Tri-Gas, 166 Keystone Dr., Montgomeryville, PA 18936, USA (215-641-2700) www.mathesontrigas.com

Sigma-Aldrich, Milwaukee, WI 53201, USA (414-438-3850) www.sigma-aldrich.com

VWR International, 1310 Goshen Parkway, West Chester, PA 19380, USA (610-431-1700) www.vwr.com

Appendix Combustion Methods

The correct combustion program is needed to prevent coking in the combustion furnace and adsorption unit. Use Table A1 as a reference to start the process of identifying the appropriate combustion program for analysis. Do not carry over combustion programs from older instruments as small differences in pyrolysis tube length and furnace insulation have a great effect on combustion programs. The analyst must create methods associated with their sample matrices. Refer to the ABC-210 Manual, Section 4-1, for further assistance.

Table A1
Combustion Programs, Showing Boat Injector Position (Pos.) and Time in Seconds

	1 st		2 nd		3 rd							
<u>Program</u>	<u>1st</u>	<u>Pos.</u>	<u>2nd</u>	<u>Pos.</u>	<u>3rd</u>	<u>Pos.</u>	<u>End</u>	<u>Cool</u>	<u>Boat</u>	<u>Home</u>	<u>Ar</u>	<u>O₂</u>
	<u>Pos.</u>	<u>Time</u>	<u>Pos.</u>	<u>Time</u>	<u>Pos.</u>	<u>Time</u>	<u>Time</u>	<u>Time</u>	<u>Speed</u>	<u>Time</u>	<u>Time</u>	<u>Time</u>
Toluene	95	90	115	30	140	15	100	60	10	30	5	300
Diesel	125	95	145	45	175	15	100	60	10	30	5	300
Tallow	145	95	165	25	215	15	100	60	10	30	5	300
Dilute Tallow	100	90	145	90	170	30	100	60	10	30	5	300
Boat Prebake	0	0	0	0	0	0	120	60	20	30	0	120

A flash of light coming from the combustion of the sample should begin within 15 seconds of the start of the first position, grow to a maximum intensity and dim by the beginning of the second position. Position 3 is typically used for a safeguard to combust any leftover sample around the temperature range of position 2 before it is sent to the end of the furnace for bake-off. Diluted samples will have two stages of combustion, one for the diluent in the first position, and one for the sample in the second position. A very intense and fast flash of light leads to coking. If coking does occur while testing combustion conditions, turn off all gases and modules. Once the furnace is at ambient temperature, disconnect the contaminated glassware and clean with the appropriate solvent. Bake glassware in a furnace for approximately 1-2 hours. All quartz glassware can be baked at 800°C. All other standard glassware should be baked at 400°C.