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Methods of Collection and Analysis of Acid Gases in Fire Tests

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16. Abstract

This report documents proven methods of collection and analysis for acid gases in fire tests conducted at the FAA Technical Center. It focuses on methods of collection and analysis requiring trapping hot acid gases at the sampling point and avoiding errors due to sample line losses. The sampling system, collection tubes and procedures are described in this report. Various ion chromatography methods are described which separate and quantify the solution concentration of the anions corresponding to the gases HF, HCl, HBr, HI, HCN, H_2S, HIO_3, H_3PO_4, NO_x and SO_x in complex combustion gas matrices. The ion chromatography methods include the separator columns, suppressor columns, eluents, detectors and autosamplers. The fluoride ion selective electrode method is also evaluated.

17. Key Words Combustion gases, ion chromatography, columns, fluoride ion selective electrode, acid gases, analysis, combustion gas, fire, sampling system, response time, toxicity, sample line losses, acid gas collection, sample tube, acid gas analysis, HF, HCl, HBr, HI, HIO_3, H_3PO_4, NO_x and SO_x	18. Distribution Statement This document is available to the U.S. public through the National Technical Information Service (NTIS), Springfield, Virginia 22161. This document is also available from the Federal Aviation Administration William J. Hughes Technical Center at actlibrary.tc.faa.gov.

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Acronyms

Acronym	**Definition**
APU	Auxiliary power unit
BPC	Bisphenol C, (2,2-bis-(4- hydroxyphenyl)-l,l-dichloroethylene)
2-BTP	2-Bromo-3,3,3-trifluoroprop-1-ene
CFR	Code of Federal Regulations
FAA	Federal Aviation Administration
FTIR	Fourier Transform Infrared Spectroscopy
HEPA	High efficiency particulate air [filter]
IC	Ion chromatography
i.d.	Inside diameter
ISE	Ion selective electrodes
M	Molarity (moles/liter)
µeq	Microequivalents
MPS	Minimum performance standard
o.d.	Outside diameter
ppm	milligram anion/liter solution (mg/l)
ppmv	liters of gas/liters of air x 10^6
PFA	Perfluoroalkoxy polymer
PTFE	Polytetrafluoroethylene
SS	Stainless steel

Glossary

Term	Definition
Analytes	The substances whose chemical constituents are being identified and measured (i.e., toxic acid gas) in the analytical procedures described in this report.
Blank sample tube assemblies	Sample tube assemblies where no sample is drawn used to address the diffusion into the tubes. They also address unintended sampling due to pressurization of the compartment during a fire test.
Breakthrough collection tube	The second of two collection tubes in series used to check the collection efficiency of the first tube or of a tube assembly.
Column capacity	Ion exchange column capacity is a measurement of the number of positive charges (cations) or negative charges (anions) that the exchange resin can bind to and is reported in singly charged ion equivalents.
Dead volume	The excess gas volume that the sampling system needs to draw that will lengthen the time for the desired flow rate to be reached (for point of sampling gas sampling systems). Large filters and long sample lines contribute to the dead volume.
Eluent	The liquid solvent in ion chromatography that transports the analytes through the separator columns and detectors of the ion chromatograph.
Eluent generator	Produces high purity eluents for ion chromatography and is a part of Reagent-Free Ion Chromatography™ (RFIC™). The entire process only requires deionized water and eluent generator cartridges, eliminating the need to handle any bases. The feed water is degassed, minimizing absorbed carbonate buildup in the eluent over time. This prevents baseline shift, increases sensitivity, improves resolution, and ensures consistent peak integration.
Eluent generator cartridges (EGC)	Eluent generator KOH cartridges produce hydroxide eluents. These cartridges eliminate the need to handle KOH solutions, which are traditionally required for the preparation of IC eluents and allows chromatographers to run a full range of gradient and isocratic separations more effectively than hand-made eluents.
Elute	Recover an absorbed or adsorbed substance by washing with a solvent.
Equivalent	The number of moles of an anion multiplied by the charge of that anion in solution.
Fluoride ion selective electrode	A transducer that converts the activity of a specific ion (i.e., in this case fluoride) dissolved in a solution into an electrical potential in units of joules per coulomb (i.e., volts). The electrical voltage is dependent on the logarithm of the ionic activity, according to the Nernst equation[1].

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[1] https://www.gstatic.com/education/formulas2/443397389/en/nernst_equation.svg

Term	**Definition**
Fourier-transform infrared (FTIR) spectroscopy	A technique used to obtain an infrared spectrum of absorption or emission of a solid, liquid or gas. A laser is used to send infrared radiation through a sample, some radiation is absorbed and some passes through the sample. A mathematical technique called the Fourier transformation is used to manipulate the measured signal to produce a spectrum. The resulting spectrum represents the unique molecular absorption and transmission of a specific molecule. FTIR spectra can be used to quantify gas concentrations.
Gradient elution	The continuous change of the mobile phase composition during a chromatographic run.
Impinger	A vessel, sometimes known as a bubbler, used with an air sample pump to collect airborne gases into a collection solution. A calibrated flow of air is bubbled through the impinger that contains a specific liquid volume which reacts with or absorbs the chemical of interest.
Ion chromatography	A method for separating and quantifying the carrier portion of the mobile phase ions based on their interactions with resin (stationary phase) and the eluent (mobile phase).
Isocratic elution	The elution method with no changes of the mobile phase composition taking place during a chromatographic run.
Matrices	The term gas matrix is used to describe everything that is present in the typical sample except for the analytes of the interest.
Milligrams per liter (mg/L)	A solution concentration unit expressed as milligram of the analyte anion per liter of solution. This term is equivalent to “ppm.”
Parts per million (ppm)	A solution concentration unit expressed as milligrams of the analyte anion per liter of solution. This term is equivalent to “mg/L.”
Parts per million by volume (ppmv)	A gaseous concentration unit equivalent to microliters of gas per liter of gas which has the units µL/L.
Pre-tube	A narrow bore tube placed upstream of a sample tube that minimizes unintended sampling due to diffusion of the analyte gas.
Primary collection tube	The first two collection tubes in a series used to check the collection efficiency of the first tube.
Sample tube	Composed of a pre-tube in a series with 1or 2 collection tubes.
Sample matrix	Everything that is present in that sample except for the analytes of interest.
Snoop® leak detector	A solution composed of deionized water and a surfactant that produces sustained bubbling. Snoop is used to detect gas leaks in plumbing.
t90	The amount of time that it takes to reach 90% of the maximum flow into a gas sample tube, where there is no sample line leading to that sample tube.

Executive summary

This report describes proven methodologies used to collect, identify, and measure toxic acid gases generated in aircraft fire tests conducted at the FAA Technical Center (FAATC). This report focuses on methods of collection and analysis requiring trapping hot acid gases at the sampling point, which avoid errors due to line loses of acids on moist sample lines.

The sampling method was developed and optimized at the FAATC. Time sequenced sampling of sample tubes are used to obtain concentration histories of acid gases. Sample tubes are used to trap the acid gases, which are then eluted with a basic solution. The solution is then filtered and analyzed.

Various ion chromatography methods are evaluated which separate and quantify the anions corresponding to the gases HF, HCl, HBr, HI, HCN, H_2S, HIO_3, SO_x and NO_x in complex combustion gas sample matrices. The methods include the separator columns, suppressor columns, eluents, detectors and autosamplers. Columns and methods are recommended for various separation. An independent fluoride ion selective electrode method is also evaluated.

The resultant toxic acid gas histories obtained from fire tests may be input into toxicity survival models. Micro-scale to full-scale fire tests have been supported with these methods.

This collection method coupled with ion chromatography analysis can be used as a primary method to check acid gas cylinders for post-calibration gas cylinder losses of the reactive acids. These methods of collection and analysis can also be used to validate other methods of analysis of acid gases generated in fires such as particular Fourier Transform Infrared Spectroscopy (FTIR) methods.

1 Introduction

1.1 Purpose

This report describes methodologies and techniques currently employed to collect, identify, and measure acid gases produced in fire tests conducted by the Fire Safety Branch at the FAATC. This report focuses on methods employing the trapping of hot acid gases in collection tubes positioned at the sampling point, avoiding errors due to line and filter losses on moist surfaces.

Specialized open-path acid gas absorption tubes, sampling system, sampling procedures and methods of analysis are described in this report. Sample tubes trap each analyte (toxic acid gas). The tubes are later eluted, and the resulting solutions are analyzed for each anion of interest using ion chromatography (IC). The sampling system described provides accurate time-sequenced sampling of acid gases in fire tests.

The sample tubes have advantages over traditional techniques of acid gas collection.

The methods of analysis described include ion chromatography (IC) and fluoride ion selective electrodes (ISE) which are demonstrated to accurately measure anions in complex combustion gas matrices. The resultant acid gas histories obtained from fire tests may be used to assess toxicity. These toxic gas histories may be input into survival models. The minimum performance standard (MPS) for aircraft applications (hand extinguishers (Webster, 2002) and cargo compartment fire suppression system (Reinhardt, Blake, & Marker, 2000) do not currently mandate acid gas analysis. However future use of these standards may require this information. Other MPS for engine/APU and lavatory trash receptacle fire extinguishers may use this information as well.

The resultant toxic acid gas histories obtained from fire tests may be input into toxicity survival models. The methods of collection and IC analysis can also be used to assess accuracy and applicability of other methods of monitoring acid gases including FTIR, which has been reported to have the disadvantage of sample line losses of acid gases. FTIR has the potential for use in continuous monitoring of many acid gases in fire tests and the FTIR results can be verified by collecting samples and analyzing them by IC.

Troubleshooting techniques are provided to ensure the accurate operation of the sampling system. Suggested methodologies for software support is also provided. This document is not intended to limit the methods of collection and analysis employed.

1.2 Background

According to Title 14, Code of Federal Regulations, Part 25.831, "Crew and passenger compartment air must be free from harmful or hazardous concentrations of gases or vapors." This includes decomposition products of aircraft materials as well as extinguishing agents and their decomposition products (FAA/DOT, 2022). In addition, Part 25.851(a) for hand extinguishers, requires "Each extinguisher intended for use in a personnel compartment must be designed to minimize the hazard of toxic gas concentration." Part 25.851(b) for built-in fire extinguishing systems, requires "No extinguishing agent likely to enter personnel compartments will be hazardous to the occupants." Agent/fume penetration is addressed in Part 25.855 (h) and 25.857(b), (c) and (f): Part 25.855 requires, "Flight tests must be conducted to show compliance with the provisions of Section 25.857 concerning-- The entries of hazardous quantities of smoke or extinguishing agent into compartments occupied by the crew or passengers." Part 25.857(b), (c) and (f) require, "There are means to exclude hazardous quantities of smoke, flames, or extinguishing agent, from any compartment occupied by the crew or passengers."

Reviews of safe exposure levels of acid gasses are available (NFPA, 2015; Technical Committee: ISO/TC 92/SC3, 2012; Speitel L. C., 1995; Speitel L. , 1996; American Conference of Industrial Hygienists, 1990-1991). Acceptable limits of acid gases are specified in the minimum performance standard (MPS) for hand extinguishers (Webster, 2002).

Gases routinely measured for fire tests conducted at the FAATC are CO, CO_2, O_2, and total hydrocarbons. These gases are measured with continuous analyzers. Other gases measured are the acid gases HF, HCl, HBr, HI, HCN, NO, NO_2, SO_2, CS_2, COS, H_3PO_4, as well as individual hydrocarbons and H_2. These gases are quantified with instrumental methods of analysis including ion chromatography (IC), fluoride ion selective electrode (ISE), Fourier transform infrared spectroscopy (FTIR), gas chromatography (GC) as well as by gas analyzers.

FTIR has been used to measure acid gas histories in fire tests (ISO/TC92, 2015; Speitel L. C., 2001). Line losses and filter losses can be minimized by using heated sample lines since the very water-soluble acid gases dissolve on moist surfaces. Some acid gases such as hydrogen fluoride (HF) have significant losses even with heated sample lines and filters heated from 165 to 180°C. These can be accounted for by rinsing lines and filters after each test and analyzing the wash solution by ion chromatography (Larson, Andersson, Blomqvist, & Mellander, 2017; Hakkarainen, et al., 1999; Blomqvist & Simonson-McNamee, 2010). However, the shape of the gas concentration history curves may not be accurately captured by elution of sample lines and filters if there are major line losses.

Ion chromatography can be used as the primary method of analysis of acid gases in fire tests. Sample line losses can be minimized by not using probes, sampling lines and filters. Semi-continuous concentrations histories can be obtained by time sequencing sample collection into a series of sample tubes. See Table 1 for different types of collection tube specifications.

Sample tubes can be used to trap acid gases, with the sample tube inlet at the sampling point. These sample tubes contain glass beads that are coated with a strong basic solution. Specialized point-of-sample tubes were developed in the 1970s by the FAA Fire Safety Branch and upgraded over time. Diffusion of the sample into the front face of tube was minimized by placing a short narrow bore tube upstream of the sample tube.

These sample tubes also provide advantages over the traditional impinger method of acid gas sampling of fire gases (Spurgeon, 1976; Hill, Brown, Speitel, Johnson, & Sarkos, 1984). These collection tubes replaced traditionally used impingers which develop flow restrictions with fire gases as tars build up at the impingers' frits and tips, respectively. Open tipped impingers have a more open flow path than fritted impingers but have a poorer collection efficiency. The poorer collection efficiency of open tipped impingers is due to the short contact time of each entrapped gas molecule in its larger bubble, and the small contact area of each gas molecule with the collection solution. As the bubble size decreases, the collection efficiency increases. The collection efficiency can be increased by decreasing the flow rate for both impingers and collection tubes. These sample tubes, unlike impingers, have an open flow path, minimizing this flow restriction problem. The tortuous path of the gas transport through the coated beads of the collection tube provides a large contact area of the acid gases with the coated beads (Spurgeon, 1976; Hill, Brown, Speitel, Johnson, & Sarkos, 1984). These collection tubes are more compact and are easier to handle, clean and reuse than impingers. This results in reduced labor hours and the potential for collecting many more samples per test.

Many collection tubes can be used to obtain concentration histories. Concentration histories provide a more accurate assessment of toxicity than time-averaged samples, since toxicity of acid gases is not directly proportional to exposure time (Speitel L. C., 1995; Speitel L. , 1996; Hartzell, Packham, Grand, & Switzer, 1985; Crane, Sanders, Endecott, & Abbott, 1985; Sakurai, 1989).

The first-generation gas sample tubes were introduced in the 1970s at the FAA as a method of simplifying the collection of acid gases and replacing more cumbersome impinger method of sampling.

Collection efficiency studies were done at that time to validate the collection method (Spurgeon, 1976; Hill, R.G., Boris, P., 1976). These early sample tubes were made entirely of glass. Various types of collection tubes have been used by FAA and others.

Table 1. Collection tube specifications

Generation	**Tube Material**	**Tube ID (mm)**	**Capacity**	**Tube Length (wide part)**	**Length of Packed Beads**	**Tube OD**	**Tube ID (mm)**	**Bead Size (mm)**	**Retainer**	**User**
1	Glass	8	Medium	15.2cm 5”	13cm 5”	10mm	8	1	Glass wool	FAA*
2a	Glass-lined SS	4	Low	16.5cm	14cm	¼”	4	1	Glass wool	FAA*
2b	Glass-lined SS	4	Low	16.5cm	14cm	¼”	4	3	Slice of Teflon™	FAA
3	PFA	6	Medium	16.5cm	13cm	8mm	6mm	3	Slice of Teflon™	FAA
4a	PFA	9	High	28cm 11”	26cm	½” 13mm	9	4	Slice of PFA tube	FAA
4b	PFA	9	High	28cm 11”	28cm	½” 13mm	9	3	½” Diam. SS mesh disk	Boeing

*No longer in use

The Generation 1 tube, shown in Figure 1, was fabricated using 10mm o.d., 8mm i.d. glass tubing cut into six-inch lengths. The tube was filled with 1mm glass beads. Glass wool retainers were used. Both ends of the collection tube were joined with heat-shrink tubing to one-inch long 2mm i.d. tubes.

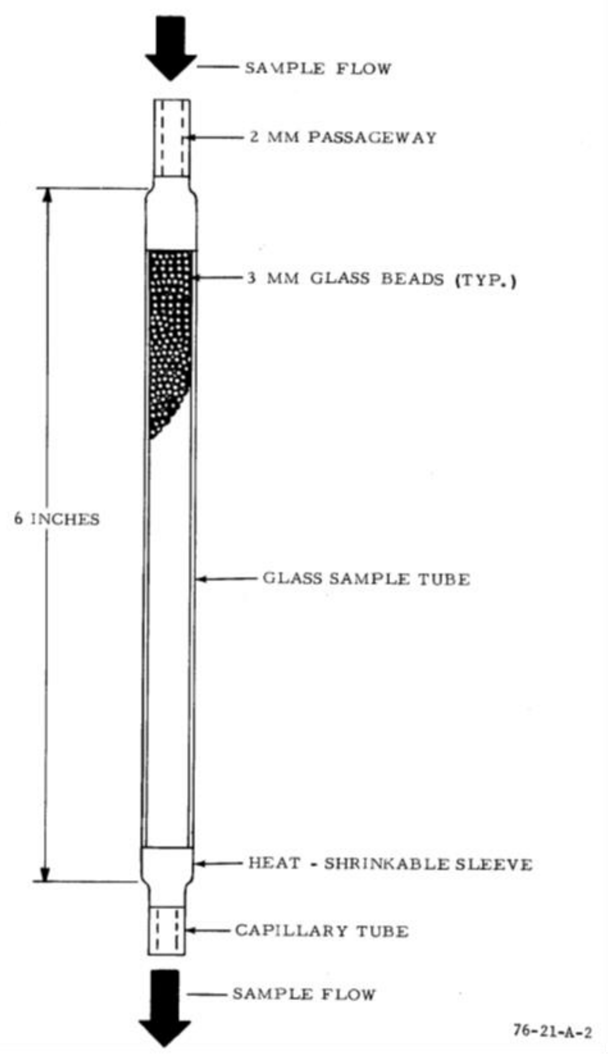


Figure 1. Generation 1 sample tube

The second generation of sample tubes were constructed of glass-lined stainless steel and were more robust than 1st generation glass tubes. The second-generation tubes were designed to facilitate cooling and to be mounted in an ice-water bath to prevent drying of the internal coating of the glass beads during the fire test and prior to sample tube recovery. The tube had a ¼” o.d, 4mm i.d and had a length of 6.5” (16.5 cm). The body of the second-generation collection tubes are shown in Figure 2.

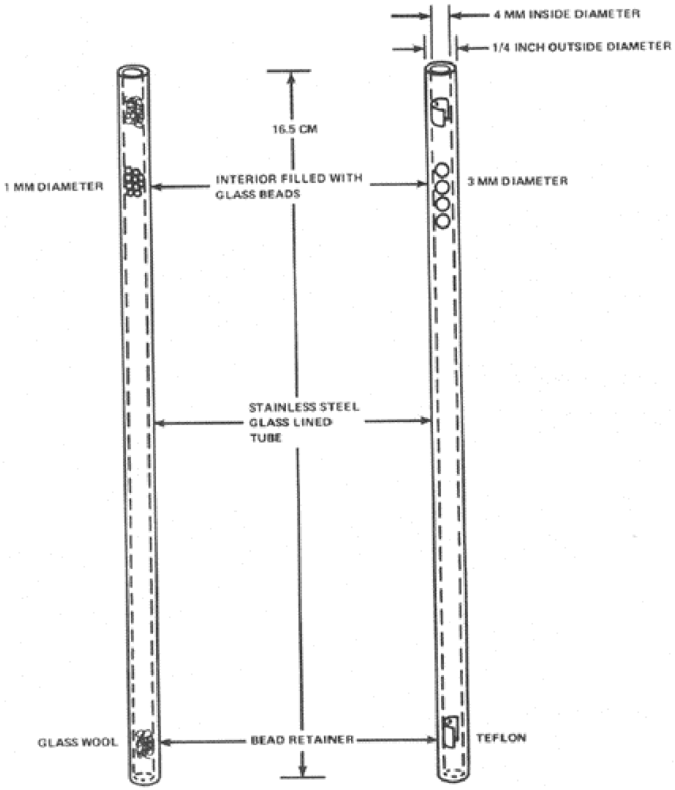


Figure 2. Second generation collection tubes, versions a and b

Generation 2a used 1mm borosilicate glass beads with a glass wool retainer (Hill, Brown, Speitel, Johnson, & Sarkos, 1984). The glass wool retainers were found to progressively restrict flow due to soot buildup during fire tests (Hill, Brown, Speitel, Johnson, & Sarkos, 1984; Guastavino, Speitel, & Filipczak, 1983). Generation 2a tube had no pre-tube.

Generation 2b has a more open flow path. The glass wool retainers were replaced with Teflon™ retainers (a slice of tubing pressed into the tube at each end) and the bead size was increased to 3mm (Guastavino, Speitel, & Filipczak, 1983). Generation 2b tubes used a three to four inch long, 2mm i.d. pre-tube. The capillary pre-tube was used to minimize diffusion, unintended sampling during a fire test.

The collection efficiencies of the improved second-generation tubes were excellent: 98percent of a 150ppm HF plus 1800 ppm HCl fire test sample was collected in the first 2/3rds of the 16.5 cm tube for a 1.8-liter sample volume. (Hill, Brown, Speitel, Johnson, & Sarkos, 1984; Hill & Speitel, 1982; Guastavino, Speitel, & Filipczak, 1983; Slusher, Wright, & Speitel, 1986).

The tube construction of the third and fourth generation collection tubes is discussed in the body of this report. These tubes are medium and high capacity, respectively. The fourth-generation gas sample tube was larger in length and in inner diameter. It was designed to trap extremely high concentrations of acid gases. HF concentrations higher that 5% have been collected using these tubes (Speitel L. , 1998). This high-capacity sample tube was introduced in the 1990s for cargo fire tests of candidate halon replacement extinguishing agents. It has a larger internal radius of 9mm and is longer than the second-generation tube. Generation 4a collection tubes are filled with 4mm glass beads. It uses a non-restrictive Teflon™ retainer and a 2mm i.d. four-inch-long glass pre-tube (Speitel L. , 2020). Boeing Aircraft Company modified these generation 4a tubes into generation 4b collection tubes for cargo fire tests conducted at their facility. They used rigid 304 stainless steel mesh ½” diameter screen disks as bead retainers which allowed them to use smaller 3mm i.d. glass beads. Heavy metal buildup is known to decrease retention time and resolution of anion exchange columns. However, no column deterioration was noticed for the test series. The same size mesh disks are also available in 316 stainless steel.

The generation 2b low capacity, the generation three medium capacity and the generation four high-capacity tubes are still in use for fire tests conducted at the FAA.

The first multi-tube sampling system for acid gases was introduced in the 1970s which used time-sequenced sample tubes with two 3 ½ liter evacuated gas bottles. As one bottle is evacuated, the other draws a sample through a sequentially determined sample tube. It required 30 seconds to draw a 3.5-liter sample (Spurgeon, 1976; Hill, R.G., Boris, P., 1976; Guastavino, Speitel, & Filipczak, 1983; Hill & Speitel, 1982). See Figure 3.

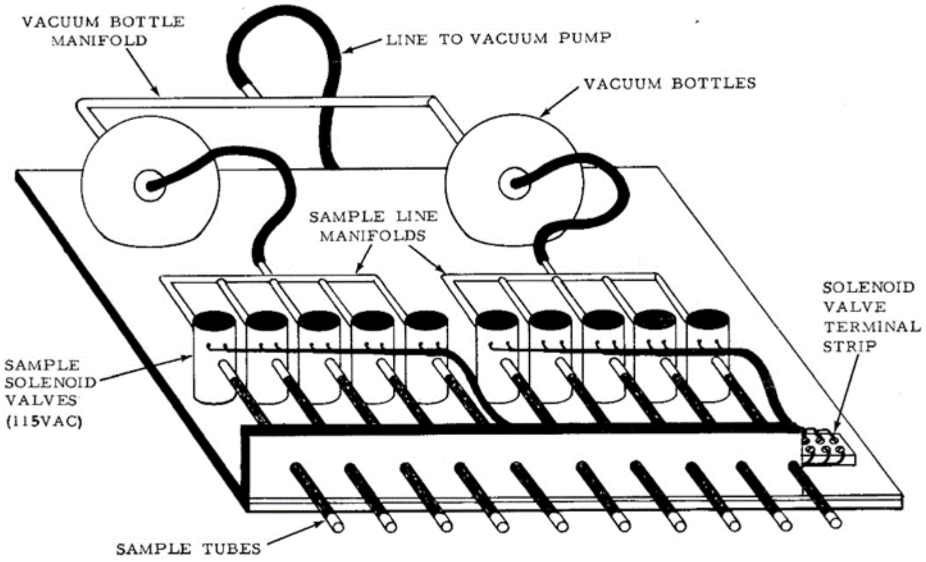


Figure 3. Sample board assembly for cabin fire tests

Flowmeters, water traps and filters were used later to set the flow and protect the downstream hardware (Hill, Brown, Speitel, Johnson, & Sarkos, 1984; Webster, 2002; Reinhardt, Blake, & Marker, 2000; Blake, 1998). This report shows the current sampling system used.

Figure 4 shows the concentration HF histories obtained for cargo fire suppression tests of Halon 1301 and HFC-125 using generation 4a sample tubes (Blake, 1998). Each time-averaged tube is shown as an average concentration for the sampling duration.

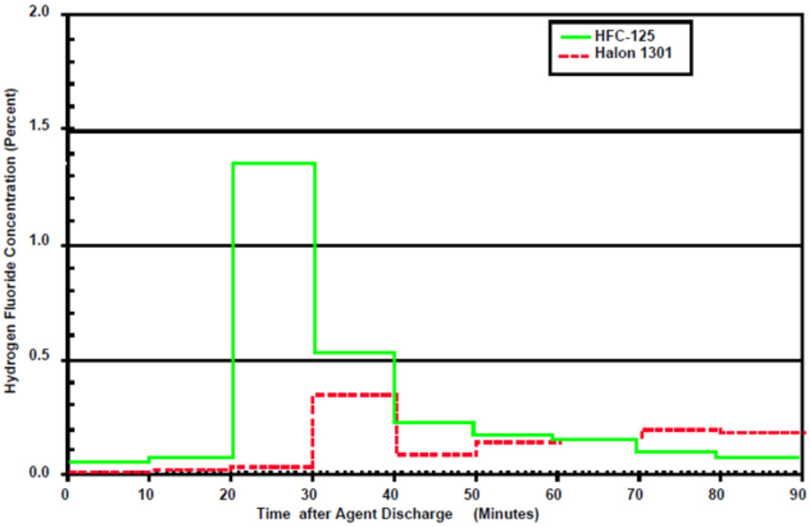


Figure 4. HF profiles in cargo compartments during bulk-loaded fire suppression tests

Historical applications of acid gas analysis at the FAA include decomposition products of burning materials for combustion tube furnace, pyroprobe, cone calorimeter and full-scale fire tests (Guastavino, Speitel, & Filipczak, 1982; Hill & Speitel, 1982; Hill, Brown, Speitel, Johnson, & Sarkos, 1984; Lyon, 2006; Webster, 2002; Quinteire, Speitel, Guo, Crowley, & Houston, 2018) (Slusher, Wright, & Speitel, 1986; Blake, 1998; Marker, 1999; Hill, Marker, & Sarkos, 1992; Marker, 1991; Hill, R.G., Boris, P., 1976). Full-scale fire tests include tests evaluating halon and halon replacement agents for handheld extinguishers to extinguish seat fires and for the suppression of cargo fires. Additional applications for acid gas analysis include lithium metal and lithium-ion battery fire tests using halon replacements handheld extinguishers.

2 Acid gas collection

Gas concentration histories are obtained by sequenced sampling of multiple gas sample tubes for the test duration. The number of tubes is selected that need to obtain the time resolution required for the toxicity assessment of a particular fire test. Tests run at the FAATC used up to 10 sequenced sample tubes per location. Time per tube has historically ranged from 30 seconds to 10 minutes depending on the test requirements. For example, 10 sample tubes and a sample time of one minute per tube would support a 10-minute test duration.

Sample tubes are positioned at the sampling point, with no tubing upstream. This avoids high sample losses from absorption of the water-soluble analyte on moist surfaces prior reaching the sample tubes. This problem is discussed in the background section of this report.

Blank sample tubes, where no sample is drawn, are used to address the diffusion into the sample tubes. They also address unintended sampling due to pressurization of the compartment during a fire test.

2.1 Gas sample tubes

The anions of the acid gases are collected based the principles outlined below:

- The open flow path enables a constant flow rate through the sample tube during sampling.
- The tortuous path of the gas transport through the coated beads of the collection tube provides a large contact area of the acid gases.
- The sampled acids passing through the collection tube react with the basic solution coating of the glass beads, to form salts which are trapped in the tubes.
- Acids and their salts are very soluble in water.

- The collection tubes are cooled in an ice water bath to prevent vaporization of the basic solution coating the glass beads, and the resultant drying of the coated beads.
- The solubility of acid gases increases as the temperature decreases.
- Sampling hot test atmospheres may dry the glass beads resulting in blow-through of the analyte salt out of the collection tube. The tubes are cooled in an ice-water bath to prevent this.
- Many sample tubes (in proximity) are time sequenced to obtain concentration histories of each acid gas of interest.
- Collection tubes in series are used to assess the collection efficiency of the first tube.

Each sample tube consists of a pre-tube, and one or two collection tubes. The first collection tube is called the primary collection tube. The second collection tube is called a breakthrough collection tube. Preparing the sample and breakthrough tubes involves coating the internal glass beads with a NaOH solution immediately prior to the test as described in section 2.1.2. The pre-tube is not coated.

- Pre-tube

  The purpose of the narrow-bore pre-tube is to reduce the diffusion into the tube when not sampling. This is done by using a pre-tube with a 2mm diameter opening. The glass pre-tube can trap significant amounts of acids when sampling. The trapped acids can be recovered in the elution step. The pre-tube is a four-inch length of narrow-bore Pyrex™ glass pre-tube (0.248" o.d. 2 mm i.d.). The pre-tubes dimensions could not be found commercially. They were fabricated by scribing and cutting Pyrex™ Vista 1 ml pipets into four-inch lengths and filing the sharp edges with a fine file. Teflon™ three mm i.d. pre-tubes can also be used when sampling at low temperatures and when diffusion is not an issue. Do not use Teflon™-pre-tubes when sampling in hot environments that can degrade the Teflon™. Orienting the tube such that the vector of the input stream is perpendicular to the direction of the smoke velocity vector also minimizes diffusion errors.

  The pre-tube is joined to the collection tube in one of two ways:

  - Option one (Recommended): A one inch length of 3/16” id, 5/16” o.d Tygon™ tubing can be used to join the glass pre-tube to the ¼” section of the collection tube butt-to-butt, minimizing contact with the gas steam.

    - Option two: The pre-tube may be connected to the collection tube replacing the one-inch PFA ¼” o.d. stub with a glass pre-tube via the same swage nut and two-piece perfluoro alkoxy polymer (PFA) ferrule. This is applicable for large collection tubes to be discussed later.

- Collection tube

  The collection tubes contain glass beads coated with a basic solution. Two collection tubes can be used in series to determine collection efficiency. The collection tube is made of either glass lined stainless steel or PFA.

    - The primary collection tube captures the sample.
    - The breakthrough collection tube can be used in series with the pre-tube and primary collection tube to check the collection efficiency of the primary collection tube and pre-tube. Once the collection efficiency is found to be acceptable for sample matrix and loading, a breakthrough tube may not be necessary if similar tests are to be run.

  Clearly number and label the tubes using an arrow to indicate the direction of sample gas flow. The sample flow direction is important to track to ensure the collection tubes can later be back flushed to maximize sample recovery. The arrow points to the downstream end of each collection tube. One labeling option is to use waterproof labeling tape marked with a wide-tipped waterproof marker pen.

- Blank sample tubes

  One or two capped sample tubes function as blanks. The pre-tube end is exposed to decomposition products during the entire test and any material that diffuses into it (or enters due to pressurization of the test article) needs to be subtracted from the total amount collected during sampling for that tube. The cap is located downstream of the High Efficiency Particulate Air (HEPA) filter such that the length of line matches the length of sample line leading to the sample solenoid valve. Blank sample tubes are constructed identically to sample tubes.

2.1.1 Collection tubes and retainers

The open path of these collection tubes enables the collection of combustion gases without the flow restrictions. For example, for high-capacity tubes, flows as high as 2.5 liters per minute can be sampled without any backpressure.

Select the tube type of sufficient capacity for the maximum sample loading expected. The capacity of the collection tube increases as the internal surface area of the tube increases. The various tube sizes are shown in this section. The selection of collection tubes based on collection efficiency and tube capacity is discussed in section 2.1.3 Parts used to construct the sample tubes are tabulated in Appendix A, Table A-1.

Low, medium, and high capacity tubes currently in use are described in this section. The low capacity tube is a generation 2b tube. High capacity tubes currently in use include generation 4a (FAA) and 4b tubes (used by Boeing). Low capacity tubes are shorter, have smaller inner diameters and are easier to handle. They have sufficient capacity for sampling low concentrations of acid gases.

One high-capacity sample tube option is shown in Figure 5. This figure shows the materials used to make these tubes along with the connectors and adapters. The overall length of each collection tube is 14”. The collection tube is constructed with ½″ o.d. PFA tubing with a 3/8″ i.d. (9 mm). The ends of the tube are reduced to ¼″ o.d. PFA tubing with reducing PFA tube unions. The ½” o.d. tubing section of the collection tube is 11 inches long. Ten inches (25.4 cm) of that length is packed with glass beads. This collection tube can be used for countless tests without disassembly. Only the Tygon™ tubing is removed, so fresh Tygon™ tubing and clean narrow bore glass tubing are used for each successive test.

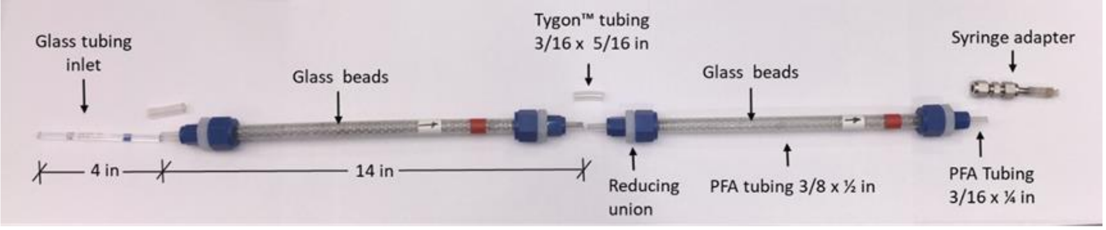


Figure 5. Generation 4a high-capacity sample and breakthrough tubes with PFA retainers

The retainer assembly used in the construction of these tubes is shown in Figure 6. This retainer assembly retains 4mm glass beads. The retainer assembly consists of two parts: the outer retainer is cut from a 1/4” length of the ½” o.d. PFA tubing: slice off approximately 1/3 of the perimeter and squeeze the remainder into the end of the sample tube, so it is flush with the surface of the outer tube. Leave an open channel on the cut ends to create an open flow path. The inner retainer is cut to ensure an acceptable tube opening, such that there is no flow restriction, and the beads are retained. Figure 6 shows the two sections of the retainer prior to pressing them into the ½ tube, such that they are flush with the end of the tube.

Figure 6. Insertion of PFA sample tube retainer

2.1.1.1 High capacity tube with SS mesh retainer

An alternative high-capacity sample tube option is shown in Figure 7. These collection tubes use ½" mesh disks as retainers in place of the cut sections of PFA tubing. The stainless steel mesh disks may leach out heavy metals which may reduce the lifetime of ion chromatography columns. These mesh disk retainers enable the use of 3mm o.d. beads which provide a larger surface area and a higher collection efficiency.

To aid in construction of the option two tubes, Figure 7 details the materials needed and general construction of the sample and breakthrough detection tubes and their various ancillary equipment. The Tygon™ 3/16-5/16 luer connection shown in this diagram is one option for rinsing the tube.

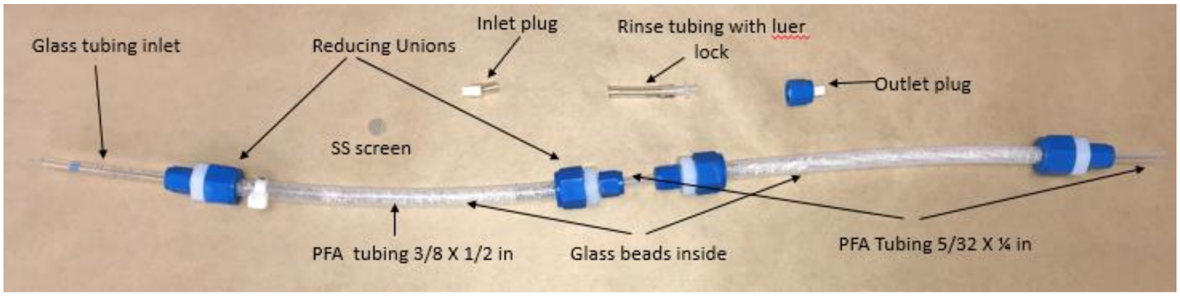


Figure 7. Components of Generation 4b sample and breakthrough tubes with screen retainers

2.1.1.2 Medium Capacity tube with Teflon™ retainer

The medium capacity tube is 16 ½ centimeters (cm) long with an 8mm o.d. and 6mm i.d. and is illustrated in Figure 8.

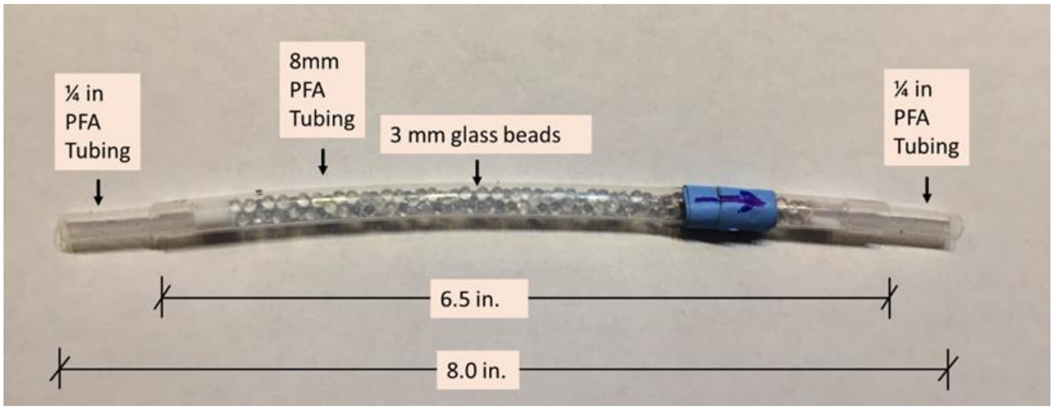


Figure 8. Generation 3 medium capacity tube: view 1

Teflon™ of PFA retainers hold the beads in place. A short length of ¼” o.d. PFA tubing is pressed inside the 8mm tube with 1.25” exposed.

The tube is packed with 3mm diameter glass beads to a depth of five inches (12.7 cm), held in place with a ¼” slice of Teflon™ cut from ¼” o.d. Teflon™ tubing such that there is an acceptable tube opening, that there is no flow restriction and that the beads are retained. The tube construction and retainer placement can be seen in Figure 9.

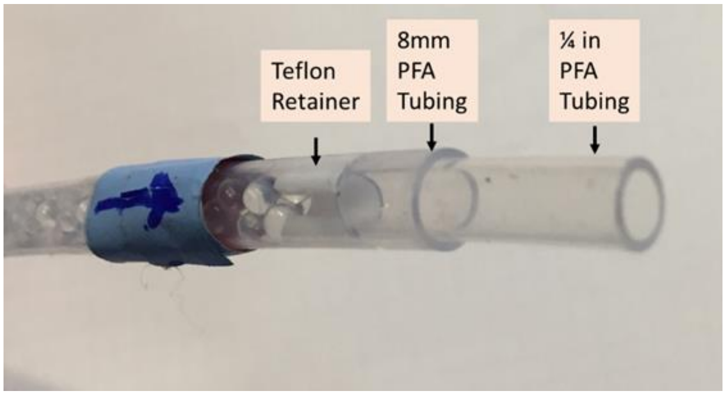


Figure 9. Generation 3 medium capacity tube: view 2

2.1.1.3 Low capacity tube with Teflon™ retainer

This tube is 16 ½ centimeters (cm) long with a 4mm i.d. and is illustrated in Figure 10. It is made of stainless steel and is lined with glass. The tube is packed with 3mm diameter glass beads to a depth of 14 cm, held in place with a slice of Teflon™ cut from ¼” o.d. Teflon™ tubing. The advantage of using a glass-lined SS tube is the enhanced heat transfer of this with the ice bath.

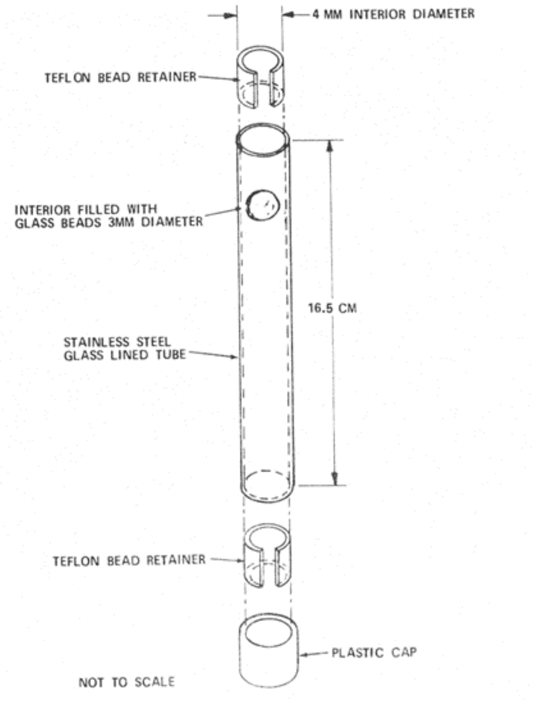


Figure 10. Generation 2b low-capacity sample tube

2.1.2 Preparing gas sample tubes

The tubes must be numbered to indicate the sampling sequence and labeled using an arrow to indicate the direction of sample gas flow. The sampling flow direction must be clearly marked on the tube to ensure it is orientated correctly when the sample is recovered. The tubes are subsequently back flushed to recover the anion, maximizing sample recovery, and minimizing contamination of the syringe adapter which is used to rinse the next collection tube. The arrow points to the downstream end of the sample tube. Use waterproof unique color labeling tape to label tubes for each sampling system location in the test article.

Chemicals required:

- 18.2 mega ohm type 1 DI water that has been degassed daily.

  Use degassed water before mixing with hydroxide. Degassing removes carbon dioxide which reduces the collection capacity of the collection tube. Carbon dioxide converts to carbonate which interferes with the chromatography for some IC methods. Degassing can be accomplished by bubbling helium for 15 minutes. Some labs prefer sonication of the water while pulling a vacuum via an aspirator or other vacuum device for 15 minutes.

Use this degassed, DI water to prepare the eluent used in IC as well as for coating and eluting sample tubes.

- One molar sodium hydroxide (made daily from 50% w/w sodium hydroxide stock solution; note 50% w/w NaOH= 18.94 Moles/Liter NaOH).
- 25 or 50mM sodium hydroxide (made daily from one molar sodium hydroxide stock solution). This solution is used to elute the tubes post-test. Select the concentration based on the column and separation requirements. Prepare daily.
- Do not use NaOH or KOH pellets to prepare NaOH stock solutions that absorb CO_2 more readily. They also have impurities that interfere with the chromatography.
- Immediately cap prepared solutions to prevent the absorption of CO_2. Diffusion of CO_2 into the tube can decrease the capacity of the sample tube. This capacity is anion dependent.

2.1.2.1 Coating collection tubes

Coat the collection tubes with 1M NaOH solution immediately before a test to minimize diffusion of CO_2 into the tube. Immediately cap the tubes after coating. Preferable, the pre-tubes are not coated. The collection tube is adapted to the syringe by using an adaptor on the downstream end of the collection tube.

The collection tube is adapted to the syringe by using an adapter.

The preferred adapter is a female Luer to Swagelok™ tube adapter constructed as shown in Figure 11. Teflon™ ferules are used for the Swagelok™ tube end of the adapter to allow hand tightening and reuse. This provides a pressure tight seal. The adapter consists of a ¼” Swagelok™ Teflon™ or PFA union, a ¼” male Teflon™ tube with a ¼-28 male thread on one end (difficult to find commercially), a ¼-28 polypropylene female connector and a polypropylene ¼-28 male to female Luer adapter which connects to the syringe.

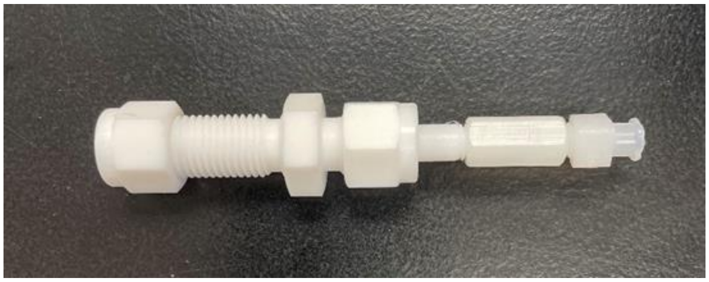


Figure 11. Female Luer to Swagelok™ tube adapter

Alternately a female Luer barbed connector and 3/16″ i.d. 5/16 ″o.d. Tygon™ tubing can be used to adapt the collection tube to the syringe per Figure 12.

Figure 12. Alternative syringe connection hardware

The procedure to coat the collection tubes is as follows:

- Use a ring stand and a support, such as a burette clamp to position each collection tube vertically into the waste beaker taking care that the arrow on the collection tube (direction of flow of the gas sampled) is directed upwards for the entire coating procedure.
- A female luer to Swagelok™ tube adapter (see Figure 11) is used to connect the downstream end of the collection tube (arrows on tube point to the syringe) to the syringe.
- With a syringe from above: backflush 10-60 ml (depending on size of sample tube) 1.0M NaOH through the downstream end of the collection tube. Let gravity drain the solution. A slight discoloration of the glass beads indicates the upstream end of the tube. Back flushing ensures that any potential residual analyte from the previous test exits the tube first.
- Remove excess solution via a 10-60cc syringe (depending on size of sample tube) by blowing from above into a vertically positioned sample tube.
- Wipe off the edges and tips of the tube with a Kimwipe™.
- Repeat coating procedure for each collection tube using the same 60 ml syringe.
- Store tubes horizontally.

2.1.2.2 Joining the pre-tubes and collection tubes and capping

After coating the collection tubes, the pre-tubes are connected as follows:

- The pre-tube, primary and breakthrough (if used) collection tubes are connected butt-to-butt to minimize contact of reactive Tygon™ tubing and gas sample. A one-inch length of 3/16″ i.d. 5/16” o.d. Tygon™ tubing is used to join the tubes.
- A pre-tube is joined to the inlet end of the primary collection tube.
- Note that the glass pre-tube was not coated with NaOH. This minimizes trapping of acid gas when not sampling.
- Use caps if there a significant delay between coating procedure and installation of the sample tubes into the test article. Caps prevent the absorption of CO2.
- From now on, tubes must be stored horizontally to prevent any fluid from escaping.
- Care must be taken to transport and handle the collection tube assembly so that there is no contact with any surfaces, which can contaminate the sample.

2.1.3 Collection tube loading and collection efficiency

The primary collection tube is capable of completely trapping the analytes of interest. Use a breakthrough tube to assess if the primary collection tube has sufficient capacity.

The collection tube size is selected based on:

- Maximum concentration expected.
- Duration of sampling for each tube.
- The sample flow rate: the collection efficiency increases as the residence time in the sample tube increases.
- The sample matrix.

The collection efficiency is determined by using a breakthrough collection tube in series with the primary collection tube.

The collection efficiency of a collection tube is best determined during a fire test, since collection efficiency is dependent on the sample matrix.

The collection efficiency of the sample tube for a particular species is expressed as the mass of that anion in the primary collection tube divided by the sum of masses of that anion collected in the primary collection tube and breakthrough tube x 100.

- The pre-tube, primary collection tube, and breakthrough collection tubes are eluted and analyzed by IC to obtain the collection efficiencies.
- Different acids have different collection efficiencies.
- Determine the collection efficiency by separately eluting the pre-tube, collection tube, and breakthrough tube with dilute NaOH solution.

The collection efficiencies and the tube loadings for historical fire tests conducted at the FAA are listed in Table 2. The high capacity tubes used were generation 4a tubes with a bead size of 4mm. Sample tube coating concentration NaOH was 1.0M. Wash solution concentration was 0.05M NaOH.

Table 2. Collection efficiencies and tube loadings of sample tubes

Fire Test	**Material/ Agent**	**Ice Bath**	**Sample tube Capacity**	**Flow rate (ml/ min.)**	**Sample time (min)**	**Wash Volume per tube (ml)**	**Gas**	**Anion concentration in ppm (mg/Lsoln)**				**Collection Efficiency = (A+B) /Total**	**Total Mass Anion collected (mg)**
								Pre-tube (P)	**Tube A**	**Tube B**	**Total (P+A+B)**		
Pyro probe	BPC Cyanate Ester	No	Medium*	600	ND	10	HCI	No	73.7	1.1	74.8	0.98	0.75 mg Cl^-
FAA Micro Calorimeter in N_2	PTFE	No	High**	100	30	100	HF	No	13.3	0.3	13.6	0.98	1.36 mg **F^-**
Cargo Bulk Load	Cardboard Boxes with shredded paper/ HFC 125	Yes	High**	31.7	5	3600	HF	9.18		No	9.18	ND	33.0 mg F^-
Flight deck Simulator	Li ion Battery Pack/ Halotron BrX agent	Yes	High**	354	1	30	HF	8.18		0.48	8.66	0.94	0.26 mg F^-
	Li ion Battery Pack / Halon 1211	Yes	High**	2,470	1	30	HF	7.56		0.64	8.2	0.93	0.25 mg F^-
							HCI	7.19		0.44	7.63	0.94	0.23 mg Cl^-

*see Figure 8 and Figure 9 **see Figure 5 ND = No data

2.2 Acid gas sampling system

Sample tubes and blank sample tubes must be positioned at the sampling point, without upstream tubing or valves. This avoids high sample losses from absorption of the analyte on moist surfaces. The combustion gas is drawn through a timed sequence of sample tubes to obtain a stepped concentration history of the gases of interest. For each sample, the gas flows through its sample tube to a cooling line, high-capacity HEPA filter, sample solenoid valve, flowmeter, needle valve and vacuum pump.

Blank sample tubes are positioned alongside the sample tubes. The sample tubes, blank sample tubes, cooling lines and HEPA-CAP filters are housed in the ice bath. Parts used to construct the sampling system for full-scale fire tests are tabulated in Appendix A, Table A-2.

The functions of the components as follows:

- Sample tubes are utilized to sequentially collect analytes.
- Blank sample tubes, where no sample is drawn, are used to address the diffusion into the sample tubes. They also address unintended sampling due to pressurization of the compartment during a fire test. Use one to two blank sample tubes.
- Cooling coils or lines are used to cool condensable gases collected downstream into cooled high-capacity HEPA filter/traps.
- Cooled high-capacity HEPA-filter/traps protect the solenoid valves and flowmeters downstream from the buildup of particulates, condensates, and tars.
- The filter also may condense out high boiling point gases such as some halon replacement agents.
- Sample solenoid valves are normally closed two-way valves used to select which tube is to draw a sample.
- Venting solenoid valves are normally closed two-way valves used to:
    - Minimize pre-sampling vacuum buildup between the vacuum pump and the sample solenoid valve which can result in drawing more than the intended volume.
    - Set and maintain sample flow rate before the test.
    - Minimize the contribution of the plumbing downstream of the solenoid valve(s) to the t90.

    - Minimize sample errors when solenoid valve does not seal properly. The venting solenoid valve is open before and after sampling.

- Flowmeter is a rotameter used to measure the flow of air. It is calibrated for dry air at 70 degrees F and one atmosphere.
- A needle valve is used to set the flow. It is positioned between the rotameter and the vacuum pump.
- A vacuum pump pulls the gas sample through the sampling system.
- The ice bath cools the tubes and prevents the volatilization of the coating on the glass beads. The ice bath increases the collection efficiency of the collection tubes since gas solubility increases as the temperature decreases. The ice bath also increases trapping efficiency of the HEPA filter.

The tubes, cooling lines, high-capacity filters and sampling valves must be mounted horizontally. The flowmeters and (condensing coils if used) are mounted vertically.

2.2.1 Sampling system design options

There are two flowmeter options for time sequenced sample tubes for full-scale fire tests. The first option uses a single flowmeter which is sufficient for most applications. The second option uses multiple flowmeters: one flowmeter per sample tube. HEPA-CAP 36mm diameter 0.3µ glass media filters are used which have a nominal internal volume of 90ml.

2.2.1.1 Single flowmeter sampling system

Figure 13 illustrates a single flowmeter sampling system with 10 sample and breakthrough tubes and two blank sample tubes. There is one venting solenoid valve which vents the space between all the sample solenoid valves and the pump when the sample solenoid valves are not sampling (before the first tubes starts sampling and at the completion of sampling for the last tube). Filters are used to protect the solenoid valves and flowmeters. Cooling lines or coils are used to precool the effluent from the sample tubes prior to filtration. If using one ice bath, cooling coils may be replaced by a cooling line to provide sufficient cooling.

Sampling systems can be fabricated for as many sample tubes needed for the required temporal resolution for the step concentration time curve. One or two blank (non-sampling) sample tubes can be used.

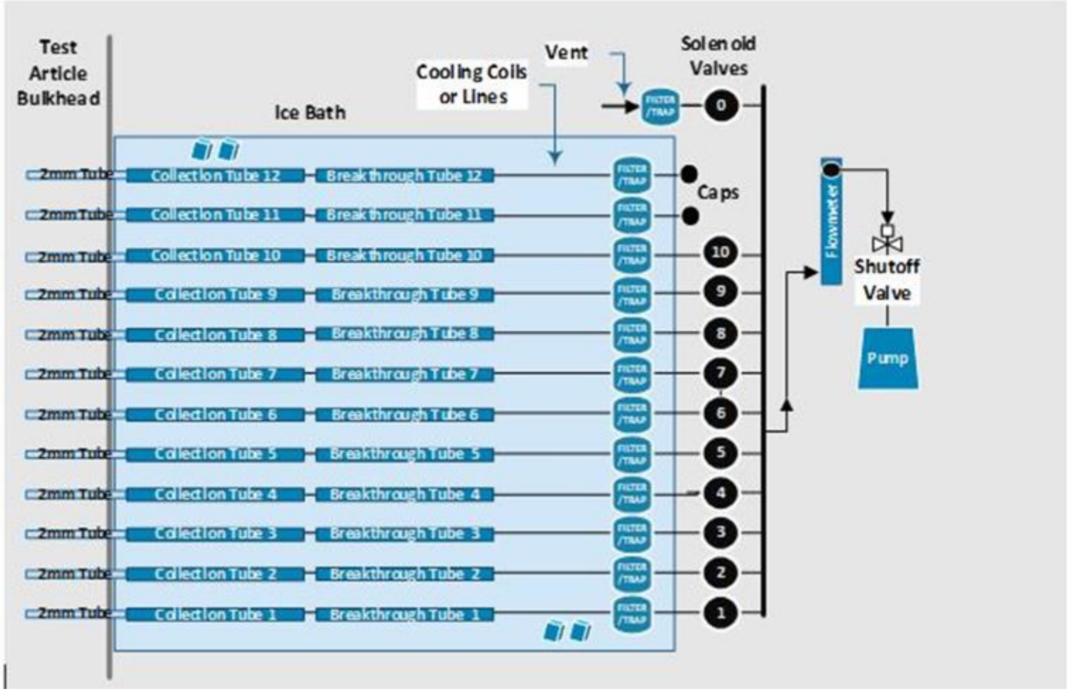


Figure 13. Schematic of a single flowmeter sampling system, top view

This schematic is drawn in a planar format, the actual orientation is described in Appendix B, along with engineering diagrams with dimensions: the sample tubes, HEPA filters and sampling valves are in one plane and the flowmeters and cooling coils that rely on gravity are in a perpendicular plane.

2.2.1.2 Multi-flowmeter sampling system

Figure 14 illustrates a multi-flowmeter sampling system. The system shown has four sample tubes and two blank tubes. For each sample tube, there is one dedicated flowmeter, venting solenoid valve and sample solenoid valve.

Each venting solenoid valve vents the space between that sample solenoid valve and the pump. It vents when its sample solenoid valve is not sampling. Each venting valve must also vent before the first tubes starts sampling and at the completion of sampling for the last tube.

This multi-flowmeter sampling system design is practical if you have a limited number of sample tubes and only one sampling station. Otherwise, consider using a one flowmeter sampling system when many sample tubes and many sample stations are used for a fire test.

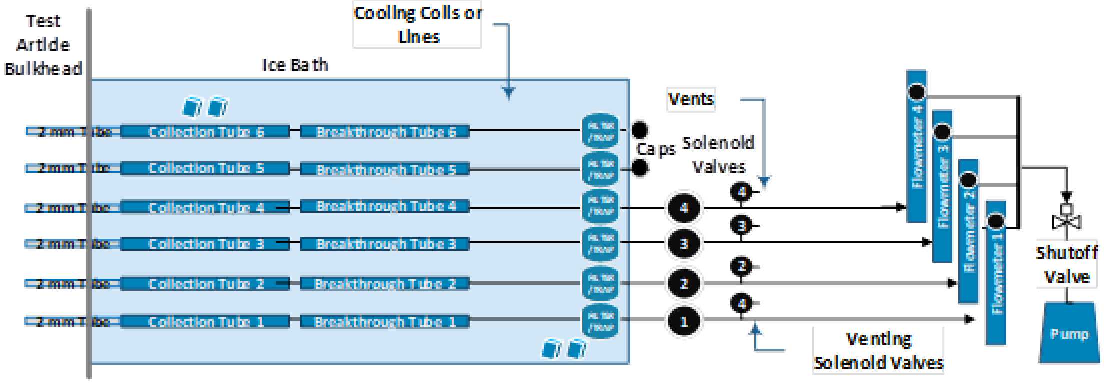


Figure 14. Schematic of a multi-flowmeter sampling system, top view

2.2.2 Solenoid valves

Each sample solenoid valve opens for a specific time. For example, given 10 sample solenoid valves, and a 10-minute test duration, each sample solenoid valve would open for one minute.

For the single flowmeter system, the venting solenoid valve is initially open pre-test and closes when sampling is initiated then opens again when sampling the last tube is completed.

For the multi flowmeter system, all venting solenoid valves are open pre-test and post-test. All venting solenoid valves, except for the one servicing the active sample tube, remain open during the entire test. The venting valve servicing the active sample tube is closed during its sampling period. When a sample solenoid valve opens, its venting solenoid valve closes; likewise, when the sample solenoid valve closes, its venting solenoid valve opens.

The solenoid valves must be mounted horizontally, with the working part of the valve at the bottom of solenoid valve rack, and the electronic part above, per manufacturer's recommendations.

2.2.3 Sample tube installation

Each sample tube is mounted horizontally in an ice water bath.

The upstream glass end of each sample tube is directly exposed to the atmosphere to be sampled. The glass portion of the tube (0.248"o.d.) slips through bored through Swagelok™ bulkhead tube fittings mounted on the front surface of the aluminum ice water bath with ¼" Teflon™, graphite or Vespel™/graphite ferrules supporting the glass portion of the tube inside the box.

- Teflon™ two-piece ferrules can be tightened by hand and reused many times.
- Graphite is a soft material so the ferrules can only be used once or twice. Hand tighten.

- Vespel™/graphite ferrules are available in various percentages of Vespel™ and graphite. Select the appropriate softness to get a good seal. Vespel™ is too hard to get a good seal with glass. These ferrules require a wrench to get a water-tight seal.

One or two blank tubes are mounted in the box with all downstream lines the same length. The blank sample tube lines are terminated with tube caps directly downstream of a circa 90ml high-capacity HEPA-filter. These blank sample tubes are used to assess errors due to diffusion into the tube during test and post-test exposures.

The 2mm bore of the pre-tubes does not restrict the flow and there is no pressure difference at each end of the sample tube in use. There is no pressure difference from the inlet of the sample tube to the downstream rotameter, since the downstream rotameter is calibrated for one atm.

The tubes must maintain their horizontal position post-test until eluted for analysis. This prevents the loss/carryover of sample.

2.2.4 Filtration and drying

Each sample line exiting the sample tube ice water bath is connected to a cooling line or cooling coil followed by a high-capacity HEPA-filter/trap to a solenoid valve. A six-inch cooling line may be sufficient.

If a cooling coil is needed, it is placed in a second ice bath. The filter and cooling line/coil is not required to be directly adjacent to the sample tube ice bath. The length of copper tubing needed in the optional coil depends on sample temperature and volume sampled per tube. Coils of four turns on 2.5” o.d. copper tubing are sufficient to cool the gas stream for sample flows of up to two liters per minute.

The HEPA filter has a high surface area, minimizing backpressures that would pose flowmeter errors. The HEPA filter is mounted horizontally to prevent wetting the entire surface area of the filter, which could impede flow.

2.2.5 Sampling system errors

The sampling system is designed to minimize sampling system, timing, flow, and deposition errors.

2.2.5.1 Sampling system timing and flow errors

The internal dead volume downstream of the sample tube is minimized to reduce sample delays which can reduce the volume and sampling duration of the gas sample collected. The HEPA filter could pose a significant delay if not sized properly. A HEPA-CAP 36 filter provides high filtration capacity at minimal, yet significant internal volume. A smaller filter may be used in its place for cleaner samples.

The system flowmeter is calibrated for one atmosphere intake pressure so routine sampling checks are needed to ensure that the HEPA filter does not buildup a backpressure over time which would result in a flowmeter error.

Check the t90 (time to get 90% of the set flowrate through the sample tube) as outlined in section 2.2.10 Post-assembly checks, and reduce the dead volume and increase the flow rate as needed.

2.2.5.2 Deposition errors

Deposition errors are minimized by:

- Minimizing dead volume between sample inlet and solenoid valve. Consider dead volume of filters, tubing, and plumbing.
- Using narrow-bore glass or PFA pre-tubes.
- Positioning the pre-tube perpendicular to the smoke velocity vector.
- Using larger sample volumes (one liter or greater) per sample tube. A minimum sample volume of 2.5 liters is effective in minimizing diffusion errors in large scale fire tests, where the tubes cannot be removed immediately after the test (Hill, Brown, Speitel, Johnson, & Sarkos, 1984).
- Minimizing post-test exposure times.
- The test article pressure ideally does not change during the test. Consider venting the test article.
- If the flowmeter is calibrated for one atm, the pressure within the chamber is ideally equal to one atm.
- If there is any pressure buildup of test article during the test, the dead volume upstream of all the sample solenoid valves will cause a positive sampling error in all tubes, whether sampling or not.
- This error can be reduced by increasing the sample flow.

2.2.6 Ice bath descriptions

The ice bath is constructed of weldable 0.125” 6061-T6 aluminum sheet. The ice baths can be designed to accommodate only the sample tubes or designed to accommodate filters and cooling coils if needed.

One or two ice baths can be used for each sampling station:

- One ice bath: sample tubes + cooling lines + filters.
- Two ice baths:
    - Sample tubes ice bath.
    - Ice bath for cooling coils and filters.

The ice bath housing the sample tubes can be positioned inside or outside the test article. If outside the test article, the ice bath must be mounted on the test article bulkhead with the glass ends of the sample tubes inside the test article. There are no sample lines upstream of the sample tubes due to potential losses of acid gases.

If the sample tube ice bath is located inside the test article:

- An inert fireproof inert insulation board covers all exterior surfaces of the ice bath.
- Insulation sleeve covers the tubing exiting the ice bath if the bath is located inside the test article to minimize temperature changes within the tubing which could introduce unintended oversampling as the tubing cools post-test.

If the sample tube ice bath is mounted to the exterior bulkhead of the test article, a fireproof inert insulation board could be used. This prevents cold spots on the interior walls of the test article surrounding the protruding glass sample tubes. Cooling of the interior walls promotes condensation of water and unintended absorption of the acid gases to be sampled.

The options for ice bath sampling systems using one flowmeter are discussed in the sub sections below. Detailed shop drawings for the two options can be found in Appendices B1 and B2.

2.2.6.1 One ice bath sampling system option

One ice bath is used for each sampling location. This ice bath contains the sample tubes, blank sample tubes (and breakthrough tubes if used). Short lengths of copper cooling connect the collection tubes to downstream HEPA 36mm filters contained in the same bath. The one ice bath sampling system option is illustrated in Figure 15 and Figure 16.

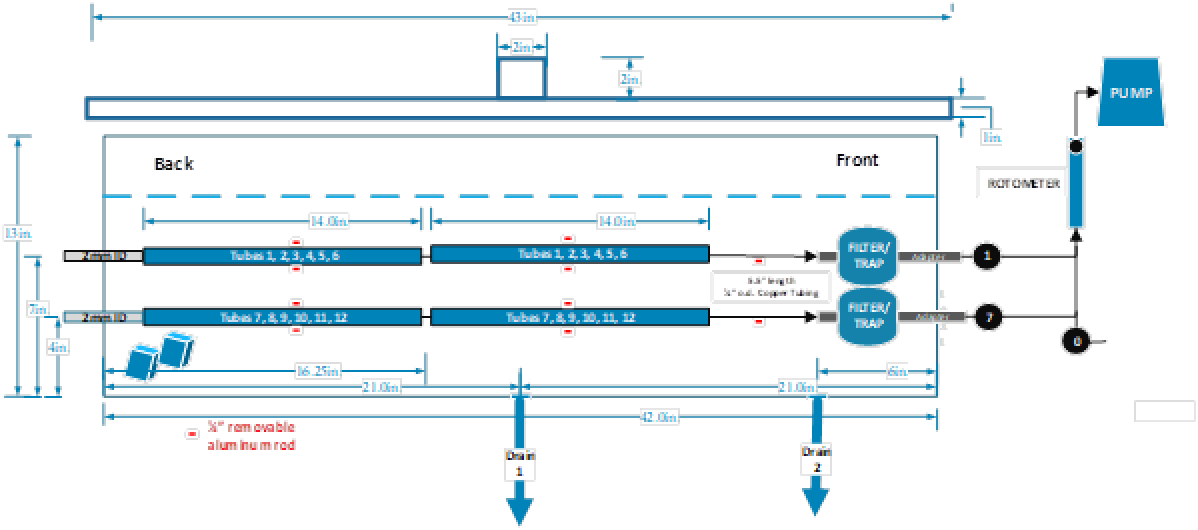


Figure 15. One ice bath sampling system, side view

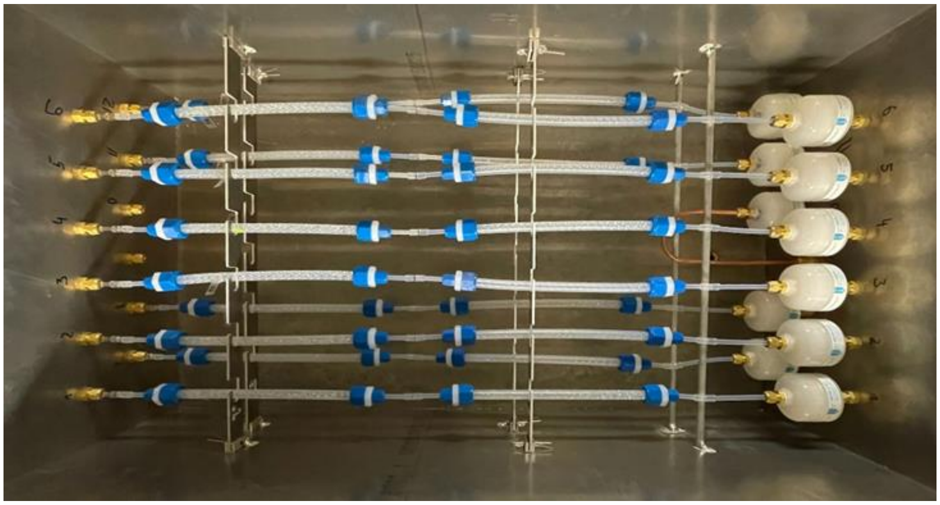


Figure 16. Fabricated one ice bath sampling system, top view

2.2.6.2 Two ice bath sampling system option

Two ice baths are used for each sampling location. One ice bath is for the sample tubes, blank sample tubes (and breakthrough tubes if used) and one ice bath is for the cooling coils and filters. Figure 17 is a side view showing the separate ice baths sized for the high-capacity sample tubes. Ice baths are positioned and tubing leading to the filter/trap is directed downwards such that condensates are trapped in the horizontally mounted high-capacity HEPA filter/trap without impeding air flow.

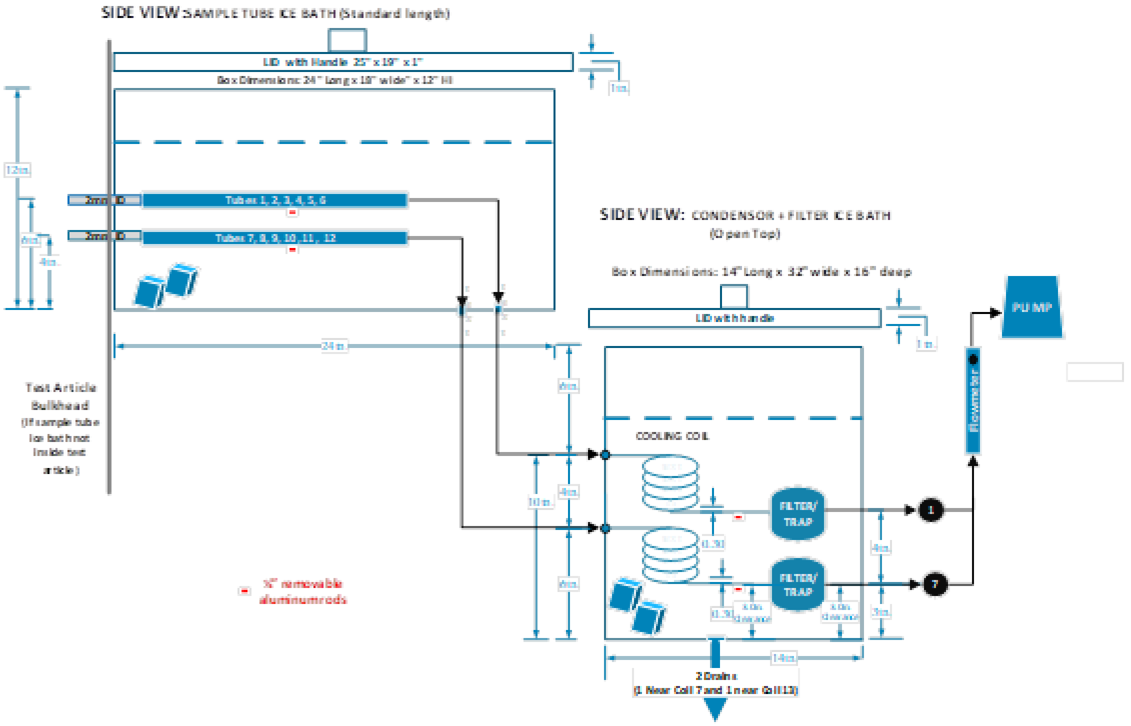


Figure 17. Two ice baths sampling system, side view

The cooling coil and filter ice bath can be positioned outside the test article, with consideration of minimizing the dead volume of the tubing. The downstream end of each sample tube is connected to 3/16” i.d., 5/16” o.d. Tygon™ tubing leading to vertically mounted one inch length of ¼ ” o.d. copper tubing stubs. The stubs are mounted to the bottom of the sample tube ice bath with ¼” brass bulkhead fittings. The ¼” o.d. copper tubing then leads from the rear bottom of the sample tube ice bath to a second ice bath containing cooling coils and HEPA filters. The coils and filters are stacked at two levels. Figure 18 and Figure 19 are top views for the upper and lower levels of the ice bath housing the condenser coils and filters. All tubing leading to the filter traps is directed either horizontally or downward such that condensates are trapped in the high-capacity HEPA filter/trap without impeding air flow.

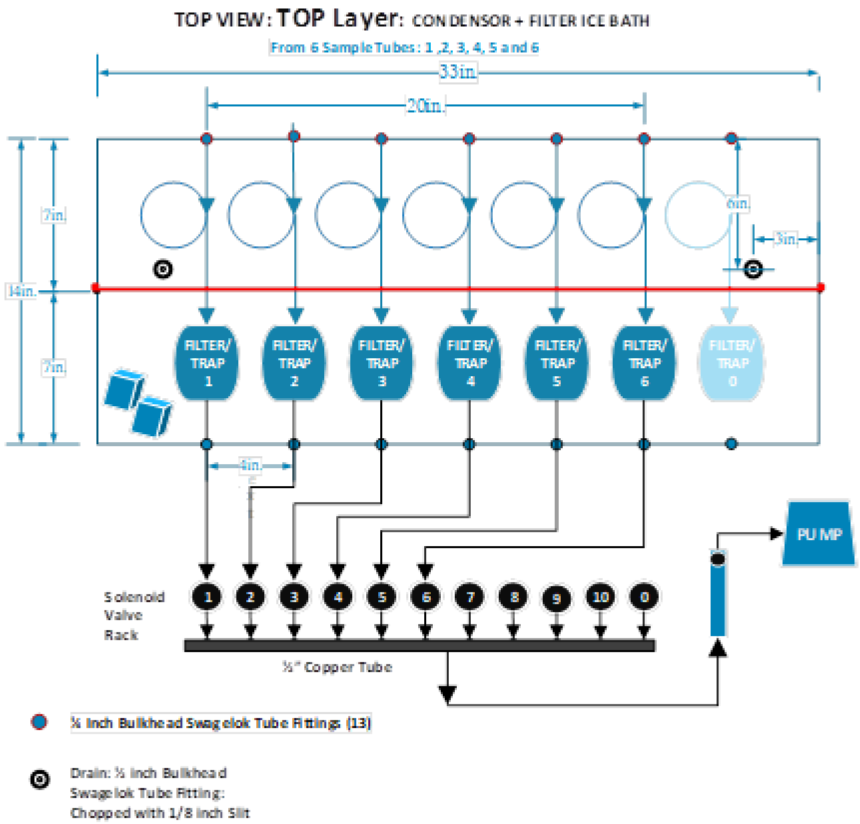


Figure 18. Ice bath containing cooling coils and filter/traps: upper level

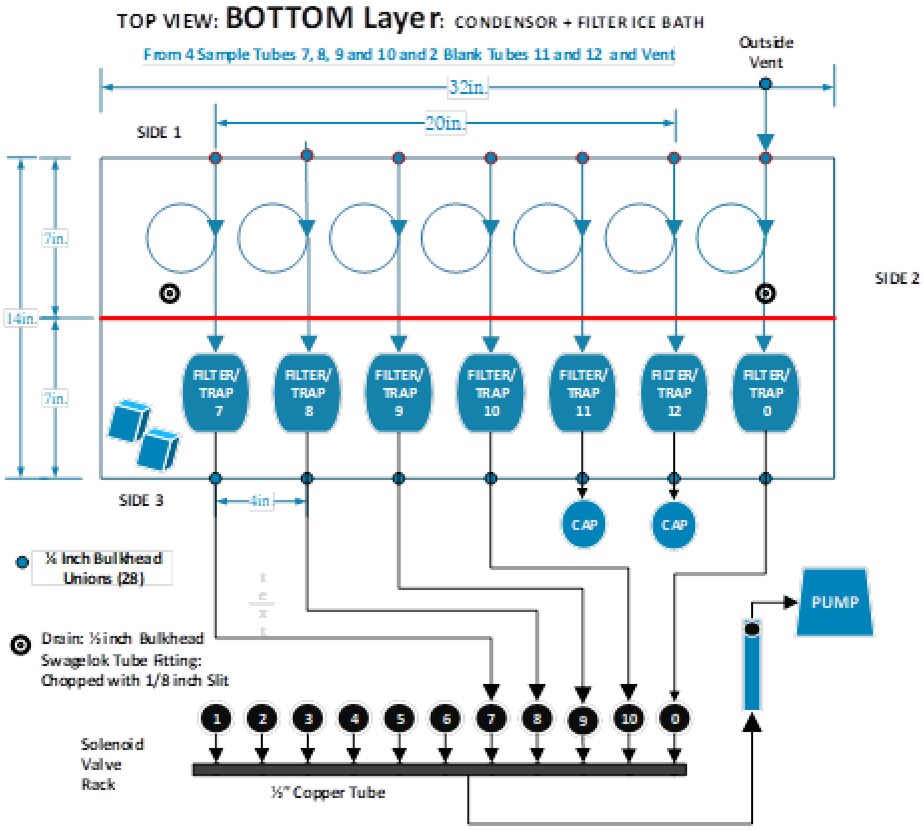


Figure 19. Ice bath containing cooling coils and filter/traps: lower level

Drains are used to remove the water post-test from all ice baths. A ½” bulkhead union is mounted to the bottom of the ice bath and leads to a ½” shutoff valve which leads to ½” copper tubing. The top end of the bulkhead fitting is cut at the base of the threads as shown in Figure 20. A 1/8” wide slit at the inside end of the fitting allows drainage from the water bath.

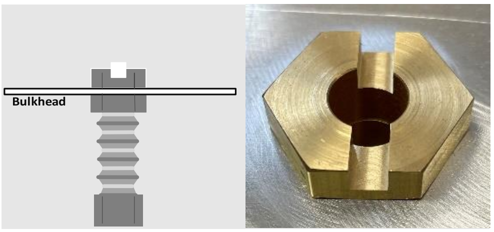


Figure 20. Half-inch bulkhead fitting drain

2.2.7 Bulkhead support for sample tube

The sample tube ice bath could be positioned either inside the test article (free standing) or attached externally to the test article. If mounted externally, the pre-tube section of each sample tubes must project into the test article by minimum of one inch. The input ends of each sample tube must project a minimum of one inch from the ice bath. This is to minimize surface sampling losses.

If the sample tube ice bath is free-standing, the glass portion of the sample tube slips through bored through ¼” Swagelok™ bulkhead tube fittings mounted on the front surface of the aluminum ice water bath as shown in Figure 21 Teflon™, graphite or Vespel™/graphite ferrules provide a water-tight seal and are used in place of brass ferrules to support the glass portion of the sample tube.

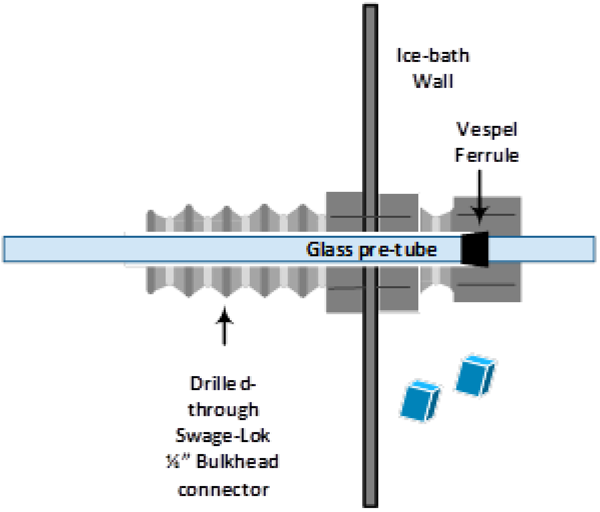


Figure 21. Bored through pre-tube bulkhead fitting tube support on free-standing ice bath

If the sample tube ice bath is externally mounted to the test article, attachment methods include:

Option one:

This option is shown in Figure 22. An appropriately sized vertical aluminum panel covers a cut out section of the test article wall. This bulkhead panel has pre-drilled holes that will accept the bulkhead fittings on the front face of the ice bath. Slide those fittings into matching holes of the aluminum bulkhead panel of the test article. Swagelok™ jam nuts secure the ice bath against the test article bulkhead and protect the glass pre-tubes from any movement of the ice bath relative to the attached test article. There is sufficient space between the ice bath wall and test article wall to place a 1/8” thick grafoil insulation sheet with a similar pattern of holes, but slightly larger diameter. The insulation sheet prevents the cooling of the bulkhead panel. The bulkhead panel cooling would otherwise result in condensation of moist acid analyte acid gases on the cold test article interior surfaces near the sample probes.

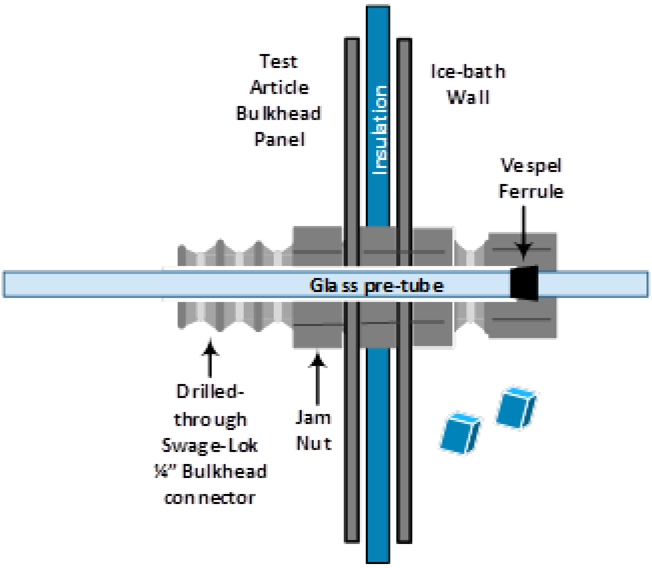


Figure 22. Pre-tube support secured to ice bath and test article walls

Option two:

Place ice bath against a cut-out rectangular section of the test article. The cut-out accommodates all bulkhead fittings on the ice bath. A soft gasket material is secured to the outside perimeter of the rectangular opening. The gasket is secured to the exterior of the test article. A length of one-inch o.d. silicone-coated fiberglass braided tubing works well as an inert gasketing material. A ceramic–based insulation board ½" Kaowool™ board with cut- out holes for the Swagelok™ unions is taped to the front surface of the ice bath prior to pressing the ice bath against the gasket. This prevents condensation losses of acid gases on the cold ice bath surface. Option two enables the use of a mobile hydraulic lift to place the entire sampling system in position when needed.

2.2.8 Acid gas sampling system operation

Higher flow rates and or test article venting may be needed if there is any pressurization of the test article to minimize the deposition errors (excess gas sampled due to diffusion and pressurization of the test article). Set the system vacuum pump to a fixed pressure for all tests e.g., 27” Hg.

The operation is dependent on the sampling system design:

- Single flowmeter sampling system: Before the test, the system venting solenoid valve must be opened and all sampling tube solenoid valves must be closed. The system flowmeter is then set for the required test flow rate. The system venting solenoid is closed for the duration of the test and opens again after all samples are collected. The first sample tube is opened at the time of fire ignition and is held in the open position for the desired sampling interval and then closed. As soon as the first sample tube is closed the second sample tube is opened to start the next sampling interval. All timed samples are obtained in this way. At the completion of sampling, all sampling solenoid valves are closed and the system venting solenoid valve opens. The pump is then turned off.

- Multiple flowmeter sampling system: Before the test, all system venting solenoid valves are opened and all sample tube solenoid valves are closed. Each sample tube flowmeter is then set for the required test flow rate. The first sample tube (not the blank) is opened at the time of fire ignition and is held in the open position for the desired sampling interval at which time the corresponding vent valve is opened and the sample valve is closed. As soon as the first sample tube is closed the second sample tube is opened and its vent valve is closed to start the next interval of sampling. All samples are obtained in this way. At the completion of sampling, all sampling solenoid valves are closed and all venting solenoid valve are opened. The pump is then turned off.

After sampling is complete and before application of water to put out a remaining fire, the sample tubes are removed quickly to minimize deposition errors. Water is drained from the ice bath holding the sample tubes. After the water in the ice bath is removed, the swage nuts connecting the sample collection tubes to the ice bath (glass tube) is loosened and the HEPA filter Tygon™ connection tubing freed from the sample tube. The sample tubes are next removed from the system, dried, cleaned, and immediately capped. Care is taken to not let any water into the ends of the sample tubes, as the anions in the water will contaminate the sample. On the glass inlet ensure to carefully wipe any deposits on the outside and on the end of the tube with a clean Kimwipe™ wetted with DI water. This prevents deposits on the outside of the glass tube from being added to trapped material. Keeping tubes in the horizontal position is necessary to prevent liquid in either the sampling or breakthrough collection tube from flowing into the other tube. The tubes are then transported to the laboratory where extraction of the sample is carried out and ion chromatography performed.

2.2.9 Solenoid valve programming

Use venting solenoid valves and sample solenoid valves that are normally closed (not powered). When a solenoid valve is powered, that valve is open. Examples of solenoid valve programming are shown below.

2.2.9.1 Single flowmeter sampling system

Refer to section 2.2.1.1 for the design and operation of the single flowmeter sampling system. Single flowmeter sampling systems have one flowmeter and one venting solenoid valve and “n” sample solenoid valves. The sample solenoid valves are numbered the same as the corresponding sample tubes: 1, 2, 3…n. The venting valve is the last valve on the solenoid rack and is labeled valve “0.”

The program powers valve “0” (vent valve) for a few minutes before the test is initiated. At the termination of the test the valve “0” is powered (opened) again. The flow is set to the desired flow pre-test with the venting solenoid valve open.

At the start of a test, the computer closes the venting solenoid valve and sequentially powers each sample solenoid valve (joined to each sample tube) for a specified time. For example, given 10 sample solenoid valves, and a 10-minute test duration, each sample solenoid valve is powered for one minute.

The controlling computer program for the single flowmeter sampling system has three modes of operation, which must run in sequence. Each successive mode can only be accessed from the previous mode. Programming instructions are provided below including instructions for controlling power to the solenoid valves.

The three sequenced modes of the program for the single flowmeter sampling system are: the no solenoid valves powered mode, the pre-test and post-test venting mode, and the test mode.

- NO SOLENOID VALVES POWERED MODE:

  The following text displays:

  - “NO SOLENOID VALVES POWERED MODE: (All venting and sample valves closed).”
  - “Check for leaking of each solenoid valve under vacuum when all solenoid valves, venting and non-venting, are closed. Use an open flowmeter. Place it at the input of each HEPA filter to check for leaks.” There is no flow for each sample and venting solenoid valve.
  - Provide button labeled “PRE-TEST and POST-TEST VENTING MODE” to progress to the next mode.
- PRE-TEST and POST-TEST VENTING MODE:

Open venting solenoid valves and set duration of sampling for each sample solenoid valve, in preparation for the test mode. The test is started in this mode. Write the program to power up only the venting solenoid valves (pre-test venting mode) enabling the pre-test venting of all the venting solenoid valves. Set the test parameters mode as sampling flow rate as well as sample duration per sample tube. Provide warning text that this mode runs for a minimum of two minutes prior to running the test to allow the system to vent.

The following text displays:

- "PRE-TEST AND POST-TEST VENTING MODE"
- "Venting Mode: All VENTING solenoid valves are powered. All sample valves are closed."
- "Elapsed venting time" (SHOW COUNTUP) ___ minutes."
- "Turn on vacuum pump. Set to 27" of Hg. and set flows."
- "Set test parameters."
    - "Select the sample time per tube in ___ UNITS."

      (Units are the same units as the time units used by the test engineer. This simplifies aligning IC data with other test data).

      The program is written so that there is an option for the operator to select either of the two options shown in the tables below:

        - "Option one: Set the same sampling durations for all tubes and the number of tubes to sample. The program indicates the sampling durations for the previous test.

Solenoid Valve	**Previous Test Sampling Duration per Tube (Minutes, Seconds)**	**Set sampling Duration per Tube (Minutes, Seconds)**	**Set the number of tubes to sample**
S1-10			

        - "Option two: Operator defined sampling duration per tube." The program indicates the sampling durations for the previous test. Print on monitor: "Set custom sampling durations." Add option to print Option one or Option two tables.

Solenoid Valve	**Previous Test Sampling Duration Time (units)**	**Set Test Sampling Duration (Time (units)**
S1		
S2		
S3		
S4		
S5		
S6		
S7		
S8		
S9		
S10		

- “This venting mode runs for a minimum of two minutes prior to starting the test to allow the system to vent (preventing oversampling of the first sample tube).”
- “Post-test venting minimizes unintended sampling if a sample solenoid valve develops a minor leak.”

  Enter data on screen: “Test Article: ___ Test Number: ___ Test Date: ___.”
- Start test from this pre-test venting mode screen by pressing this button. Venting must stop when the first sample solenoid valves open. Print alongside the button: “Sample sequencing starts instantly when the start test button is activated.”

- TEST MODE

  The sample solenoid valves are sequentially powered on for the sampling duration of each corresponding sample tube. Venting must stop while sample solenoid valves are open and start again post-test when all sample solenoid valves are closed.

  The venting solenoid valve is labeled valve “0.” The Sample solenoid valve numbers match the sample tube numbers.

  The following text displays on the computer monitor during and after sampling:

  - “TEST MODE.”
  - “Sampling has started.”
  - “Time into test = ___ minutes.”

- "Solenoid valves states for each solenoid valve: GREEN (open), RED (closed)."
- Show the test number, test date and a list of all valves and a green light adjacent to the valve that is on. This table continues to display after sample tubes complete sampling, indicating that the venting solenoid valve is now open.

Test Article: _____ Test Number: ______ Test Date: _______

Solenoid Valve	**Status Light**	**Elapsed Time into test (count from start of test to final sample time for that tube) (xx.xx minutes)**	**Elapsed Time into sampling for each sample tube (x.xx minutes) (count to planned sample time/ tube)**
Vent, S0	○	N/A	N/A
S1	○		
S2	○		
S3	○		
S4	○		
S5	○		
S6	○		
S7	○		
S8	○		
S9	○		
S10	○		

- Provide option to stop sampling early: Add "Stop sampling button." Stay on "TEST MODE" screen. (If test is terminated early, the program displays the actual duration of the last sample.
- When all sampling is completed, indicate:
  - "Sampling stopped at ___ minutes into test."
  - "Elapsed time from the end of sampling ___ minutes."
  - "Only vent solenoids valves powered."
  - "Reminder: Post-test venting minimizes unintended sampling if a sample solenoid valve develops a minor leak."

    - Provide option to print table above with test number and test date.
    - "Do not stop program until vacuum pump is turned off."

2.2.9.2 Multi-flowmeter sampling system

Refer to section 2.2.1.2 for the design and operation of the multi-flowmeter sampling system. The multi-flowmeter sampling systems (with multiple (n) flowmeters, has "n" sample valves, and corresponding "n" venting valves). The venting valves are labeled Vent1, Vent2, Vent3… Vent n; corresponding to sample valves S1, S2, S3… Sn.

All venting solenoid valves are powered pre-test and post-test. Flows are adjusted pre-test for each flowmeter to a set flow rate. When sampling is initiated, the computer sequentially powers each sample solenoid valve (joined to each sample tube) for a specific time. All venting solenoid valves, except the one servicing the active sample tube, remain powered during the entire test. When a sample solenoid valve is powered, its venting solenoid valve is not, likewise when the sample solenoid valve is not powered, its venting solenoid valve is powered.

2.2.10 Post-assembly checks

It is important to do systematic checks post-assembly to ensure proper installation of the sampling system.

2.2.10.1 Proper orientation of solenoid valves

Check that all solenoid valves are plumbed in the required flow direction: the markings on the valves indicate the in and out ports. The valve will not close properly if not positioned correctly.

2.2.10.2 Sequencing of solenoid valves

- The solenoid valves are sequentially numbered and mounted in numerical order.
- Check that the solenoid valves are wired to the correct computer outputs.
    - Turn vacuum pump on to 27" Hg. Set the system flowmeter to the maximum flowmeter calibration setting.
    - Run the computer program in the "PRE-TEST AND POST-TEST VENTING MODE." Select a short sample time per tube (e.g., 30 seconds).
    - Start sampling. Press the "Start Test Button" from the "PRE-TEST AND POST-TEST VENTING MODE" screen. Computer initiates sampling and switches to the "TEST MODE."

- While in the “TEST MODE”: check valve sequencing, and the solenoid valves sequence in the order the valves are mounted.
    - Check by verifying the light on each valve or by touching the inlet tube leading to each solenoid valve for vacuum to determine if each sample solenoid valve is drawing a sample in the correct numerical order, left to right.
    - The program (monitor) indicates the valves are sequenced properly.
    - The correct order for various sampling system options is shown in Appendix B. Correct the plumbing as needed.

2.2.10.3 Post-assembly check for leaks

Check the sampling system for leaks in the solenoid valve assembly with the HEPA filters not yet installed. The source of the leak may also be the threaded fittings attached to each solenoid valve. The leak may also be due to a solenoid valve that does not seal in the closed position properly, resulting in unintended sampling. Refer to the sampling system diagram, Figure 13.

- Check to see if any fittings are leaking from vacuum pump to the solenoid valves (with the HEPA filters not yet installed):
    - Close all sample and vent solenoid valves. Open needle valve fully.
    - Cap all lines in the ice bath leading to the solenoid valves.
    - Set vacuum to 10 psi.
    - System flowmeter goes down to zero flow.
    - If flow is observed, tighten all fittings until flow is zero.
    - If leaking and the source of the leak cannot be identified: do a leak check to identify the source of the leak. Either of these methods are acceptable:
        - Helium leak check: With all valves closed, set vacuum to 10 Hg. Spray helium at each fitting and place helium leak detector probe between the solenoid valve assembly and the flowmeter.
        - Snoop® test: Alternately, for the single flowmeter system, in the vent mode with all valves closed, replace the flowmeter with a source of 10 psi air with a pressure gauge and shutoff valve. Pressurize the line leading to

        the “out” port of the solenoids in the manifold. Apply Snoop® to each pressurized fitting. Check for bubbles to identify leaks.

        - Alternate Snoop® Test: For the single flowmeter system, in the vent mode with only the vent valve open, introduce 10 psi air with a pressure gauge and shutoff valve into the vent inlet. Snoop® each pressurized fitting. Check for bubbles to identify leaks.

- Check to see if any fittings are leaking from solenoid valves to the interior of the ice bath: pressurize fittings one-by-one upstream of each solenoid valve (from the interior of the ice bath with the HEPA filters not yet installed):
    - Select the “NO VALVES POWERED MODE” (All vent and sample solenoid valves closed) or turn off power to all solenoid valves (normally closed).
    - Use 5 psi air with a shutoff valve, and pressure gauge, connecting the pressurized air one-by-one to each copper tube in the sample tube ice bath that leads to each sample solenoid valve (For the multi-flowmeter sampling system, follow this same procedure). While each line is pressurized Snoop® the fittings upstream of that sample solenoid valve and or vent valve. Note which fittings are leaking. Fix leak (tighten fittings and/or add Teflon™ tape) and retest.
    - Pressurize fittings one-by-one upstream of each solenoid valve: (with the HEPA filters installed) using the same procedure as above.
- Check to see if the solenoid valve internal seals are leaking (potentially drawing samples when the valves are closed). Note: If there are no leaks at the fittings (determined in the previous steps), any leaks measured will be due to leakage at the valve seals.
    - Set the computer to “NO SOLENOID VALVES POWERED MODE (all valves closed)”
    - Set vacuum pump to 10 psi vacuum.
    - Open the flowmeter valve to the fully open position so that the system flowmeter is pegged.
    - Check the flow at each sample tube position with additional (second) flowmeter of the same type and flow range as the system flowmeter, but without a valve.

    - There is no flow at any sample tube position. If there is flow, there is a leak at that valve's seating seal. Replace that valve.
    - Repeat for venting solenoid valves inlets. By changing the computer program to the "PRE-TEST AND POST-TEST VENTING MODE" (Vent valve open, all sample solenoid valves closed).
    - Tabulate the flows for each solenoid valve.
    - Replace solenoid valves as needed.

2.2.10.4 Post-assembly flow checks

Two types of flow checks are needed post-assembly. Use the flow rate intended for the test series:

- Check the flow rates upstream and downstream of each solenoid valve. Ensure both flowmeters have the same readings. Backpressure and flow restrictions can affect the main flowmeter reading. Since the main flowmeter is calibrated for atmospheric pressure, a vacuum buildup on the upstream end of the flowmeter can cause an error.
    - The flow leading to each HEPA filter (using a flowmeter with no valve) matches the flow of the main flowmeter.
    - Determine the flow of each sequenced sample tube line upstream and downstream of each HEPA filter. Use the main flowmeter for the downstream reading.
    - Correct restrictions to flow. Replace HEPA filters as needed.
- Check t90s: The time for 90% increase in flow, t90, for each sample tube should be a small percentage of the sampling time for that tube. Check the flow response time for each sample tube position (upstream of each HEPA filter): record the time it takes to achieve 90% of the desired steady-state flow (t90) setting after opening the corresponding solenoid valve. The installed plumbing dead volume (cooling cline/coil, HEPA-filter, flowrate, and flowrate changes due to particulate/tar buildup contribute to the t90. Use the t90 form in Appendix D to record the t90s for each sample line. The upstream flowmeter should be open with no needle valve.
    - Open solenoid valve control program.
    - Set the program to "PRE-TEST AND POST-TEST VENTING MODE" (only venting solenoid valves open).

- Set the flow at main flowmeter setting for the intended test flow.
- Enter intended sample time for each sampling solenoid valve for the upcoming test.
- Start sampling. Press “Start Test Button” from the “pre-test and post-test venting mode” screen.
- Measure the time to 90% set flowrate using a flowmeter upstream of each HEPA filter. Repeat for each HEPA filter. (Record the t90, the upstream flowmeter setting and the upstream steady-state flowmeter setting.
- Record this t90 for each sample line and for each for each station.
- Reduce the dead volume as needed.

2.3 Acid gas collection procedure

This section outlines pre-test, test, and post-test procedures to ensure reliability of the acid gas collection. It includes pre-test sampling system checks, sample tube installation and removal procedures, the test procedure and post-test recordings.

2.3.1 Pre-test and post-test sampling system checks

System verification is necessary days before the test date so there is a sufficient time to remedy problems without affecting the test schedule. Ferrules, solenoid valves, HEPA filter, or other hardware may need to be replaced, rewired, or serviced.

The possible complications that may need to be remedied include:

- The ferrules supporting the tubes in the ice bath must be checked for water-tightness. Water leaking onto the front face of the sample tubes will contaminate the tubes. Teflon™ and graphite ferrules require hand tightening. Vespel™/graphite ferrules should provide a leak-proof seal on first use with hand tightening followed by a ¼ turn with a wrench. If not, use a ferrule with a higher percentage of the softer graphite material. Replace all ferrules when any is showing signs of a poor seal.
- Solenoid valves may not fully close due to valve sticking, particulate or tar build up. This would result in some unintended flow through “closed” solenoid valve.
- Closed solenoid valves may not seal properly due the corrosion of working valve surfaces or seal failure.

- High-capacity 0.3-micron HEPA-Cap36 (36mm diameter with estimated internal volume of 90ml) filter may develop a back pressure resulting in flowmeter errors, since the flowmeters are calibrated for atmospheric pressure. Change filters as needed as particulate and tars start to restrict flow. It is important to check flows upstream of the filter and at the downstream flowmeter before and after each test.

2.3.1.1 System checks days before test

- Check the ice bath ferrules supporting the sample tube for water tightness. Perform this test every few tests.
    - Replace every sample tube with a placeholder tube ¼” o.d. tubes the length of the collection tube.
    - Mount the tubes as in an actual test and fill with water above the tubes.
    - Note any water leakage by observing the front outside face of the sample tube ice bath.
    - Replace all ferrules if one has a problem.
    - A schedule for ferrule replacement can be set based on leakage history.
- Check for sample solenoid valve leakage in the closed position. Determine if the valves are seating properly and enter the check data in the “Days before test” solenoid valve leakage data form:
    - Set pump to 27” Hg. vacuum.
    - Set computer program to “NO SOLENOID VALVES POWERED MODE: (all valves closed).”
    - Open the main flowmeter valve to the fully open position so that the flowmeter is pegged.
    - Check the flow at each sample tube position with a flowmeter of the same type as the system flowmeter.
    - Tabulate the flows for each solenoid valve.
    - There should be no flow at any sample tube position. If there is flow, there is a leak is at that valve’s seating seal.
    - Repeat for venting solenoid valves inlets.

    - Replace solenoid valves as needed.
- Check for filter back pressure flowmeter errors:
    - Set computer program to “PRE-TEST AND POST-TEST VENTING MODE.”
    - Set the flow to be the desired flow for the test at the main flowmeter.
    - Set sampling time for each tube to two minutes.
    - Start sampling by selecting the “START TEST BUTTON” on the “pre-test and post-test venting mode” screen.
    - Measure and tabulate on the “Days before test” filter restriction data form (example form found in Appendix D) the flow at the main flowmeter and the flow directly upstream of each HEPA filter (with no sample tube). Include the rotameter model number and type of float valve recorded (e.g., glass or stainless steel) as well as the readings.
    - If the volumetric flows at any tube position varies from the volumetric flow corresponding to the main rotameter by more than 10% then there is a significant flow restriction and the HEPA-filter for that tube may be causing that restriction. If so, replace it. Also record the flow after filter replacement.
- Check for t90 for each tube position using the procedure outlined in Appendix D. Replace HEPA filters as needed.

2.3.1.2 System checks same day of test

The following flow checks should be performed before and after each test upstream of each HEPA filter as well as at the main flowmeter. Both the upstream and downstream flowmeters should be the same flowmeters type. An open rotameter (without the valve) should be used at the tube position. Record the flowmeter readings on the test data form, as this will be needed to determine the net flows for each sample tube and to identify any sampling problems. The sample test data form can be found in Appendix D. System checks are run as follows:

- Before inserting the sample tube prior the test: set the main flowmeter to the intended test flowrate.
    - Record the main flowmeter reading.
    - Record the flow at each tube position.

- After removing the sample tube post-test: do not change the vacuum pump setting or main flowmeter valve setting until all flows are recorded:
    - Record the main flowmeter reading.
    - Record the flow at each sample position.

Ideally, the flows have not changed during the test.

2.3.2 Sample tube installation

Sample tube assemblies are installed immediately prior the test to minimize diffusion of CO_2 into the sample tubes. Prolonged exposure to CO_2 reduces the collection efficiency of the sample tube. Sample tubes are removed immediately after the test to minimize post-test diffusion of combustion gases into the sample tubes. CO_2 is an interference for some analytes in ion chromatography.

Care must be taken to handle the collection tube assembly such that there is no contact with any surfaces, which can contaminate the sample. The sample tube assemblies are installed by removing the caps from both ends, placing them in a clean container, carefully inserting the glass tube end through the bulkhead fitting.

Before tightening the swage nut on the glass pre-tube, the other end (the breakthrough tube outlet) is connected to the ¼” o.d. cooling coil (or cooling tube) which leads to the HEPA filter using a short length of 3/16" i.d. 5/16" o.d. Tygon™ tubing. Next, tighten the swage nut on the glass pre-tube end. The swage nut only needs to be finger tight if graphite ferrules are used. Confirm that the tubes are notable to rotate. If graphite/Vespel™ ferrules are used, a slight turn with a hand wrench may be necessary to ensure the tube does not rotate.

Ice and water can now be added. Minimize the amount of ice used so that tubes can be quickly recovered after draining the ice bath. Add sufficient ice so some ice remains after the test. Next, add water to completely cover the tubes and HEPA filters.

2.3.3 Pretest-setting flow rates

The flow rate is selected with the following considerations:

- The duration of the test and the levels of analytes to be expected.
- The limit of detection of the method of analysis for each analyte.
- The capacity of the sample tube.

- The potential diffusion and deposition errors. Although minimized with the design of the sampling system, diffusion errors will occur.
- In general, a minimum volume of 1 L per tube is sampled to minimize the deposition errors.

The procedure to set flow rates is as follows:

- Turn vacuum pump on. Set vacuum to 27" Hg.
- Start the computer program.
- Set the computer program to “PRE-TEST AND POST-TEST VENTING MODE,” (only the venting solenoid valve is open, and no sample is being drawn through sample tubes).

Adjust the flowmeter metering valve to the intended flow for each sampling station. Indicate this required flow rate on the flowmeter housing.

2.3.4 The test

- Start the video cameras to monitor and record each system flowmeter during the test. Each camera shows the time into the test.
- Press the “Start test button” to start the test.
- Do not adjust the flow during the test.
- Record the following flowmeter readings for each sampling station:
  - Set flowmeter reading for each system flowmeter,
  - Range of flowmeter readings for each sample tube during test with sample times.
  - Final flowmeter reading for each flowmeter after sampling completed (vent mode).
- Those flow rates are needed to perform the calculations detailed in Appendix C. The “Test and post-test data form” can be found in Appendix D.
- Do not adjust the flow after the test since post-test flows must be measured.

2.3.5 Sample tube removal

Sample tubes are removed from the ice bath as soon as possible to minimize diffusion errors (before the activation of post-test extinguishing system). Immediately after the test, water is drained from the ice-water bath. Protective breathing equipment may need to be donned by the individual recovering the samples.

After the water in the ice bath is drained, the tubes are dried with a clean paper towel as well as the swage-nut and Tygon™ unions connecting the sample tube to the sampling system. Be careful to not let any water, a contaminant, enter the ends of the sampling or breakthrough collection tubes. On the glass inlet make sure to carefully wipe any deposits on the outside and on the end of the tube with a clean Kimwipe™ wetted with DI water. This prevents deposits on the outside of the glass tube from being added to material trapped.

The front face and exposed sides of each glass pre-tube are wiped clean a second time with DI-wetted clean Kimwipe™ to prevent the contamination of the sample to be recovered. After drying and cleaning, cap the tubes if not eluted shortly. The samples tube assemblies for each station are placed in a separate clean tray.

The sample tubes (and breakthrough tubes if used) are maintained in a horizontal position. Keeping tubes in the horizontal position is necessary so any liquid in either the sampling or breakthrough detection tube is not allowed to flow into the other tube. The tubes are transported to the laboratory where the tubes are eluted and the eluted sample is analyzed. Elute the tubes as soon as possible after the test.

2.3.6 Post-test sample recovery from sample tubes

Again, clean the front face and leading edge of the tube with Type 1 deionized water. Use a wetted Kimwipe™. Repeat with a clean slightly wetted Kimwipe™ so that any acids deposited on these surfaces are removed. Only the internal contents of the sample tube are to be recovered and analyzed.

The pre-tube and primary collection tubes are eluted in series and the breakthrough collection tubes are eluted separately. Each section is typically washed with a 30.0 ml or 100 ml (for large sample tubes) of 0.025 M or 0.050M NaOH solution. The concentration of the NaOH wash solution depends on the level of anions collected and the column used in the ion chromatography method. The hydroxide concentration must not significantly affect the retention time of each analyte. Additional dilutions with the NaOH wash solution may be needed to obtain concentrations within the calibration curve of each analyte.

The washing and sample recovery procedure is as follows:

- Each tube is mounted vertically, with the arrows pointing upward and is back flushed (the opposite direction from gas sampling) with the prescribed volume of NaOH wash solution.
- This post-test rinsing is done in the similar manner as used for coating (downstream end up). Note that the NaOH solution concentration is much lower for rinsing than coating.
- Back flushing ensures that the most concentrated analyte exits the tube first, optimizing analyte recovery.
- The prescribed volume of NaOH wash solution is dispensed with a Luer tipped disposable syringe into a polypropylene sample bottle, which has been previously rinsed with deionized water and dried.
- Let gravity drain the solution. Remove excess solution by pushing 60cc of air from above with a syringe. Wipe off the edges and tips of the tube with a Kimwipe™.
- When a collection efficiency study is done, each section of the sample tube is eluted separately.
- The contents of the pre-tube must be collected for analysis since significant concentrations of acids deposit in the interior of the glass pre-tube.
- The recovered solution is further diluted with 0.025 or 0.050 M NaOH when any analyte concentration exceeds the calibration range of the method of analysis.
- The collected fire test samples are stirred and filtered through a PTFE 13 or 25mm 0.2-micron disposable syringe filter directly into the autosampler cuvette of the IC. Use polypropylene or another suitable plastic, not glass, cuvettes if fluoride is to be analyzed.

2.3.7 Post-test flow recordings

Flow rates at the sample tube position (upstream of the HEPA filter) may need to be determined immediately post-test if flows at the main system flowmeter changed during the test. The flows at the sample tube positions are needed for determining acid gas concentration sampled, as well as information on which lines have flow restrictions that need to be corrected for subsequent tests.

- First, remove samples for analysis
- Follow guidance outlined in 2.3.1.2 system checks same day as test: restated in more detail. If there was a significant change in the main flowmeter setting during the test,

check flows for each sample tube and vent tube at both the main flowmeter and upstream of each HEPA filter: Use an open rotameter of the same flowmeter type with no valve and flow range as the main flowmeter as shown using the same vent flowrate as recorded for the end of test. See section 2.3.3. Include the rotameter model number and type of float valve recorded (e.g., glass or stainless steel) as well as the readings. Record on the appropriate form in Appendix D.

  - Wait for the air to clear after the test. Continue when it is safe to enter the test area.
  - Set computer to the “PRE-TEST AND POST-TEST VENTING MODE” and check that flows at the main flowmeter match the end of test flows after all tubes sampled (venting solenoid). Ideally, the flows do not change during the test.
  - Press the “Start Test” button.
  - Without changing the main flowmeter needle valve or vacuum post-test, record both the flow upstream of the HEPA filter and at the simultaneous flow at the main flowmeter.
  - Note if there are significant delays in the flow for each sample position. If so, measure the t90s.
  - Measure the vent flow at the venting solenoid inlet. Record the vent flow.
  - Enter data into the post-test data form in Appendix D and provide a copy to the chemist.
  - Replace HEPA Filters as needed.
- Provide flow data sheet and programmed valve timing data sheets to the principal investigator.

3 Acid gas methods of analysis

After collecting samples, each sample tube is eluted: use 30 ml of a 0.05M NaOH solution into 30ml polypropylene container. The concentration of the NaOH elution solution may be adjusted to be compatible with the method of analysis. The eluted 30 ml sample is diluted for further analysis when any analyte is outside the calibration range of the method of analysis. If any tubing was used upstream of the sample tube, it is also eluted for analysis. If there are breakthrough tubes, they are be analyzed separately to determine collection efficiency (see section 2.1.3).

The following data is needed to calculate the gas concentration of each acid gas in the combustion gas collection solution:

- The gas volume sampled per sample tube (based on sample time and sample flowrate).
- The liquid wash or extraction volume.
- The calibration curves obtained using the calibration standards for the concentration range of the method.
- The resulting solution/anion concentration determined by from the analysis of the liquid sample
- The molar mass (g/mole) of the anion if calibration solutions have units of ppm (mg anion/liter solution).

Calibration curves using anion standards must be developed for each anion and each method. The measured concentration of each anion in the analyzed solution are determined by applying the calibration curves.

There are two units that are customarily used for anion concentrations in solution: either of these is acceptable. Calibration standards containing seven anions are commercially available for both units.

- ppm, milligram anion /liter solution (mg/L).
- micromoles/liter solution (μmol/L).

The units of μmol/L are based on the molar quantities, providing a direct comparison of the molar quantities of each anion. Note that μmol/L gives the relative concentration of each anion and can be related to the stoichiometry of the reaction.

The units of ppm are convenient when the goal is to measure gas yields (e.g., grams of analyte/grams of sample). The units of ppm are based on the molar mass of the anion for each calibration salt that is dispensed into a given volume of solution. When you are inputting molar mass in the calculations you need to convert from grams of anion per liter solution to moles of acid per liter of solution to obtain the acid gas concentration in the sampled air.

There are three units that are customarily used for acid gas concentrations for fire gas studies.

- ppmv, equivalent to μL/L (liters of gas/liters of air x 106).
- μL/L, equivalent to ppmv (liters of gas/liters of air x 106).
- percent, %, liters of gas/liters of air x 100.

Other units used for acid gas concentrations for other applications include:

- $g * m^{-3}$, grams of gas per cubic meter of air.
- $mg * m^{-3}$, μg of gas per cubic meter of air, equivalent to ppm. This is used to quantify air pollution levels. This is distinct from the ppm mentioned in the solution section above. This is also different unit than ppmv.
- ppm, μg of gas per cubic meter of air. See above for more details.

The calculations of acid gas concentrations for fire gas analysis can be found in Appendix C.

Two methods of analysis are used by Fire Safety Branch laboratory for analysis of anions: ion chromatography and fluoride ion-selective electrodes.

3.1 Ion chromatography

As stated in section 2.1.2 all water used to prepare the NaOH solutions for coating and eluting of sample tubes should be prepared from 18 mega Ohm water that is subsequently degassed to remove CO_2. The presence of CO_2 results in a carbonate peak, which may potentially co-elute or interfere with anions of interest.

All water used to prepare eluents is prepared and then blanketed with an ultrapure gas with low water solubility at 15psi. This prevents the slow acidification of the eluent which can affect the chromatography. Helium has a lower water solubility, but nitrogen may be sufficient if the there is a degasser downstream of the water feed to an eluent generator.

Some IC columns and suppressors are not compatible with strong basic solutions that are required for collection and rinsing/eluting the samples tubes for analysis. It is suggested working with high-capacity columns and suppressors that are compatible with strong basic solutions. If this is not possible, consider using a more dilute NaOH solution for coating and eluting of sample tubes.

3.1.1 Ion chromatography general principles

By varying the concentration of the eluent during the chromatographic separation, ions with widely different affinities for the separator resin may be separated in one run. Elution can either be isocratic or gradient. Isocratic elution is the elution method with no changes of the mobile phase composition taking place during a chromatographic run. Gradient elution is the continuous change of the mobile phase composition during a chromatographic run. The order of elution is dependent on the column, the eluent, and the gradient.

Traditional gradient systems have two separate feeds of water and stock hydroxide solutions and separate pumps.

Some IC systems use eluent generator cartridges (EGC) to generate gradients by programmed mixing of a sodium or potassium hydroxide salt with water. The EGCs have continuously (electrolytically) regenerated trap columns (CR-TC) that remove ionic contaminants, notably carbonate, from the deionized feed water to the EGC, providing low drift during gradient elutions. Offline chemical regeneration is not needed with these systems.

The first few inches of the analytical column are the first to be poisoned, trapping anions and other materials that will not elute through the column, resulting in shorter retention times. A short guard column is used prior to the analytical column to protect it. The guard column is cheaper to replace and extends the life of the analytical column. The guard column trap anions and other materials that will not elute through the column. The guard column is replaced frequently.

3.1.2 Anions of interest

Common anions seen for combustion products of materials include fluoride, glycolate, acetate, formate, chloride, nitrite, carbonate, sulfite, sulfate, bromide, nitrate, and phosphate. Common anions seen for the decomposition products of current halon replacement fire extinguishing agents include fluoride, chloride, bromide, iodide, and iodate.

The weak acids glycolate, acetate and formate may interfere with the anions of interest. The separation the weak acid interferences may be enhanced by starting with a low concentration of the eluent. Gradient methods provide the best separation of early eluting organics from fluoride. For this reason, gradients are preferred for samples containing fluoride.

3.1.3 IC calibration of anions

Guidelines for anion calibration:

- Anion calibrations are based on peak area, not peak height since peak height is subject to sample matrix effects. For example, the peak height of an anion changes significantly with changing hydroxide concentrations.

- Calibration concentrations ideally have a range of about three orders of magnitude.
- The calibration curves are often nonlinear. The number of calibration points needed depends on the calibration curve linearity.
- The curve linearity for a particular ion depends on the column, the separation method, sample loop size, the column capacity and the separation method.
- The retention time shift as the concentration of the analyte increases and the hydroxide concentration in the sample increases. Care is taken to avoid misidentifying shifting peaks. The peak identification windows are enlarged to properly identify analytes.
- Anions are quantified using external standardization with a four to seven point calibration curve with anion concentrations that do not exceed the capacity of the columns. Consider decreasing the size of the sample loop from 25 µL to 5 µL if sample concentrations are very high.
- The calibration curve should pass through the origin.
- The following calibration concentrations can be considered if using a 25-microliter sample loop with a 4mm x 250mm AS 15 column, with the method described in Table 5,
    - ppm fluoride: 0.5 ppm, 1ppm, 2ppm 5 ppm, 10 ppm, 15 ppm, and 20 ppm,
    - µM fluoride: 25µM, 50µM, 100 µM, 250 µM, 500 µM, 750 µM, and 1000 µM.

A common mix of calibration anions commercially available is shown in Table 3.

Table 3. 7-Anion standard solution

Anion	**Concentration (mg Anion/L)**
Fluoride	20
Chloride	100
Nitrite	100
Sulfate	100
Bromide	100
Nitrate	100
Phosphate	200

Dilutions can be made from this standard solution to construct a calibration curve. Fluoride calibration curves are the most nonlinear relative to the seven anions listed in Table 3. The calibration curve for fluoride is shown in Figure 23, fluoride calibration curve using AS15 column with the method shown in Table 5.

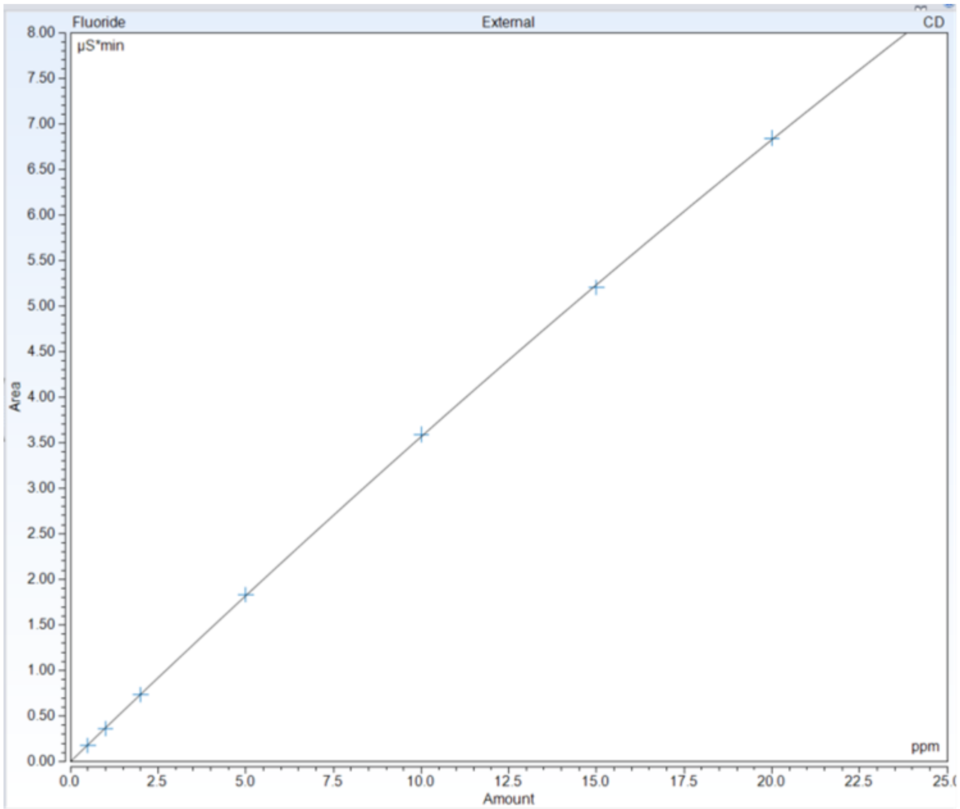


Figure 23. Fluoride calibration curve using AS15 column

The autosampler may be used to perform serial dilutions of this standard solution mix to create the calibration standards.

The IC is calibrated with the anions of interest daily or less often if it can be demonstrated by daily calibration checks that calibration is not needed.

Calibration solutions are available with units of mg anion/liter solution or µmole anion/liter solution. (See Appendix C for conversion between units.)

The following other calibration solutions are available commercially:

- A stock solution containing a mix of 0.1M concentrations of the 7 anions fluoride, chloride, bromide, nitrate, nitrite, phosphate, and sulfate is available commercially.
- Single anion calibration solutions for 0.1M concentrations of the anions glycolate, acetate and formate are also available commercially.

- Stock calibration solutions with units of mg/liter (mg anion) are also available with a mix of anion concentrations.

It is important to calibrate and check calibration regularly since the retention time can shift with concentration and poisoning of the column which can be expected from fire test samples. This ensures that correct identification for each anion for all test sample concentrations within this calibration range. Adjust the lowest test calibration sample to capture the anion just above the level of detection.

It is recommended that calibration checks be performed every 10 – 20 fire test samples: e.g., 4µM (or lower) and 1000µM standard anion solution. If the quantified concentration changes markedly, correct the problem, recalibrate, and reanalyze the samples.

Solutions of cyanide and sulfide are far less stable and must be prepared daily from reagent grade potassium cyanide and potassium sulfide respectively: Prepare a 0.1M solution of potassium cyanide or potassium sulfide daily, if it is to be analyzed. Cyanide and sulfide calibration and sample solutions need to be stored at 10°C. Temperature controlled autosamplers are available that can hold the samples at 10°C. Sodium salts are more hydroscopic, and potassium salts are preferred. Sulfide reacts readily with oxygen in solution, so the diluent water is purged with helium prior to preparing the sulfite standard solutions.

3.1.4 Peak identification

Retention times shifts with column loading. Shifting is minimized by using high-capacity columns. Shifting retention times can cause misidentification of peaks. A high-capacity column is desirable for this reason and is recommended for fire gas analysis. For a particular column and method, column loading is a function of the sample loop size, the separation method, the ion concentration, and the sample matrix. Retention times for a given anion decrease as the hydroxide concentration in the sample increases.

Retention times of a given anion time shift as that ion concentration increases. The IC program may not identify the retention time of the peak if the concentration is lower than the lowest concentration used in the calibration curve, so it is important to select the lowest calibration concentration with that in mind.

The peak identification windows are adjusted further to enable proper identification of analytes in basic solution.

3.1.5 Scheduling of IC samples

An autosampler is necessary due to extended duration of the analysis of many calibration standards and samples. Calibration samples can be prepared by manual dilution or by dilution of a sequence of empty vials using the sample prep option of the IC autosampler.

A non-sequential autosampler with a sample prep option can be set up to program the sequence of vial positions for calibration standards and samples. Stock calibration standards can be placed in vial positions to be used for preparation of additional calibration standards by dilution. The sample prep feature dilutes the calibration standards into a sequence of empty sample prep vials. Standards may be robotically prepared from a stock calibration solution, shaken, and analyzed in the prescribed order. Use the sample preparation feature to serial dilute (with distilled, deionized, purged water blanketed with Helium) the starting standard solution mix to obtain sealed vials of calibration standards with concentrations ranging from 25µM to 1000µM. This serial dilution may be done on the day of the analysis, just prior to running chromatographs of these same standards, and the test samples.

The program controlling the autosampler and IC includes the vial position, injection volume, sample description, calibration dilution levels when applicable and the IC method to be run for each sample. Additional parameters include the column oven setting and the sample loop flush volume.

The program can be modified while the schedule is running to accommodate additional dilutions for samples with anions exceeding the calibration limit. Diluted samples can be further diluted as needed. Empty vials for dilution can be added to the sample trays to allow for further dilutions. Some autosamplers have a feature that will automatically dilute samples for any anion whose quantification falls above the calibration range.

Chromatographic reports are generated for each sample in the order of the analysis.

3.1.6 IC column selection

A high-capacity column is needed for high ionic strength eluent and samples used in this analysis. Columns are selected based on separation requirements.

- The Dionex Ionpac AG15 guard column (4mm x 50mm) and AS15 Analytical Column (4mm x 250mm) are the preferred columns for all the anions of interest described below except for iodide, which is retained by this column (Thermo Scientific, 2014). An excellent separation can be obtained for fluoride, light organic interferences, carbonate, chloride, nitrate, nitrite, phosphate, bromide, sulfite, and sulfate (conductivity detection).

Iodate co-elutes with glycolate, one of the light organic interferences. This column separates fluoride from early eluting organics anions glycolate, acetate and formate. These columns are even higher capacity than the AG10 and AS10 columns (see bullet below) previously used by our lab (Lyon, 2006; Thermo Fisher, 2008).

- AS15 columns have a markedly improved separation and separate the interference iodate from fluoride which the AS10 and the AS18 columns cannot do. However, iodide is retained in the column. A gradient separation is used to obtain the required resolution for fire gas samples, particularly the separation of fluoride from early eluting organics.
- The Dionex Ionpac AG20 guard column (4mm x 50mm) and AS20 Analytical Column (4mm x 250mm) allow the separation of the late eluting iodide from the other anions (Thermo Scientific, 2012). The separation of some of the other anions of interest is not satisfactory, particularly fluoride from glycolate; carbonate from sulfite, and sulfite from sulfate.
- The Dionex Ionpac AG10 guard column (4mm x 50mm) and AS10 Analytical Column (4mm x 250mm) are high-capacity columns used for the gradient separation of the seven standard anions as well as HCN and H2S.
- The Metrohm Supp A 5: A 250mm column, used by Arkema, is used for the isocratic separation of the seven standard anions. The separation of fluoride and glycolate, the earliest eluting organic acids is poor with this column, however separation can be obtained with further dilution. According by the manufacturer a gradient elution will not improve the fluoride and glycolate separation by much. This column may be considered if the analysis of fluoride is not required.
- Metrohm Supp A 7: A 250mm column is used for isocratic separation of fluoride, early eluting organics (acetate and formate), chloride, nitrite, bromide, nitrate, phosphate, sulfite, and sulfate. The separation of fluoride from glycolate and acetate can only be obtained for very dilute solutions. The separation is improved compared to Metrohm Supp 5 250mm column in that sulfite and sulfate are separated. According by the manufacturer a gradient elution will not improve the fluoride and glycolate separation by much. This column may be considered if the analysis of fluoride is not required.
- The Acclaim WAX-1 Analytical Column (4mm x 150mm) has been used for the separation of Iodate and Iodide.

The separations obtained with these columns are discussed in the sections below.

The column properties and separation highlights are summarized in the Table 4.

Table 4. IC columns

Column	**Column size (mm x mm)**	**Anion Exchange Capacity (μeq/ column)**	**pH**	**Eluent**	**Max. Operating Pressure** (psi)**	**Detector**	**Separation Highlights**	**Well Separated from Interferences**
Dionex AS10 *	4 x 250	170	0-14	KOH	3,500	Conductivity	Iodate and fluoride well resolved. Glycolate interference for fluoride at high fluoride conc.	Fluoride Chloride Nitrite Sulfate Bromide Nitrate Phosphate
Dionex AS15*	4 x 250	225	0-14	KOH	4,000	Conductivity	Excellent separation of fluoride from iodate and glycolate which coelute.	Fluoride Chloride Nitrite Sulfate Sulfite Bromide Nitrate Phosphate
Dionex AS20	4 x 250	310	0-14	KOH	4,000	Conductivity	Iodate coelutes with fluoride, iodate, and acetate. Poor resolution of carbonate, sulfite and sulfate. Excellent separation of Iodide.	Chloride Nitrite Bromide Nitrate Iodide Phosphate Iodide
Metrohm A Supp 5*	4 x 250	___	3-12	K2CO3	2,180	Conductivity	No separation of fluoride and glycolate at high fluoride concentration	Chloride Nitrite (Sulfate & Sulfite co-elute) Bromide Nitrate Phosphate
Metrohm A Supp 7*	4 x 250	___	3-12	K2CO3 + KHCO3 mix	2,180	Conductivity		Chloride Nitrite Sulfate Sulfite Bromide Nitrate Phosphate

Acclaim WAX-1	4.6 x 150	___	2.5-7.5	Na2HPO4 + H3PO4	5200	UV, 223 nm, 10 nm bandwidth	Excellent separation of Iodide. Concern of running close to the pH limitation of the column.	Iodide

* Iodide retained in the column

** Operating a column above its recommended operating pressure can cause irreversible loss of column performance.

3.1.7 IC columns and methods –current

Analytical columns and methods are now available that provide improved separations compared to those obtained by previous columns used by FAA Fire Safety Branch chemists.

3.1.7.1 Ionpac AS15 IC column

The AS15 column set provides an improved separation compared to the historically used AS10 column set, for the separation of fluoride and nitrite from early eluting carboxylic acids found in combustion gas samples (glycolate $HOCH_2COO^-$, acetate, CH_3COO^- and formate H_3COO^-). This column also separates the later eluting anions of interest from the carboxylic acids propionate $CH_3CH_2COO^-$, butyrate $CH_3CH_2CH_2COO^-$ and oxylate $[O_2CCOO]^{2-}$. Carboxylic acid interferences can be expected from lithium-ion battery thermal runaway vent gas samples. Iodate co-elutes with glycolate. This column retains iodide.

The chromatographic method developed by Thermo Fisher Scientific for FAA fire test samples is tabulated in Table 5. A 4 x 250mm AS15 column with a 4x 50mm AS15 pre-column was used. A pre-injection equilibration time of 10 minutes was utilized. After sample injection, a gradient of 2 to 60 mM NaOH is ramped for 28 minutes, and the concentration holds at 60mM until 35 minutes.

Table 5. Ion chromatography 10-Anion Dionex AS15 Method for FAA Samples

<table>
<tr><th>Anions</th><th>Instrument</th><th>Columns</th><th>Method</th></tr>
<tr><td>Fluoride
Glycolate
Acetate
Formate
Chloride
Nitrite
Carbonate
Sulfite
Sulfate
Bromide
Nitrate
Phosphate</td><td>Dionex Integrion system,
Eluent source: eluent generation cartridge- Dionex 500 EGC II KOH with continuously generated anion trap column- Dionex CR-ATC 600
Detection: Suppressed conductivity,
Dionex Integrion CD Conductivity Detector and Integrated cell
Suppressor: Dionex ADRS600, 4mm</td><td>Dionex IonPac AG15 Pre-column,
4 x 50 mm
Dionex IonPac AS15,
4 x 250mm</td><td>IC Gradient Elution.
Column T: 300C
Total flow: 1.25ml/min
Injection volume 25µL<table><tr><td>Time, (min)</td><td>mM KOH</td></tr><tr><td>-10-0</td><td>2 (equilibrate)</td></tr><tr><td>0-28</td><td>2-60, ramp</td></tr><tr><td>35-45</td><td>60</td></tr></table>Standby mode: 20mM NaOH</td></tr>
</table>

Note that the anion trap column used in the method removes anion interferences, such as carbonate, from the eluent prior to the injection valve. This reduces the background conductivity, enabling lower limits of detection.

Figure 24 shows a chromatogram of a calibration standard of 10 anions using this method. These 10 anions are commonly found after eluting combustion gas sample tubes. The prepared anion concentrations are shown in Table 6.

Table 6. Anion concentrations for Figure 24

Anion	**Amount (ppm)**
Fluoride	20
Glycolate	~60
Chloride	100
Nitrite	100
Carbonate	unknown
Sulfite	~100
Sulfate	~100
Bromide	100
Nitrate	100
Phosphate	200

No attempt was made to stabilize sulfite, so it partially oxidized to sulfate. The carbonate concentration is primarily due to absorbed CO_2.

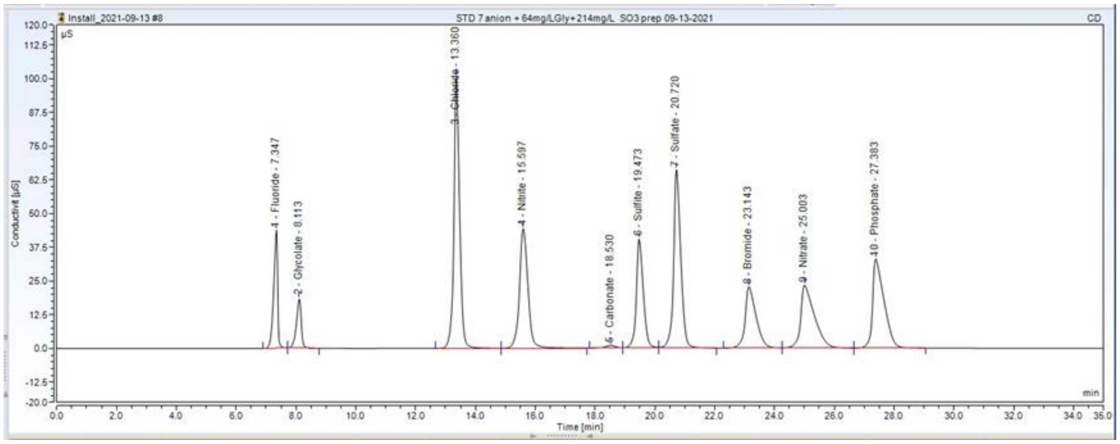


Figure 24. Ion chromatogram of standard anions using AS15 4mm column set

The application of this 10-anion method for lithium-ion battery vent gas samples was evaluated for an 18650 cell. Bomb calorimeter vent gas samples were obtained in air using large sample tubes. A vent gas sample taken after the thermal runaway reaction was completed.

Figure 25 shows a chromatogram obtained of the battery anions. This chromatographic method provides an excellent separation of the anions of interest. The carbonate anion does not pose an interference in this analysis. The quantified anion concentrations are shown in Table 7.

Table 7. Anion concentrations for battery sample in Figure 25

Anion	**Amount (ppm)**
Fluoride	55.8
Glycolate	4.1
Chloride	0.3
Nitrite	0.6
Carbonate	Unknown
Sulfite	87
Sulfate	1.6
Bromide	0.1
Nitrate	0.2
Phosphate	3.9

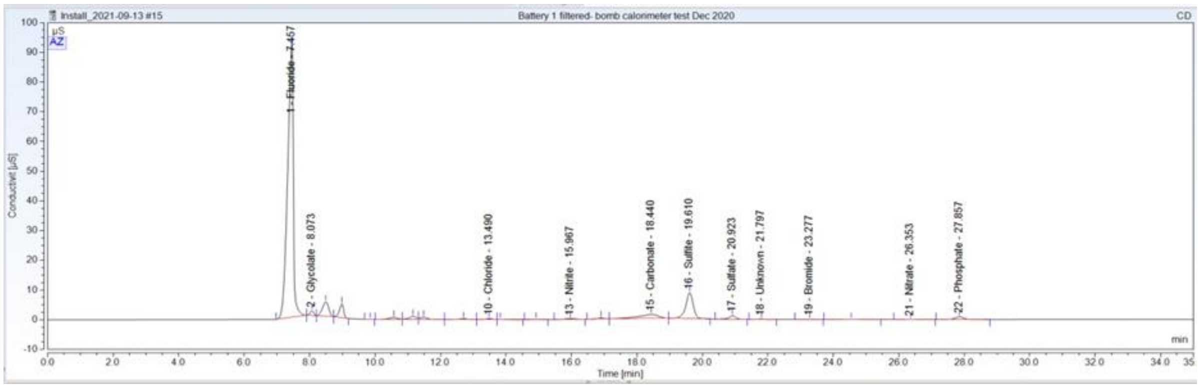
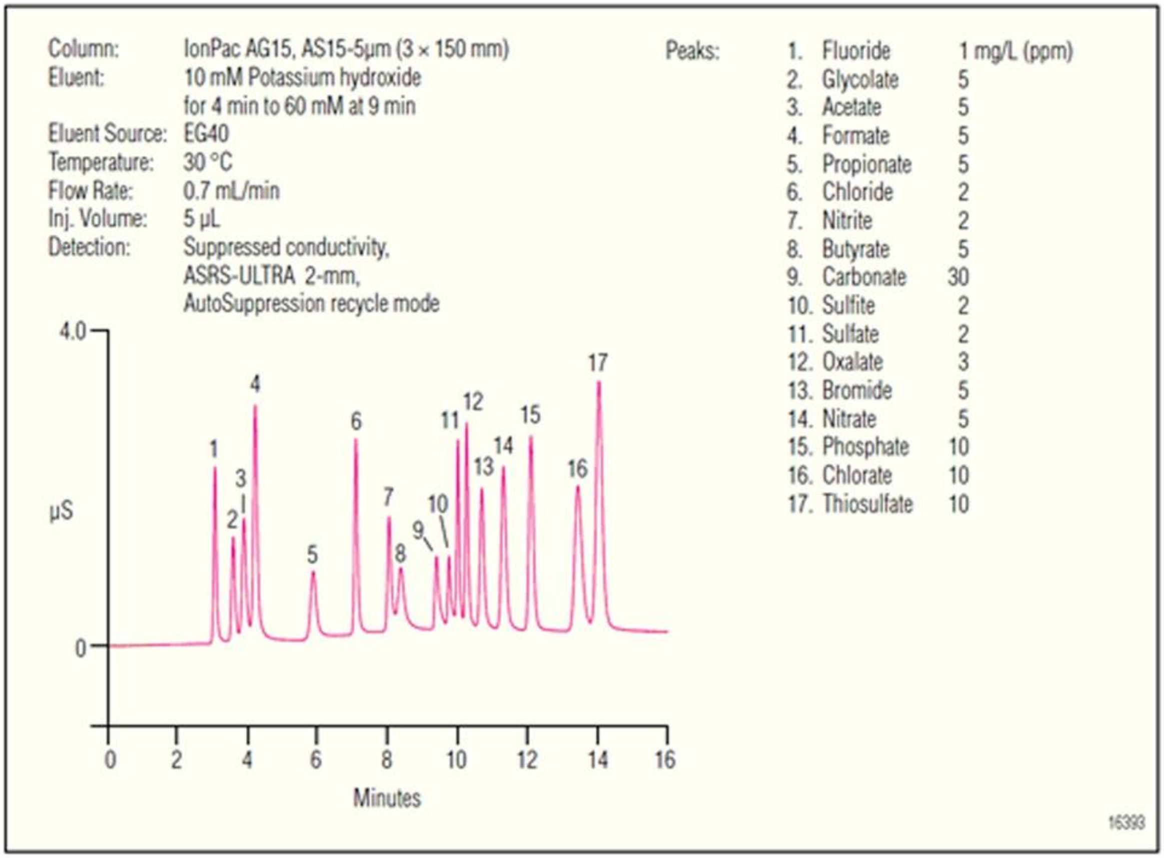


Figure 25. Ion chromatogram for battery sample using AS15 4mm column set

The separation and method using a fast 3 x 150mm AS15 column for a low concentration of 17 anion standard is illustrated in Figure 26 (Fisher, 2011). This fast (short and narrow) AS15 column has insufficient capacity and insufficient resolution for combustion gas samples but illustrates the separation potential of the larger AS15 columns which have improved capacity and resolution.


Column: IonPac AG15, AS15-5µm (3 × 150 mm)
Eluent: 10 mM Potassium hydroxide for 4 min to 60 mM at 9 min
Eluent Source: EG40
Temperature: 30 °C
Flow Rate: 0.7 mL/min
Inj. Volume: 5 µL
Detection: Suppressed conductivity, ASRS-ULTRA 2-mm, AutoSuppression recycle mode

Peaks:		
1.	Fluoride	1 mg/L (ppm)
2.	Glycolate	5
3.	Acetate	5
4.	Formate	5
5.	Propionate	5
6.	Chloride	2
7.	Nitrite	2
8.	Butyrate	5
9.	Carbonate	30
10.	Sulfite	2
11.	Sulfate	2
12.	Oxalate	3
13.	Bromide	5
14.	Nitrate	5
15.	Phosphate	10
16.	Chlorate	10
17.	Thiosulfate	10

Figure 26. Gradient separation of anions using 3mm AG15 and AS15 columns

Note that this chromatogram includes six carboxylic acids which may be expected interferences for lithium-ion battery vent gas samples.

3.1.7.2 Ionpac AS20 IC column

This column has a much poorer separation for many of the anions of interest. However, it provides a good separation of iodide from the other anions. This column could be used for measuring iodide, a decomposition product of the extinguishing agent CF_3I. Iodate, another decomposition product of CF_3I coelutes with fluoride and is an interference. An AS15 column or fluoride ion selective electrode can be used to measure fluoride in this case.

Figure 27 was obtained using Dionex virtual column software to predict the chromatogram of the anions of interest using an AS20 4mm x 250mm virtual column for the single gradient of 2mM to 25mM at 29 minutes shown on the same figure. The column temperature was set at 30°C, the flowrate was 1.25 ml/minute and a 5µL injection volume was simulated. The anion concentrations are listed in Table 8.

Table 8. Anion concentrations for Figure 27

Anion	**Concentration (mg/L)**	**Co-eluting Anion**
Fluoride	40	Iodate
Acetate	40	Glycolate, Propionate
Formate	40	
Chloride	40	
Nitrite	100	
Bromide	100	
Nitrate	100	
Carbonate	100	
Sulfite	100	
Sulfate	100	
Oxylate	100	
Iodide	100	
Phosphate	200	

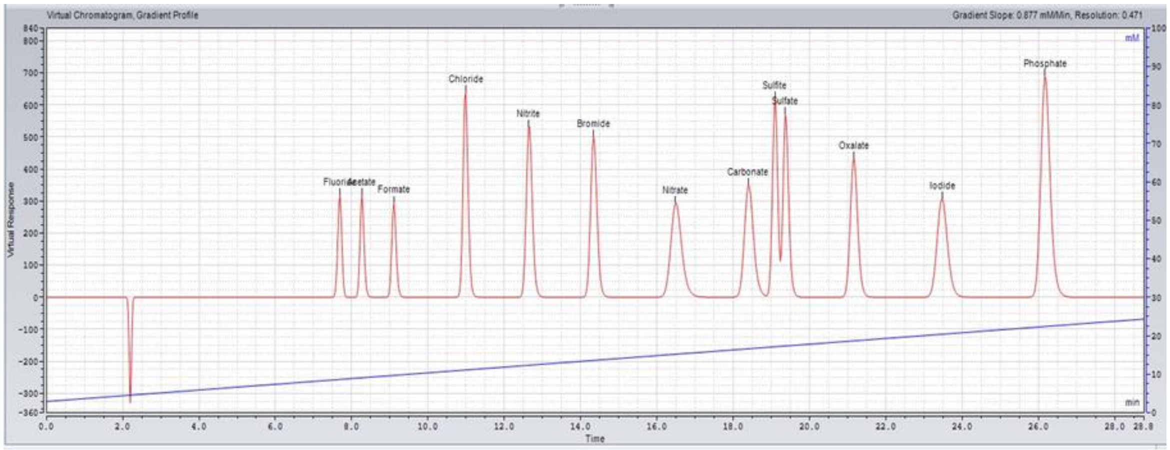
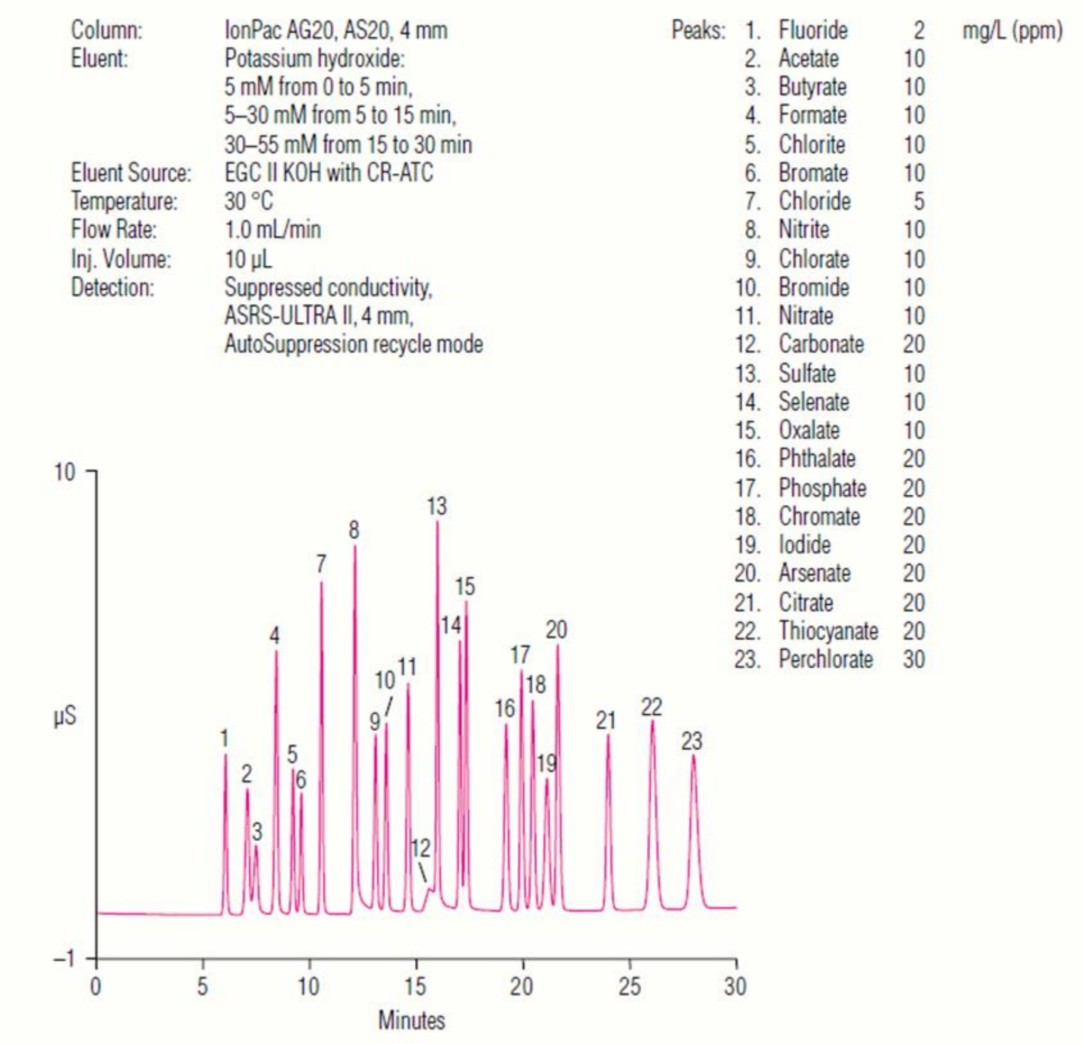


Figure 27. Simulated separation of anions using 4mm x 250mm virtual AS20 column

The AS20 column provides a good separation for iodide which is retained by the AS15 column. The separation of some of the anions of interest is not satisfactory, particularly fluoride from glycolate (not shown); carbonate from sulfite, and sulfite from sulfate. Iodate co-elutes with fluoride. Glycolate, iodate and proprionate coelute with acetate. The gradient/gradients may be altered to improve separation of carbonate, sulfite, and sulfate. This column is not capable of an acceptable separation of fluoride and iodide. In contrast, the AS15 column provides an optimal separation for the anions except for iodide which is retained by the AS15 column.

Figure 28 shows the actual AG20 /AS20 column set with multiple gradients (Thermo Fisher, 2021). This figure contains many organic anions not encountered in fire gas anion samples. It shows a poor separation of carbonate from sulfate. Sulfite, not shown, elutes between carbonate and sulfate, so these anions cannot be resolved with this method.



Column: IonPac AG20, AS20, 4 mm
Eluent: Potassium hydroxide:
5 mM from 0 to 5 min,
5–30 mM from 5 to 15 min,
30–55 mM from 15 to 30 min
Eluent Source: EGC II KOH with CR-ATC
Temperature: 30 °C
Flow Rate: 1.0 mL/min
Inj. Volume: 10 µL
Detection: Suppressed conductivity,
ASRS-ULTRA II, 4 mm,
AutoSuppression recycle mode

Peaks:			mg/L (ppm)
1.	Fluoride	2	
2.	Acetate	10	
3.	Butyrate	10	
4.	Formate	10	
5.	Chlorite	10	
6.	Bromate	10	
7.	Chloride	5	
8.	Nitrite	10	
9.	Chlorate	10	
10.	Bromide	10	
11.	Nitrate	10	
12.	Carbonate	20	
13.	Sulfate	10	
14.	Selenate	10	
15.	Oxalate	10	
16.	Phthalate	20	
17.	Phosphate	20	
18.	Chromate	20	
19.	Iodide	20	
20.	Arsenate	20	
21.	Citrate	20	
22.	Thiocyanate	20	
23.	Perchlorate	30	

Figure 28. Gradient separation of anions using 4mm AG20 and AS20 columns

3.1.7.3 Metrohm A Supp 7 column

This isocratic method provides a much poorer separation of fluoride from light organic acids than can be provided by the Dionex AS15 column. The method is shown in Table 9. The separation of fluoride, glycolate and acetate is poor and could not be improved much with a gradient due to column limitations. However, the separation for acetate, formate, chloride, nitrite, bromide, nitrate, phosphate, sulfite, and sulfate is good as can be seen in Figure 29. This figure shows the isocratic separation of 50 ppm standard anions in 2mM NaOH.

Table 9. Ion chromatography analysis of anions by Metrohm A Supp 7 column

Anions	**Instrument**	**Columns**	**Method**
Fluoride Glycolate Acetate Formate Chloride Nitrite Bromide Nitrate Phosphate Sulfite Sulfate	Metrohm 940 Isocratic IC	A Supp 7 250mm/4.0mm	IC isocratic Eluent: 3.6 mM sodium carbonate Oven T: 40°C Flow rate: 0.7ml/min Injection volume 1.5µL Runtime: 32 min

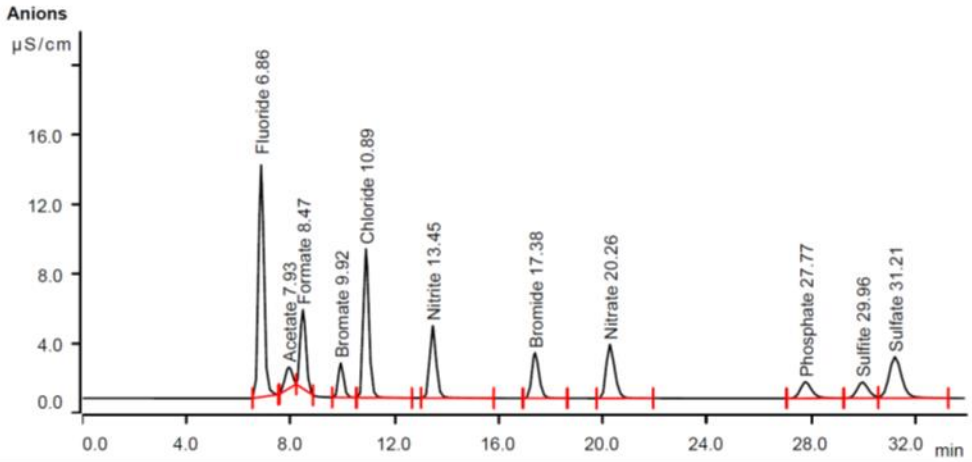


Figure 29. Isocratic separation of anions using a Metrohm A Supp 7 column

3.1.8 IC columns and methods –historical

Columns and methods are now available (see section 3.1.7) that provide improved separations to the historical columns and methods discussed in this section. Columns historically used for fire gas samples include the Ionpac AS10 (FAA and Boeing), Metrohm A Supp 5 (FAA contract lab) and the Acclaim WAX-1(Boeing). The chromatographic methods and separations for these columns are discussed below.

3.1.8.1 Ionpac AS10 methods and chromatograms for standard anions

The sampling system, instrumentation and IC gradient elution method used by the FAA is described in Table 10. This column is no longer used by The FAA Fire Safety Branch since a superior separation is attained with the AS15 column.

Table 10. FAA Ion chromatography methods for Dionex AS10 column- historical (gradient)

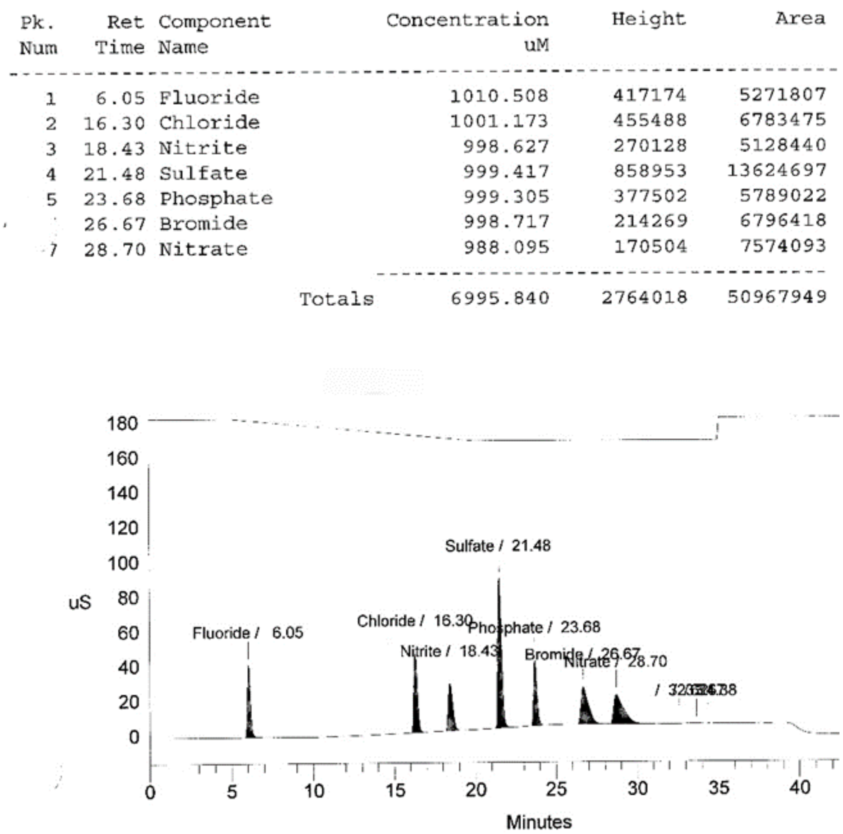
<table>
<tr><th>Anions</th><th>Instrument</th><th>Columns</th><th>Method (FAA)</th></tr>
<tr>
<td>Fluoride
Chloride
Nitrite
Sulfate
Phosphate
Bromide
Nitrate</td>
<td>Dionex DX 500 Chromatography System with GP40 Gradient Pump w/Degas,
LC30 Chromatography Oven,
ED40 Electrochemical Detector with *conductivity cell*,
DS3 Detection Stabilizer (temperature control chamber for conductivity cell)
AS3500 programmable Autosampler with sample prep,
Peaknet Chromatography Data Acquisition System</td>
<td>Dionex
Ionpac AG10 Guard Column
(4 x 50mm),
Ionpac AS10 Analytical Column
(4 x 250mm),
suppressor</td>
<td>IC Gradient Elution.

Oven T: 30^0C
Total flow: 1.0ml/min
Sample loop = 25um

<table>
<tr><th>Time, (min)</th><th>mM NaOH</th></tr>
<tr><td>0-5</td><td>20</td></tr>
<tr><td>5-20</td><td>20-150, ramp</td></tr>
<tr><td>20-35</td><td>150</td></tr>
<tr><td>35-45</td><td>20</td></tr>
</table>
</td>
</tr>
<tr>
<td>Cyanide
Sulfide</td>
<td>Same as above, but replace conductivity cell with *Ag/AgCl amperometric cell*</td>
<td>Same as above</td>
<td>Same as above. but
The sample must be kept at 10C before analysis.</td>
</tr>
</table>

The primary difference between the two methods listed in Table 10 is the detector used. A conductivity detector cannot be used at the same time as an amperometric detector. A separate analysis needs to be run to analyze the samples containing cyanide and sulfide using the amperometric detector. Studies have shown that cyanide and sulfide should be run at low sample temperatures since they have short lifetimes at room temperature. Cooled autosamplers are available for this application. Improved high-capacity columns have since been developed for the analysis of cyanide (Thermo Fisher Scientific, 2015).

Figure 30 illustrates the separation of the highest calibration concentrations of the seven standard anions. This illustrates the types of separations that are possible for a gradient elution using an AS10 high-capacity ion chromatography column and the FAA gradient method previously described in Table 10.

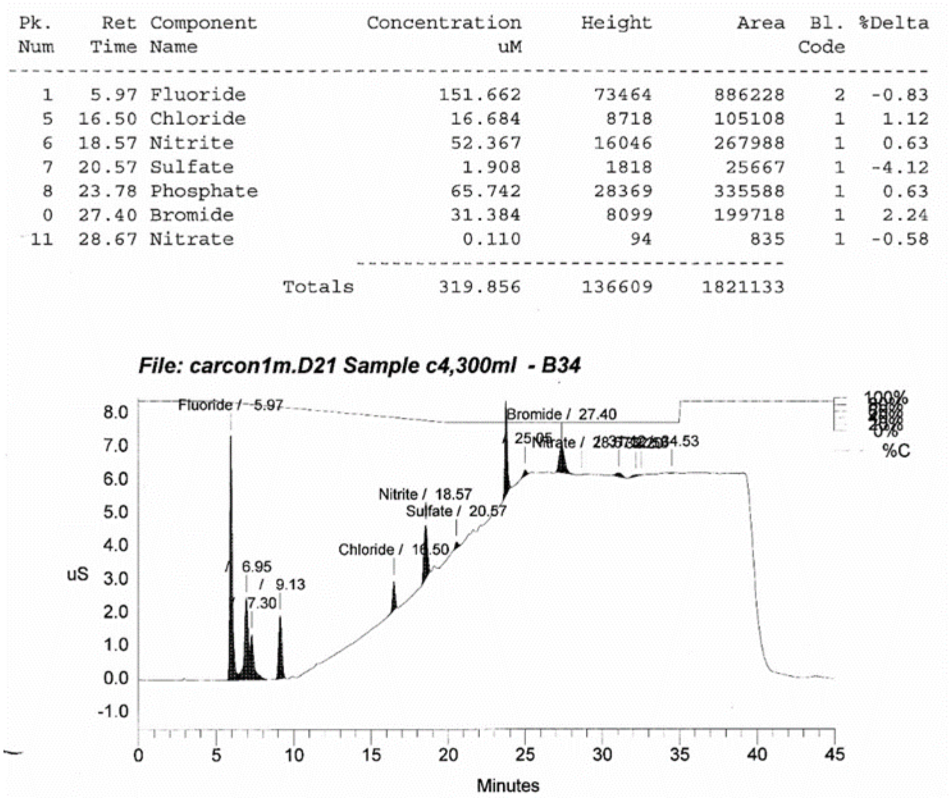


```
Pk.     Ret Component             Concentration      Height          Area
Num    Time Name                             uM
--------------------------------------------------------------------------
  1    6.05 Fluoride                   1010.508      417174       5271807
  2   16.30 Chloride                   1001.173      455488       6783475
  3   18.43 Nitrite                     998.627      270128       5128440
  4   21.48 Sulfate                     999.417      858953      13624697
  5   23.68 Phosphate                   999.305      377502       5789022
      26.67 Bromide                     998.717      214269       6796418
  7   28.70 Nitrate                     988.095      170504       7574093
                               ------------------------------------------
                        Totals         6995.840     2764018      50967949
```

Figure 30. Dionex AS10 separation of standard anions by FAA

The initial low concentrations of NaOH eluent enables separation of the early eluting organics from fluoride as can be seen in the next figure.

Figure 31 illustrates the decomposition products in the cargo compartment for cardboard boxes loaded with paper using bulk fire load extinguishing agent Halon 1301 (CF_3Br) to suppress the fire. The 30ml solution used to rinse the sample tube was diluted 10-fold to give an effective rinse volume of 300ml for this sample. This is historical data from the FAA fire tests conducted in 1997. The elution gradient is shown above the chromatogram.



```
Pk.     Ret Component          Concentration      Height        Area  Bl. %Delta
Num    Time Name                          uM                          Code
---------------------------------------------------------------------------------
  1    5.97 Fluoride                 151.662       73464      886228    2  -0.83
  5   16.50 Chloride                  16.684        8718      105108    1   1.12
  6   18.57 Nitrite                   52.367       16046      267988    1   0.63
  7   20.57 Sulfate                    1.908        1818       25667    1  -4.12
  8   23.78 Phosphate                 65.742       28369      335588    1   0.63
  0   27.40 Bromide                   31.384        8099      199718    1   2.24
 11   28.67 Nitrate                    0.110          94         835    1  -0.58
                                 ------------------------------------
                      Totals         319.856      136609     1821133
```

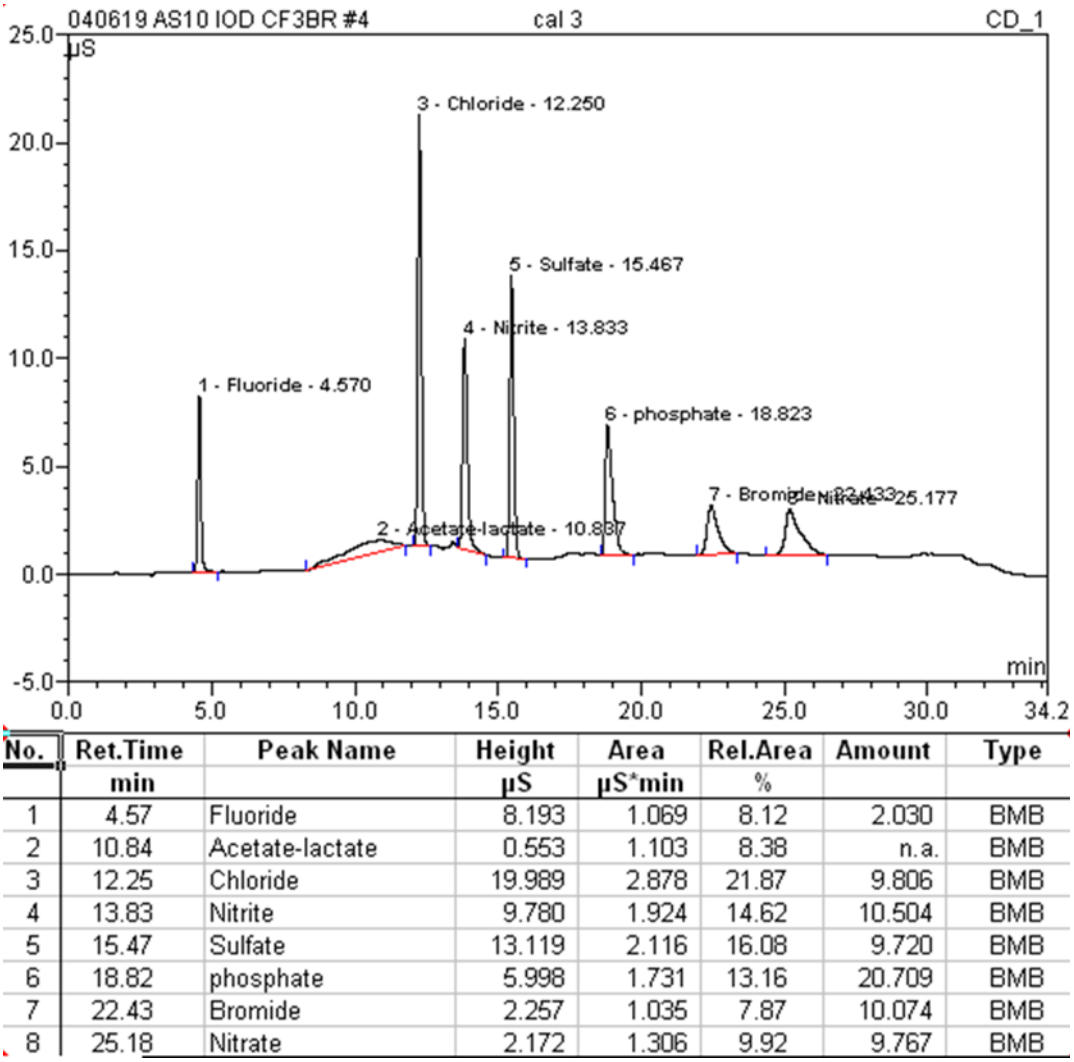
Figure 31. Dionex AS10 separation for CF_3Br extinguishing bulk-load cargo test by FAA

The same AS10 analytical column and a different gradient was used by Boeing chemists analyzing post-discharge decomposition products for a cargo fire. This method is preferred to the FAAs method since a lower maximum concentration of hydroxide eluent is needed for the separation and all analytes of interest after the fluoride peak are captured in the gradient. Some ion chromatographs are not capable of running gradients to concentrations above 100mM NaOH. The Boeing method is illustrated in Table 11.

Table 11. Boeing Ion chromatography method for Dionex AS10 column

<table>
<tr><th>Anions</th><th>Instrument</th><th>Column</th><th>Method (Boeing)</th></tr>
<tr><td>Fluoride
Chloride
Nitrite
Sulfate
Phosphate
Bromide
Nitrate</td><td>Dionex ISC3000 chromatography system with eluent generation and conductivity detection.
Suppressor AERS 500 at 255 mA</td><td>Column: Ionpac AS10
(4mm X 250mm)</td><td>IC Gradient Elution.
Oven T: 35^{0}C
Total flow: 1.0ml/min
<table><tr><td>Time, (min)</td><td>mM KOH</td></tr><tr><td>0-5</td><td>20</td></tr><tr><td>5-28</td><td>20-100, ramp</td></tr><tr><td>28-35</td><td>20</td></tr></table></td></tr>
</table>

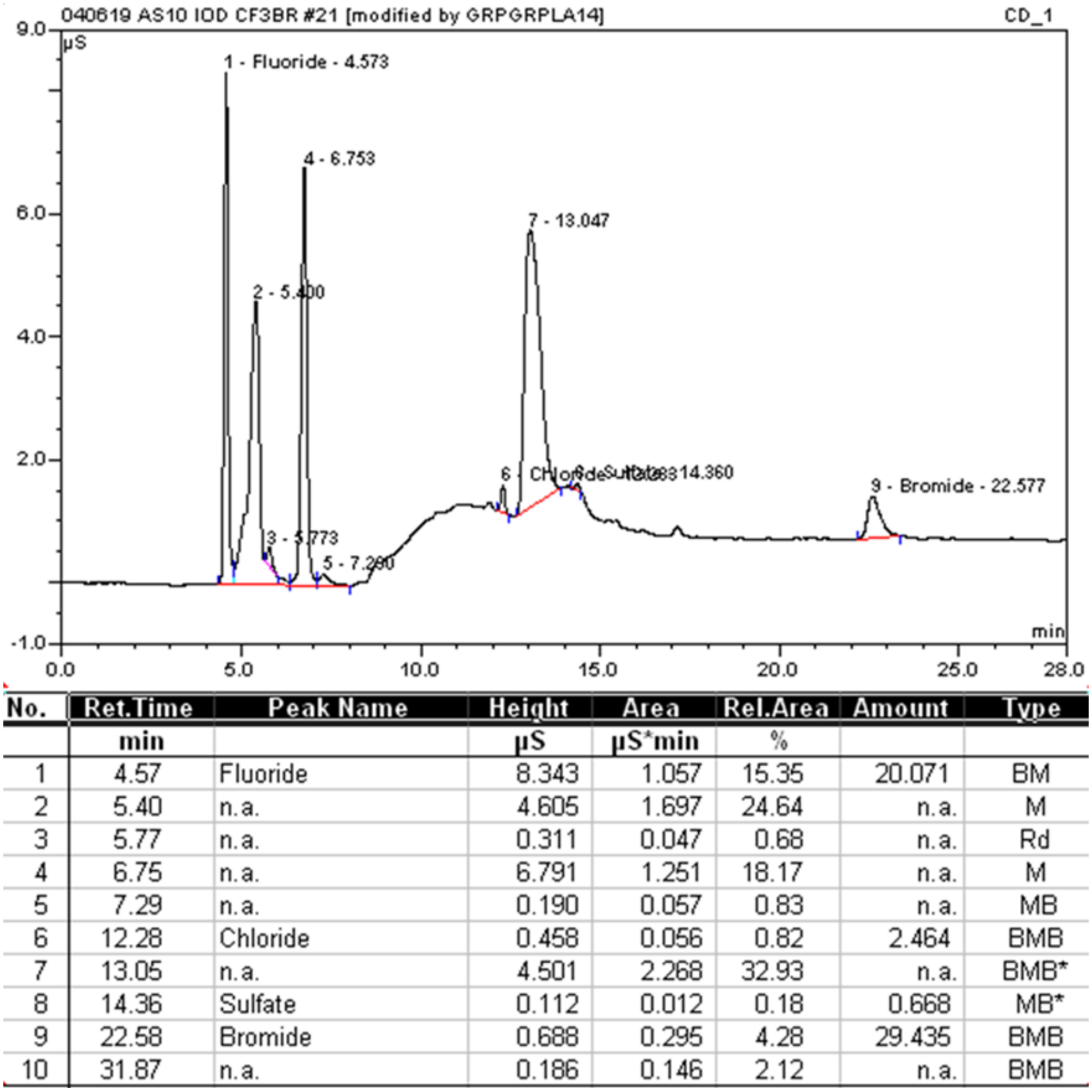
Although not shown in the above figure, iodate is well resolved from fluoride with this method. Iodate co-elutes with glycolate. Figure 32 illustrates a separation using this method for a standard anion solution. Note that the units of anion concentrations are ppm.



No.	Ret.Time min	Peak Name	Height µS	Area µS*min	Rel.Area %	Amount	Type
1	4.57	Fluoride	8.193	1.069	8.12	2.030	BMB
2	10.84	Acetate-lactate	0.553	1.103	8.38	n.a.	BMB
3	12.25	Chloride	19.989	2.878	21.87	9.806	BMB
4	13.83	Nitrite	9.780	1.924	14.62	10.504	BMB
5	15.47	Sulfate	13.119	2.116	16.08	9.720	BMB
6	18.82	phosphate	5.998	1.731	13.16	20.709	BMB
7	22.43	Bromide	2.257	1.035	7.87	10.074	BMB
8	25.18	Nitrate	2.172	1.306	9.92	9.767	BMB

Figure 32. Dionex AS10 A separation of standard anions by Boeing

Figure 33 illustrates the decomposition products for bulk load cargo compartment fire tests of cardboard boxes filled with shredded paper. The extinguishing agent Halon 1301, CF_3Br, was used to suppress the fire. The tests were conducted by Boeing engineers at their Boeing facility in 2019. This is using the Boeing AS10 gradient method described in Table 11. It can be seen from this figure that this method also provides an excellent separation for the fluoride from the light organic anions. The units of anion concentrations are ppm.



No.	Ret.Time	Peak Name	Height	Area	Rel.Area	Amount	Type
	min		µS	µS*min	%		
1	4.57	Fluoride	8.343	1.057	15.35	20.071	BM
2	5.40	n.a.	4.605	1.697	24.64	n.a.	M
3	5.77	n.a.	0.311	0.047	0.68	n.a.	Rd
4	6.75	n.a.	6.791	1.251	18.17	n.a.	M
5	7.29	n.a.	0.190	0.057	0.83	n.a.	MB
6	12.28	Chloride	0.458	0.056	0.82	2.464	BMB
7	13.05	n.a.	4.501	2.268	32.93	n.a.	BMB*
8	14.36	Sulfate	0.112	0.012	0.18	0.668	MB*
9	22.58	Bromide	0.688	0.295	4.28	29.435	BMB
10	31.87	n.a.	0.186	0.146	2.12	n.a.	BMB

Figure 33. Dionex AS10 separation for CF_3Br cargo test by Boeing

Both gradient methods described in Table 10 and Table 11 and illustrated in Figure 31 and Figure 33 provide an excellent separation of fluoride from the early eluting organics.

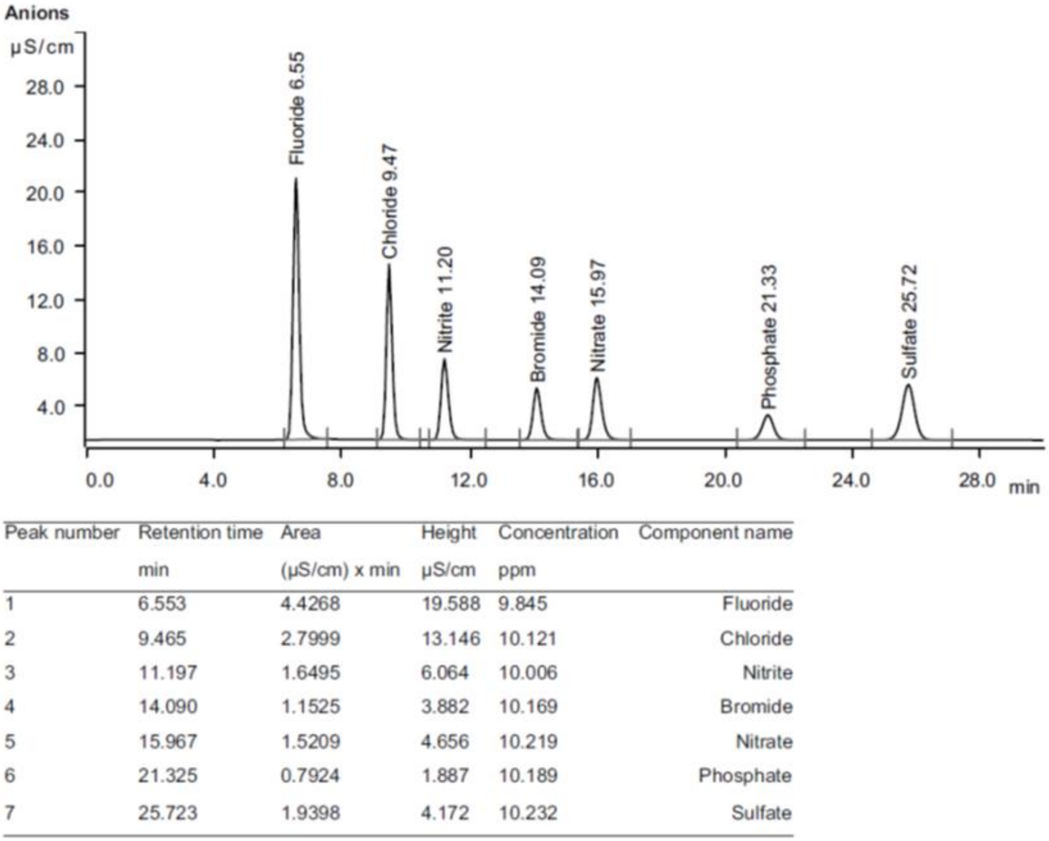
3.1.8.2 Metrohm A Supp 5 method and chromatograms

Isocratic elution is the elution method with no changes of the mobile phase composition taking place during a chromatographic run. The samples mentioned below were run for the FAA by the Arkema Corporation. The samples were filtered through a Pall™ IC Acrodisc™ 25mm x 0.45-micron syringe filter and injected neat into the IC, except for samples that needed to be further diluted. The method is shown in Table 12.

Table 12. Metrohm A Supp 5 Chromatographic Analysis of anions (isocratic)

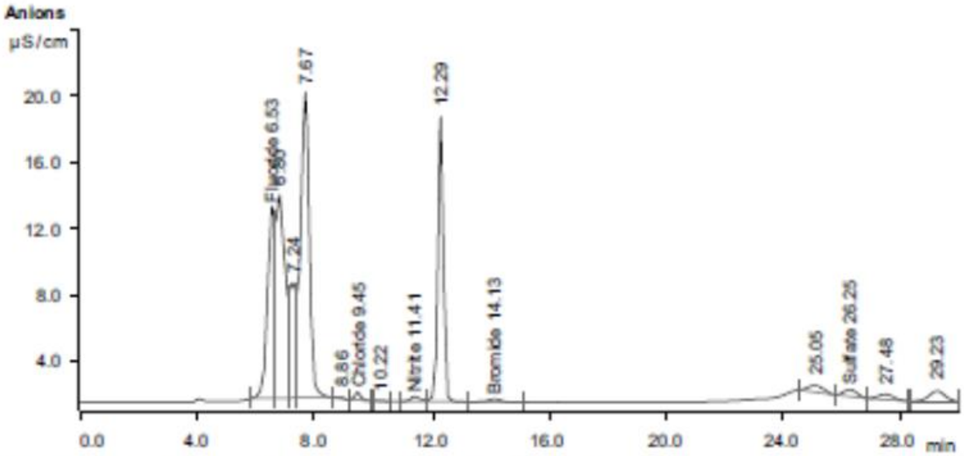
Anions	**Instrument**	**Columns**	**Method**
Fluoride Chloride Nitrite Bromide Nitrate Phosphate Sulfate	Metrohm Prof 850 IC Detection: Suppressed Conductivity, 300 mA	Column: Metrohm A Supp 5 – 250mm	IC Isocratic elution. Flow: 0.7 ml/min Oven T: 30^0C Injection volume: 20 μM Run time: 30 min Eluent: 3.2 mM Na_2CO_3/1.0 mM $NaHCO_3$

Figure 34 illustrates the chromatogram obtained using 10 ppm solutions of the standard anions. Figure 35 shows the chromatogram of anions collected during a bulk load FAA cargo fire tests where Halotron BrX (2-BTP plus a stabilizing additive) was used as the extinguishing agent. The chemical name for 2-BTP is 2-bromo-3, 3, 3-trifluoroprop-1-ene (Halotron BrX Cargo Test 10-20 min after initial discharge) (McIntosh, 2019).



Peak number	Retention time min	Area (µS/cm) x min	Height µS/cm	Concentration ppm	Component name
1	6.553	4.4268	19.588	9.845	Fluoride
2	9.465	2.7999	13.146	10.121	Chloride
3	11.197	1.6495	6.064	10.006	Nitrite
4	14.090	1.1525	3.882	10.169	Bromide
5	15.967	1.5209	4.656	10.219	Nitrate
6	21.325	0.7924	1.887	10.189	Phosphate
7	25.723	1.9398	4.172	10.232	Sulfate

Figure 34. Metrohm A Supp 5 isocratic separation of standard anions by Arkema



Peak number	Retention time min	Area (µS/cm) x min	Height µS/cm	Concentration ppm	Component name
1	6.528	3.2737	11.597	5.992	Fluoride
2	6.798	4.2759	12.284	invalid	
3	7.238	2.0614	6.963	invalid	
4	7.672	6.2873	18.488	invalid	
5	8.863	0.0239	0.104	invalid	
6	9.447	0.1105	0.485	0.496	Chloride
7	10.223	0.0067	0.026	invalid	
8	11.408	0.1169	0.295	0.852	Nitrite
9	12.292	3.6421	17.231	invalid	
10	14.132	0.0842	0.193	0.859	Bromide
11	25.052	0.2512	0.403	invalid	
12	26.245	0.2181	0.418	1.195	Sulfate
13	27.482	0.1953	0.324	invalid	
14	29.227	0.3785	0.628	invalid	

Figure 35. Ion chromatogram of anion sample from FAA Halotron BrX cargo fire test

It can be seen from Figure 35 that this isocratic method and column are not sufficient to separate fluoride from early eluting organic anions. The separation of all anions is generally poor. This method is not recommended for fire gas samples. The FAA used this method since at that time a contractor could not be found that would use the preferred AS 10 or AS15 columns and methods. A gradient method using the Metrohm A Supp 5 column cannot improve the fluoride and glycolate separation by much. Fluoride ion selective electrode method was employed for the quantification due to the poor separation attained with this IC method.

Note: High concentrations of sodium hydroxide wash solution shift the chromatograms relative to the calibration chromatograms compromising the identification and quantification of the fluoride using some columns. Likewise, there is also a retention time shift with the concentration of an analyte in IC, which can further degrade the resolution of fluoride and early eluting organic acids.

The same analytical conditions were used for a cone calorimeter test of a military tank headliner material (Quinteire, Speitel, Guo, Crowley, & Houston, 2018). See Figure 36.

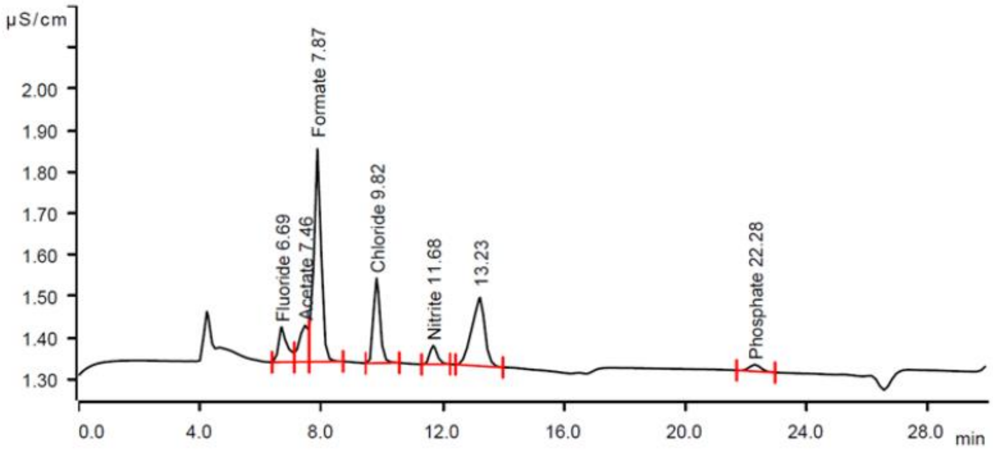


Figure 36. Ion chromatogram for gray foam sample from FAA cone test at 65 kW/m^2

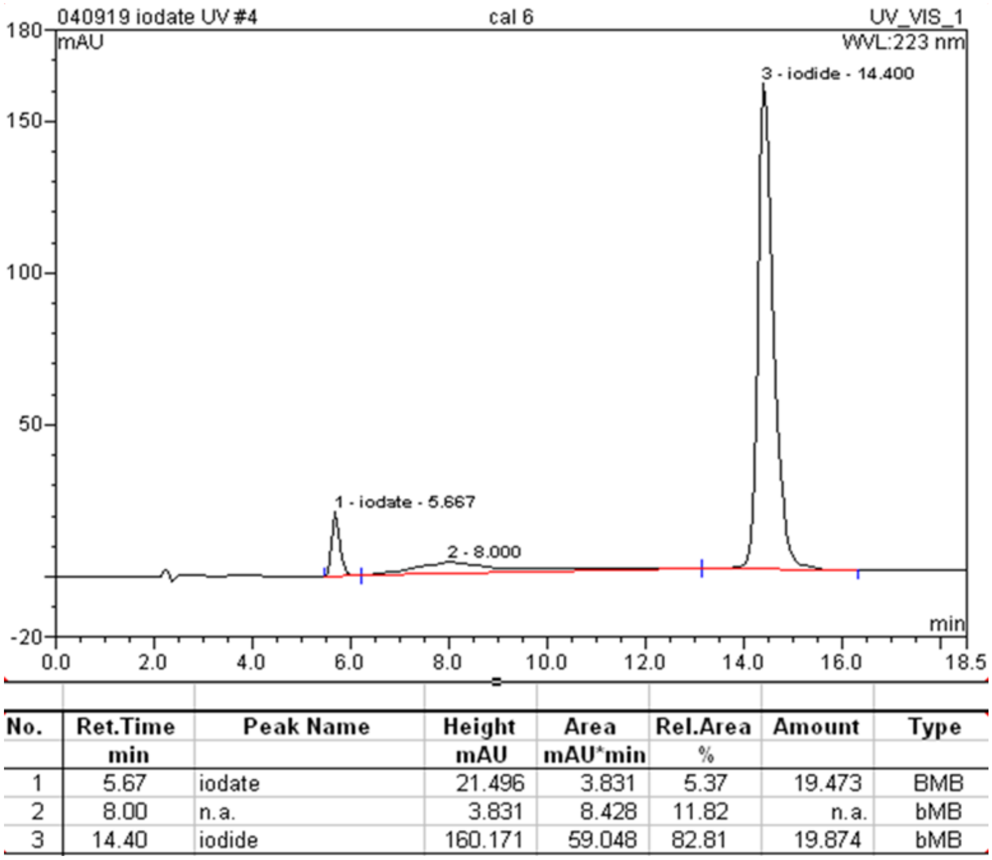
3.1.8.3 Acclaim WAX-1 method and chromatogram for iodide and iodate (Boeing)

Table 13 shows the isocratic method used by Boeing chemists to quantify iodide/iodate collected using high-capacity sample tubes. A summary of instrumentation and method of analysis is described here.

Table 13. Boeing Ion chromatography method Iodide and Iodate anions (isocratic)

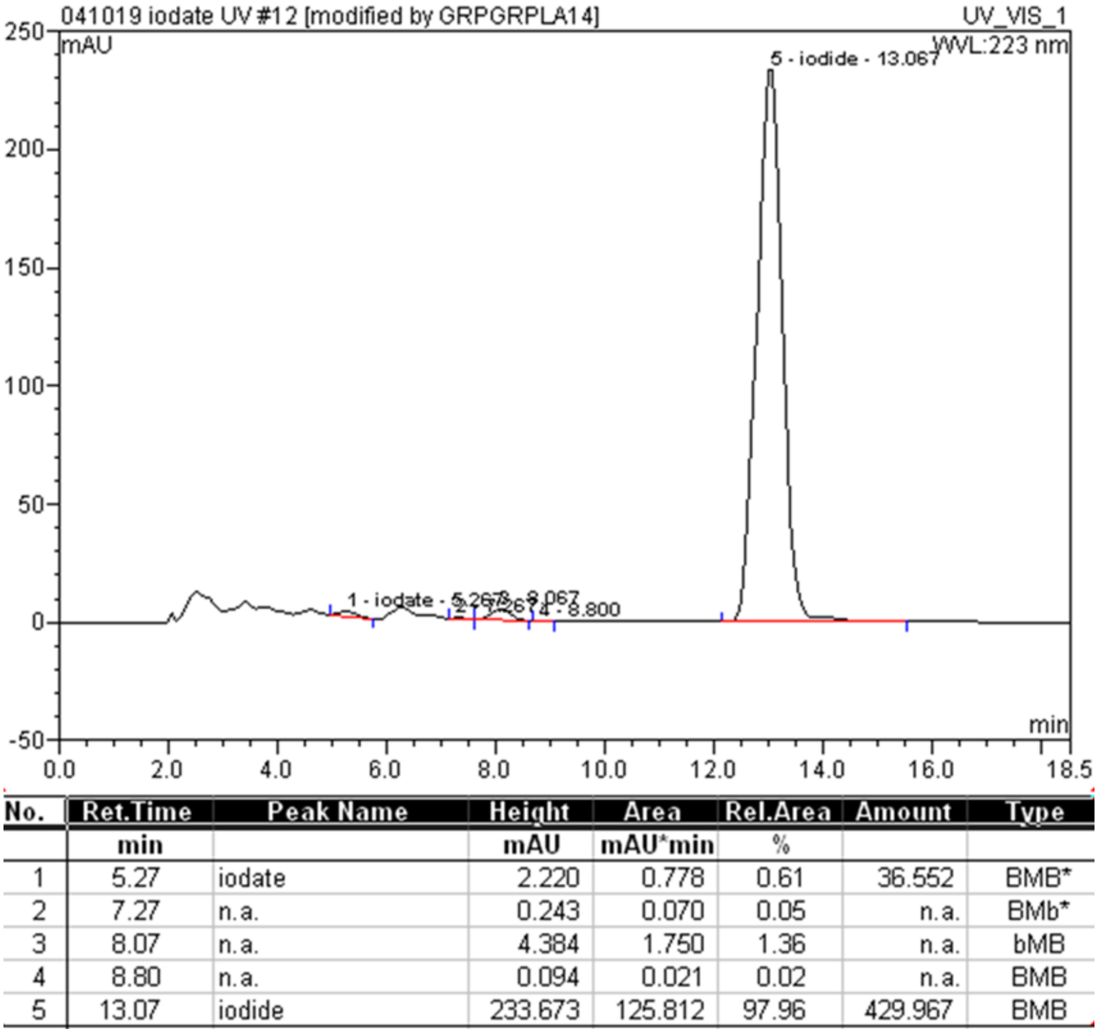
Anions	**Instrument**	**Columns**	**Method**
Iodide Iodate	Dionex ICS3000 chromatography system with Photodiode Array (PDA) UV detector. Detector wavelength: 223 nm, 10 nm bandwidth.	Acclaim WAX-1 Analytical Column (4.6 x 150mm), suppressor	IC Isocratic elution. Flow: 1 ml/min Oven T: 35^{0}C Eluent: 50% 120mM sodium phosphate monobasic adjusted to pH 3 with phosphoric acid 50% methanol

Figure 37 shows the chromatogram of a standard iodate/iodide solution obtained using this method. Note that the units of anion concentrations are ppm. Figure 38 illustrates an ion chromatogram obtained for a cargo fire test suppressed with CF$_3$I fire extinguishing agent (Reinhardt, Blake, & Marker, 2000) using the method shown in Table 13.



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	5.67	iodate	21.496	3.831	5.37	19.473	BMB
2	8.00	n.a.	3.831	8.428	11.82	n.a.	bMB
3	14.40	iodide	160.171	59.048	82.81	19.874	bMB

Figure 37. Ion chromatogram of 20 mg/L Iodide and Iodate standards



No.	Ret.Time	Peak Name	Height	Area	Rel.Area	Amount	Type
	min		mAU	mAU*min	%		
1	5.27	iodate	2.220	0.778	0.61	36.552	BMB*
2	7.27	n.a.	0.243	0.070	0.05	n.a.	BMb*
3	8.07	n.a.	4.384	1.750	1.36	n.a.	bMB
4	8.80	n.a.	0.094	0.021	0.02	n.a.	BMB
5	13.07	iodide	233.673	125.812	97.96	429.967	BMB

Figure 38. Ion chromatogram of gas sample from cargo fire test using CF_3I agent

3.2 Fluoride ion selective electrodes

The fluoride ion selective electrodes (ISE) have been shown to be specific for fluoride in combustion gas samples. The fluoride ISE is a good back-up procedure to IC if a good separation for fluoride cannot be achieved by a particular column.

3.2.1 ISE method description

The details of the method can be found in “Orion fluoride ISE user’s manual 254792-001 Revision B” (Thermo Scientific , 2016).

The equipment needed is as follows:

- Fluoride ion selective electrode (ISE). Orion part number 940900 fluoride half-cell ISE.

- Reference electrode Thermo Orion™ 900200 double junction reference half-cell.
- Orion pH millivolt meter.
- Magnetic stirrer.

The following solutions can be obtained commercially:

- Reference electrode inner filling solution: Orion Part number 900002.
- Reference electrode outer filling solution: Orion part number 900003.
- 0.1M fluoride standard: Orion Part Number 940906.
- TISAB II with CDTA: Orion Ionplus™ application solution: Orion part number 940909.

The samples and standards are prepared for analysis by adding 10 ml to the empty beaker plus 10 ml of Orion TISAB II solution with CDTA which acts as a buffer.

Prepare fluoride standards by serial dilution of 0.1 M fluoride standard with deionized water. Use concentrations of 10^{-1}, 10^{-2}, 10^{-3}, 10^{-4} and 10^{-5} moles/liter solution. Calibration standards must be prepared daily.

A small Teflon™ stirrer is used at the bottom of a polypropylene beaker which contains the fluoride ISE and reference electrodes.

The fluoride concentration (moles/liter) is plotted against millivolts reading. The resulting equation is used to solve for the concentration of fluoride in the test samples. The calibration curve must be obtained daily. See Figure 39.

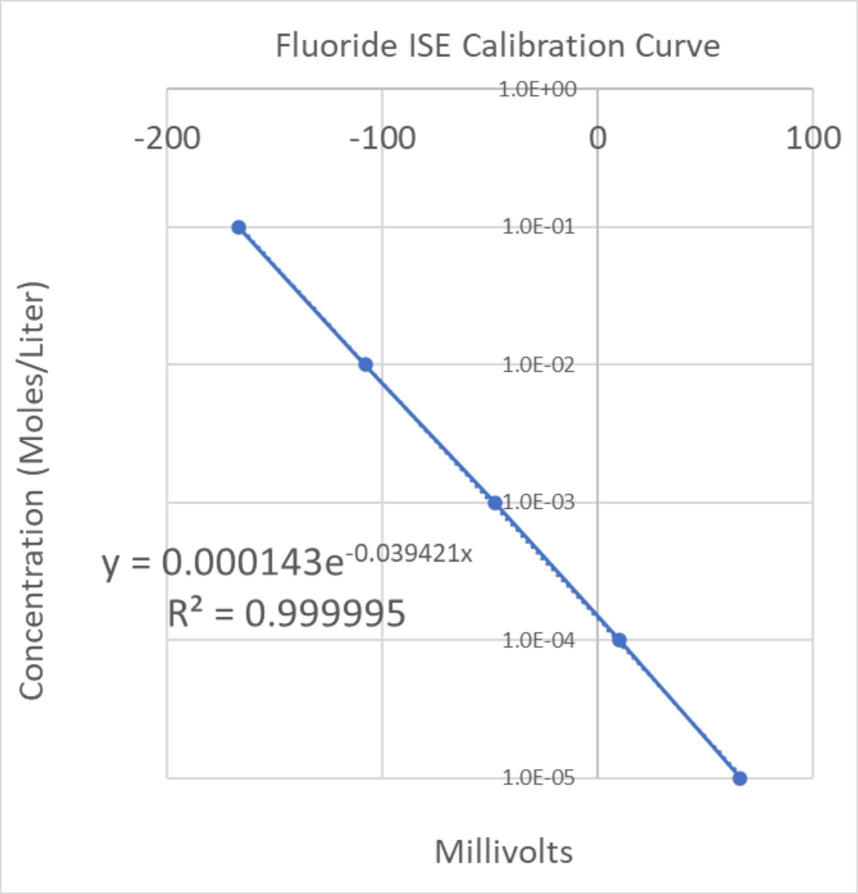


Figure 39. Fluoride ISE calibration curve

3.2.2 Comparison of fluoride using IC and fluoride ISE

A comparison of yields with fluoride ISE and IC method using the Dionex AS10 column is shown in Table 14 for two samples collected at different times into the test. This cargo container tests had cardboard boxes and shredded paper as the fuel. Halon 1301 was used as the fire extinguishing agent.

Table 14. Comparison of fluoride ISE and IC method

Test Description	**Test ID**	**Tube Type**	**Volume Solution (ml)**	**Sample duration (min)**	**IC Conc. (µM)**	**F ISE Conc. (µM)**	**Volume gas sampled (liters)**
Halon 1301 Cargo Test	9701	High Capacity, 4mm beads	30	5	100	102	0.633
Halon 1301 Cargo Test	9701	High Capacity, 4mm beads	30	5	210	215	0.633

As can been seen from Table 14, the IC gradient method has a good agreement with the fluoride ISE for these samples. In some cases where only fluoride needs to be detected, fluoride ISE can be a convenient alternative method to IC. The accuracy of the fluoride ISE decreases markedly for fluoride concentrations lower than 10^{-5} M.

4 Conclusions

This report describes the state-of-the-art methods of collection and analysis of fire-generated acid gases. Significant improvements have been developed by the Fire Safety Branch and others over the years since the method was developed in the mid-1970s. Detailed guidance provided in this report aids the user to accurately collect and analyze acid fire gases in fire tests. Accurate gas measurements are important inputs into toxicity assessments.

Gas concentration histories are obtained by sequenced sampling of multiple gas sample tubes with each sample tube inlet at the sampling point. Sample line losses are eliminated by not using probes, sampling lines or pre-filters. Specialized point-of-sample collection tubes were developed by the FAA Fire Safety branch and upgraded over time. A sample tube type of the appropriate capacity is selected for the maximum sample loading expected.

The sampling system is designed to minimize sampling system delays, deposition, and flow errors. In the acid gas sampling system, the gas flows from each timed sequenced sample tube to a cooling line/coil, high-capacity micrometer pore sized filters, sample and venting solenoid valves, flowmeter, needle valve and vacuum pump.

Ion chromatography (IC) methods have been developed which accurately measure anions in complex combustion gas matrices. A high-capacity column is needed for high ionic strength sample matrices used in the analysis of combustion gas samples. Columns are selected based on separation requirements. Improved analytical columns and methods (AS15, AS20 and Metrohm A Supp 7) provide improved separations than those obtained by previous columns and methods used by the FAA Fire Safety Branch.

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A Materials and suppliers

Table A-1 lists materials used to construct sample tubes, suppliers, and part numbers.

Table A-1. Gas sample tube materials, supplies and suppliers

Item	**Supplier**	**Part Number**
PFA Tubing 3/8 x ½ in, 50 feet (used for large collection tubes)	Penn Fluid Systems	PFA-T8-062-50
PFA Tubing 5/32 x ¼ in, 100 feet	Penn Fluid Systems	PFA-T4-062-100
PFA Tubing 8mm o.d. x 1mm wall (used for mid-sized collection tubes)	Penn Fluid Systems	PFA-TM-1M-30M
PFA Tubing, ¼" o.d x 0.062" wall (used for mid-sized collection tubes)	Penn Fluid Systems	Part # PFA-T4-062-100
Tygon™ E-3603 PVC tubing 3/16 id x 5/16 in od	Amazon	
Pyrex™ Vista 1 ml pipets (pre-tubes are cut from these pipets ~0.248" o.d., 2 mm i.d.)	VWR	89090-166
PFA reducing union ½ tube to ¼ tube	Penn Fluid Systems	PFA-820-6-4
Borosilicate Glass beads 3 mm	Thomas Scientific	5663F29
Borosilicate Glass beads 4 mm	Thomas Scientific	5663F35
30 mL Luer Lock™ plastic syringes	Medline	SYR130010Z
60 mL Luer Lock™ plastic syringes	Medline	SYR160010
Female Luer Lock™ to male ¼-28 adapter, 0.05 in bore, polypropylene	Cole Palmer	UX-02023-38
¼-28 female to ¼-28 female adapter	Cole Palmer	UX-02013-94
1/4 in Teflon™ Swagelok™ union	Penn Fluid Systems	T-400-6

Item	Supplier	Part Number
¼” Swagelok™ Groove Cutter	Penn Fluid Systems	MS-GC4
½” Swagelok™ Groove Cutter	Penn Fluid Systems	MS-GC8
Plastic End Caps for ¼” Tubes	Ohio Valley Specialty Company	2-0014

Table A-2 lists parts and materials used to construct sampling system, suppliers, and part number.

Table A-2. Sampling system materials and suppliers

Item	Supplier	Part number
Whatman	Whatman 2609T Hepa-Cap 36 In-Line Venting Filter	2906-T
Tygon™ PVC Tubing, clear 3/16”/ 5/16”	Many suppliers	Tygon™ E-3603
Solenoid Valves	Many Suppliers	HONEYWELL SK 71215SN2VN00N0C111P3
¼” Ferrules 60% Vespel™/40% Graphite, 1 piece	CRS	213400
¼” Ferrules Graphite, 1 piece	Ohio Valley Specialty	GF-03 ¼”
¼” Ferrules Teflon™ 2 pieces, sets	Penn Fluid Systems	T-400-6
Flexible Graphite Sheets, 1/8”	Equal seal	N/A
1//2” Brass In-line ball valves	Many Suppliers	
FM1050 Series High Accuracy Flowmeter, with valve	Matheson	SE QE14D151E406
FM1050 Series High Accuracy Flowmeter, no valve	Matheson	SE QE14G151E406

B Sampling system engineering drawings

The drawings below show recent designs of sampling systems used by our lab. There is no intention to limit the cooling methodologies of the sample tubes, the flowmeter type, or any other aspects of the sampling system to these designs.

The engineering drawings for the construction of the sampling system using high-capacity collection tubes are shown below. It is helpful to refer to this drawing when fabricating the ice bath housings. The baths are constructed of 0.125” 6061-T6 aluminum sheet. The tube numbers and corresponding solenoid valve numbers are indicated. The tubes are sequenced left to right when observing from the front of the box. The tubes are positioned such that tubes 7 to 12 are inserted in the bottom level and tubes 1-6 are positioned in the top level as indicated in the figures below. If breakthrough tubes are used, they are joined to the sample tube downstream end but to butt with a short length of 3/16 i.d. x 5/16” o.d. Tygon™ tubing. Two design options are shown below.

B.1 One ice bath sampling system option

The side view of the one ice bath option, long length per the schematic shown is shown in Figure B-1. This is the long option of the ice bath that accommodates the 12 main sample tubes and 12 breakthrough tubes.

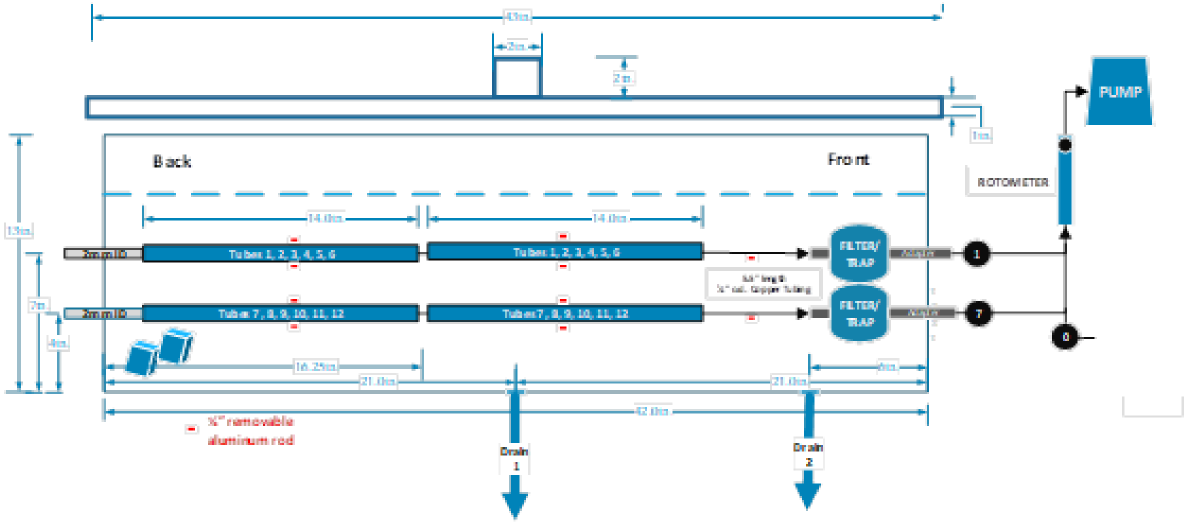


Figure B-1. Single ice bath option, long length: side view

The details of the construction of this box are shown in Figure B-2. This figure also shows the tube number connected to each position in the box.

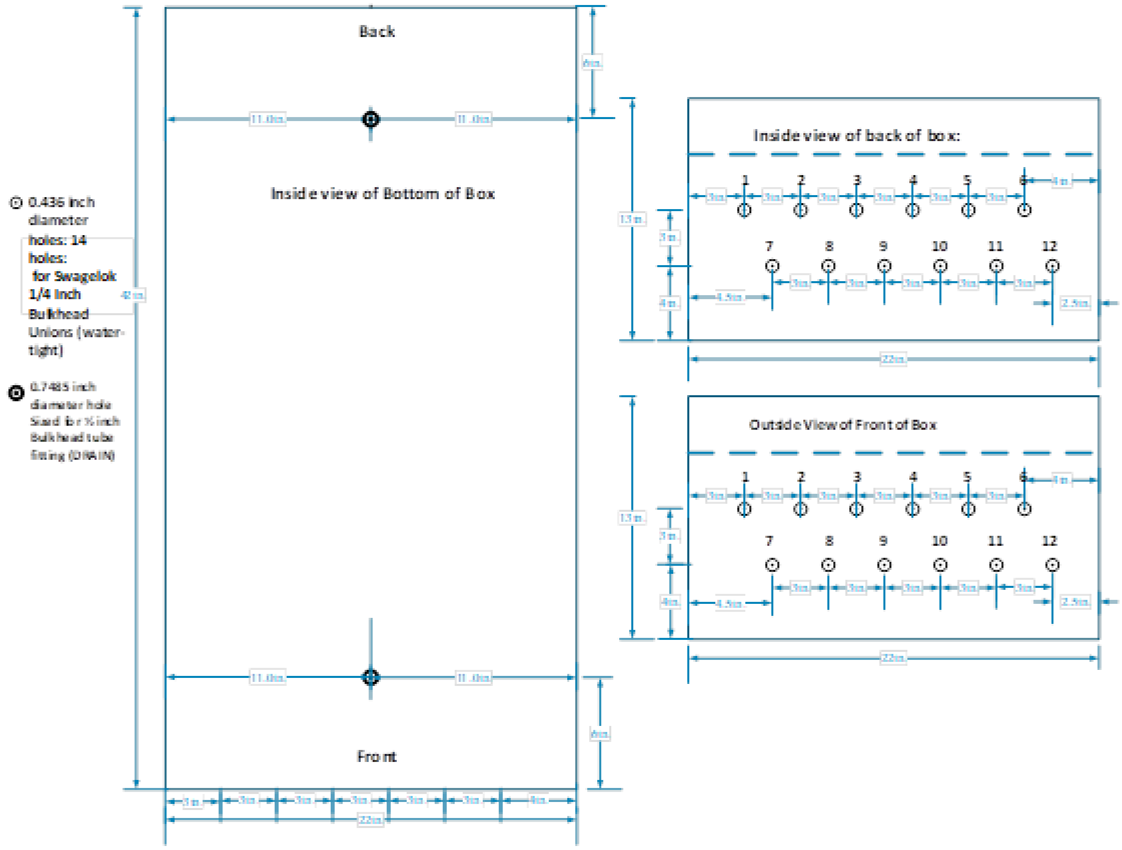


Figure B-2. Single ice bath option, long length, and construction

The details of the construction of the standard length option, where breakthrough tubes are not used is illustrated in Figure B-3. The front and back of the box are the same as the long option.

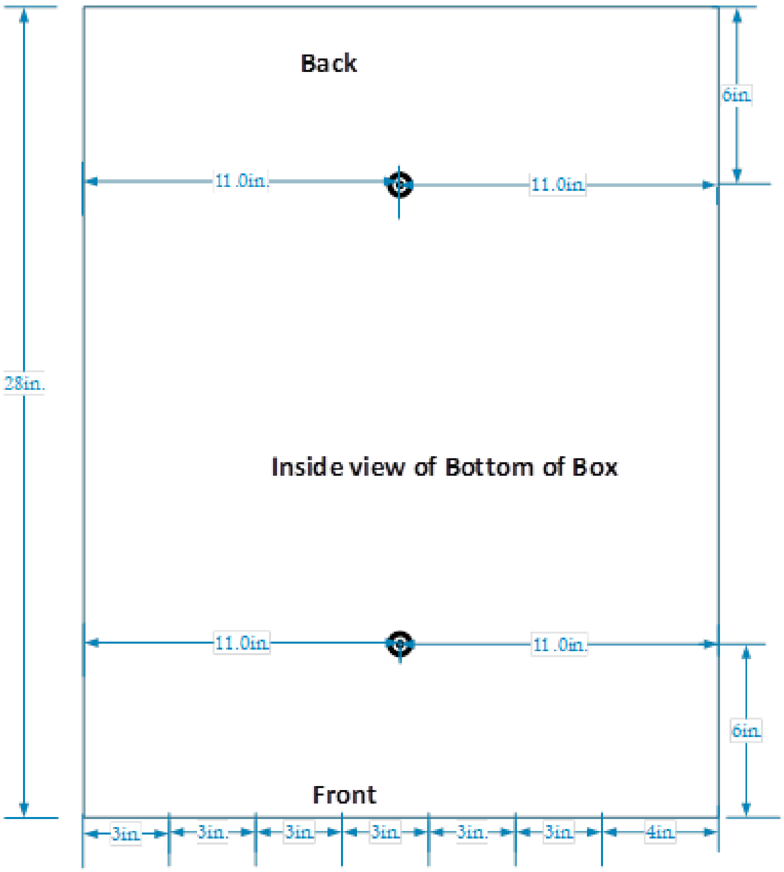


Figure B-3. Single ice bath option, Standard length, and construction

B.2 Two ice bath sampling system option

This option provides additional cooling prior to filtration. It includes a separate bath that accommodates cooling coils and the filters. The side view of the two ice bath option, standard length is shown in Figure B-4. The long length version is 14” longer and accommodates breakthrough collection tubes.

The first bath houses the sample tubes. The second ice bath houses the cooling coils and filters. The removable ¼” rod supports the weight of the filter. Note that the flow path is either horizontal or sloped downward, trapping any condensate in the filter/traps.

As shown in Figure B-4, each sample line runs from the sample tube ice bath to the to this filter ice-water bath. The lines exiting the first ice bath for tubes 7 to 12 are inserted in the bottom level of the second bath and the lines exiting tubes one to six are positioned in the top level as indicated in the figures below. This prevents the sampling lines from crossing.

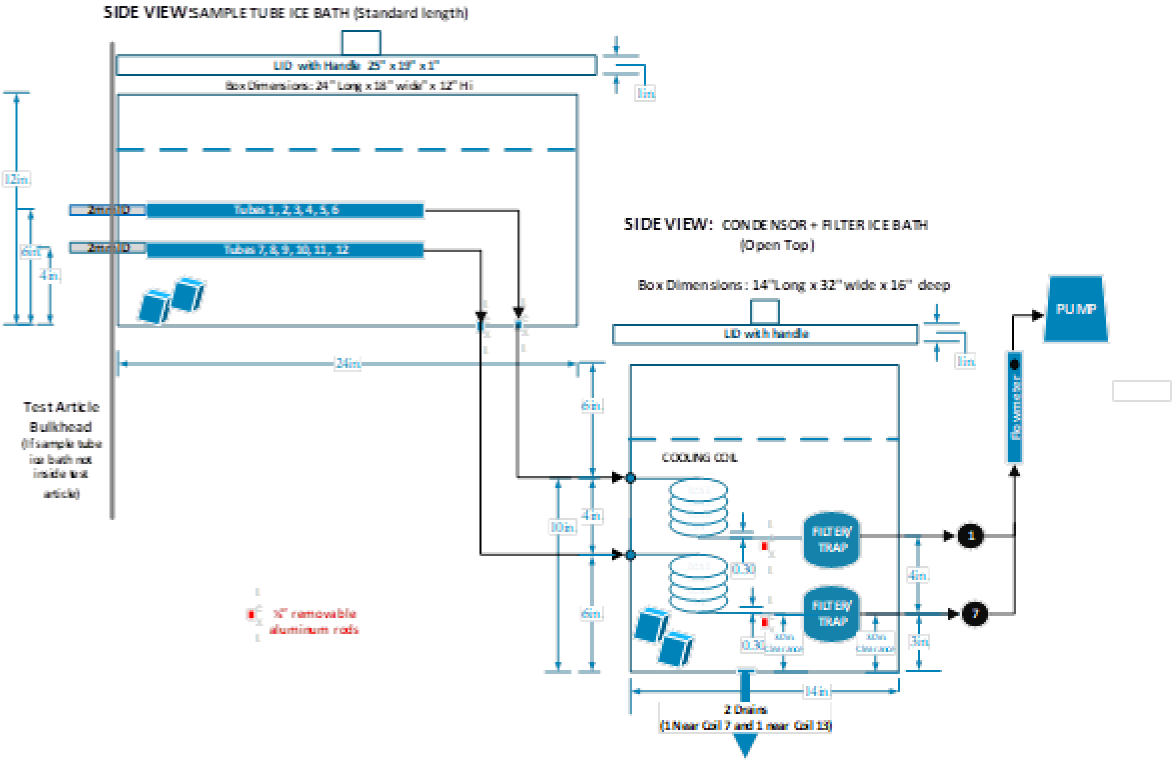


Figure B-4. Two ice bath option, standard length: side view of two baths

Figure B-5 shows the construction of the first bath in Figure B-4: Sample tube ice bath, standard length. Figure B-6 shows the construction of the long version first bath: sample tube ice bath, long length which accommodates breakthrough tubes.

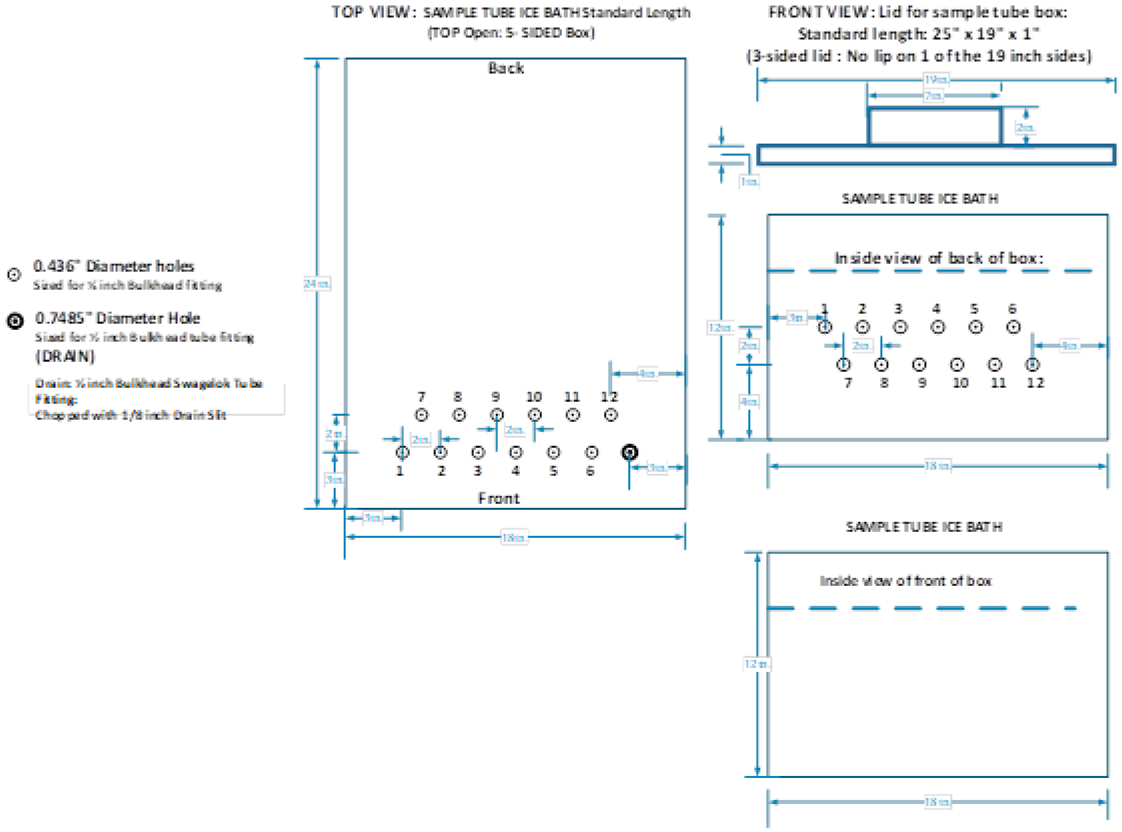


Figure B-5. Two ice bath option, sample tube bath, standard length: construction

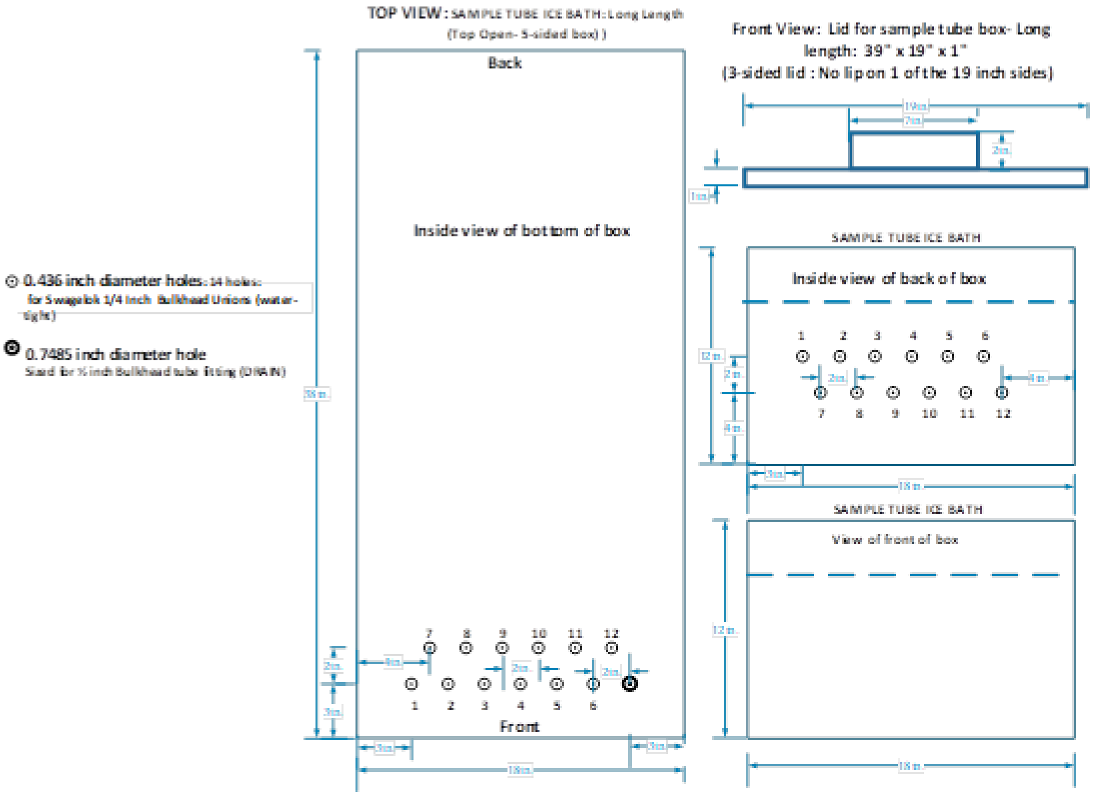
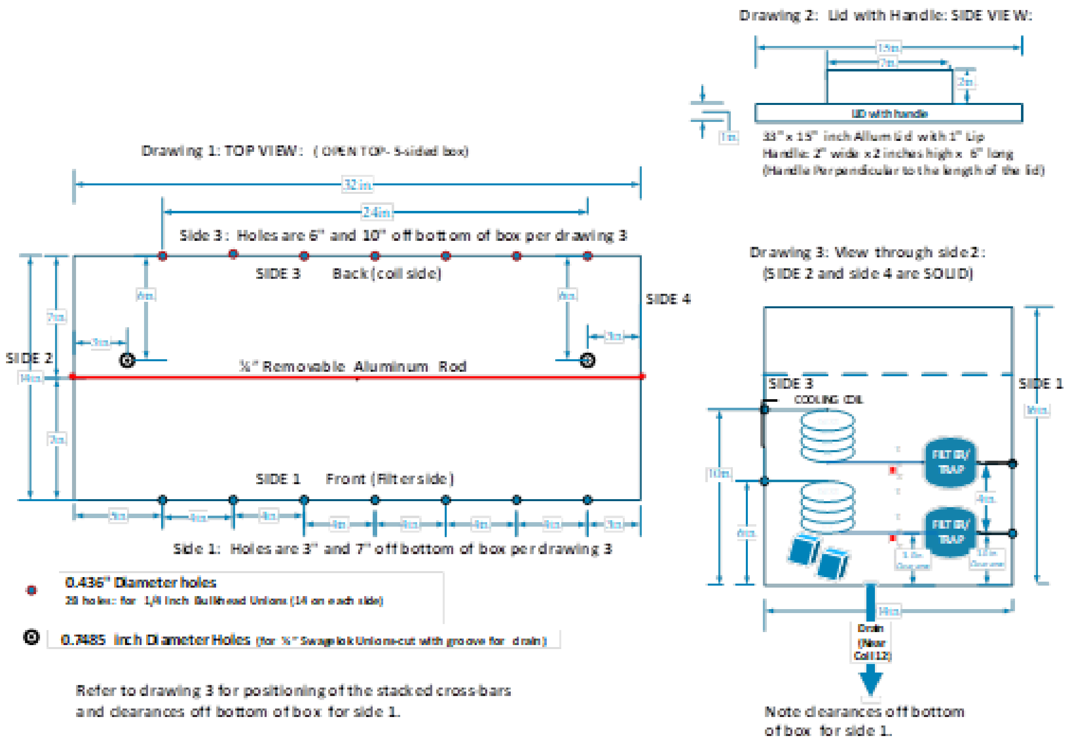


Figure B-6. Two ice bath option, sample tube bath, long length: construction

Figure B-7 and Figure B-8 present the shop drawings for the second ice bath, the filter ice water bath.

The ¼” diameter aluminum rods at each level, illustrated in red, serve to support the weight of the upstream ends of the filters.

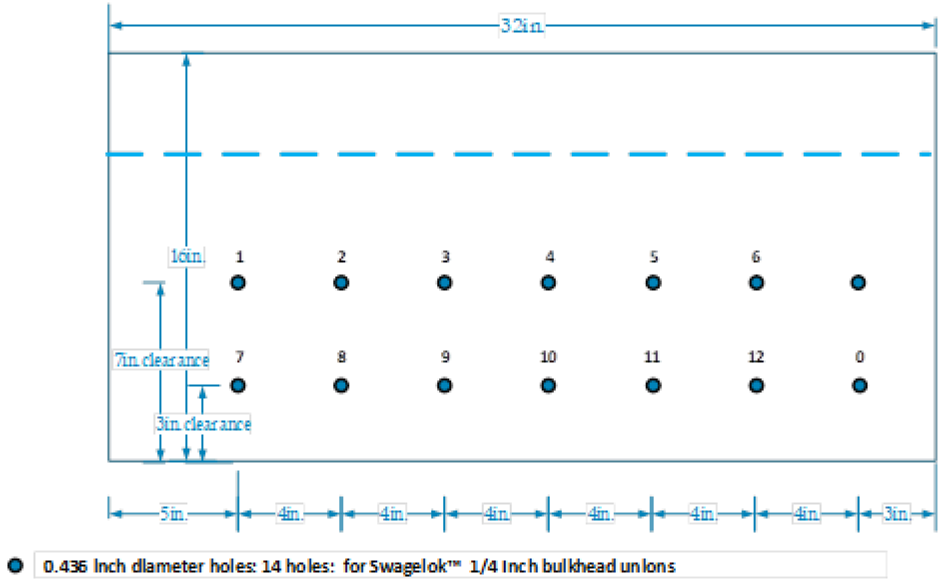


Refer to drawing 3 for positioning of the stacked cross-bars and clearances off bottom of box for side 1.

Note clearances off bottom of box for side 1.

Figure B-7. Two ice bath option: filter ice water bath, construction: drawings 1-3

Drawing 4: SIDE 1: Outside: Filter Side



Drawing 5: SIDE 3: Inside: Coil Side

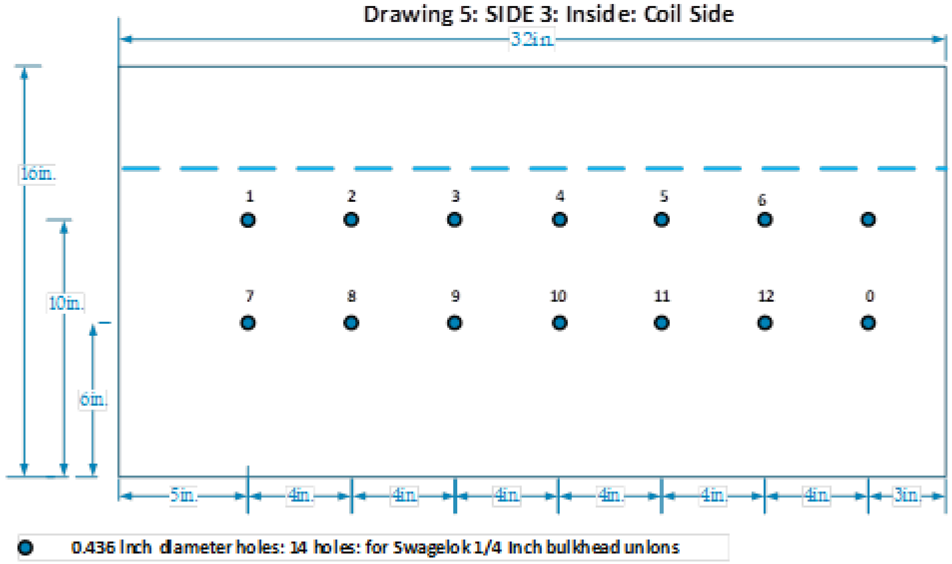


Figure B-8. Two ice bath option: filter ice water bath: construction: drawings 4-5

C Calculation of gas concentrations

The following data is needed to calculate the gas concentration from the corresponding anion concentration in the combustion gas collection solution:

- The gas volume sampled per sample tube (based on sample time and sample flowrate).
- The liquid wash or extraction volume.
- Any additional dilution factor for each ion chromatography analysis.
- The calibration curves obtained using the calibration standards for the concentration range of the method.
- The resulting solution anion concentration determined by from the analysis of the liquid sample
- The molar mass (g/mole) of each anion calibration solution if calibration solutions have units of ppm.

Either of 2 units of concentration may be used for calibration anion solutions:

- ppm (mg anion/liter solution) (more commonly used)
- µmoles/liter solution

To convert solution concentration to gas concentrations:

- See Appendix C1 for converting ppm (solution) to ppmv (gas)
- See Appendix C2 at the end of Appendix C for converting µmoles/liter solution to ppmv gas.

C.1 Convert from ppm anion (solution) to ppmv acid (gas)

The acid gas concentration of acid H_nX, where n=1,2, or 3, can be calculated from the anion concentration in solution as follows: H_nX is expressed as HX, for simplicity since the equation below is based on the concentration of each anion.

Since # µmoles anion = # µmoles acid and using molar mass of the anion expressed in units (mg anion/moles anion), and the volume of 1 mole of an ideal gas at 70°F (21.11°C) is 24.13 liters as a conversion factor. The molar mass of the anion was used as a conversion factor, where:

$$\mathrm{MW} = \frac{\_\_\_\boldsymbol{mg\ \ anion}}{\boldsymbol{mmole\ anion}} = \frac{\_\_\_\boldsymbol{mg\ X}}{\boldsymbol{mmole\ X}} \tag{C-1}$$

Note, this equation below holds for multi-protic acids with one anion:

$$\text{Fractional volume} \quad = \frac{\left(\frac{\_\_\_\_\cancel{mg\ X}}{\cancel{liters\ sol.}}\right)\left(\frac{1\ \cancel{liter\ sol.}}{1000\ \cancel{ml\ sol.}}\right)(\_\_\cancel{ml\ sol.})\left(\frac{\cancel{mmole\ X}}{\_\_\_\_\cancel{mg\ X}}\right)\left(\frac{\cancel{mole\ X}}{1000\ \cancel{mmoles\ X}}\right)\left(\frac{\cancel{mole\ HX}}{\cancel{mole\ X}}\right)\left(\frac{24.13 liter\ HX}{\cancel{mole\ HX}}\right)}{(\_\_liters\ gas\ sampled\ )} \tag{C-2}$$

$$\text{ppmv acid} = \boldsymbol{Fractional\ volume\ acid} * \ \mathbf{10^6} \tag{C-3}$$

Sample calculation of ppmv HF from Ion chromatography

In this example, the anion calibration solutions measured by ion chromatography have units of ppm based on the molar mass of each individual anion. Also note that the acid gases were sampled at 70°F with a flowmeter/s calibrated at 70°F, or 21.11°C.

See Table C- 1 for other sample information. Note that in this example the initial 30 ml extraction volume needed to be further diluted with 0.05M NaOH for the final IC analysis to a concentration that falls on the fluoride calibration curve. This further 10 –fold dilution results in a sample extraction volume of 300ml.

Table C- 1. Input data used to calculate acid concentrations in cargo compartment simulators

Value Description	**Example Value**	**Unit**	**Chemical Species**
Molar mass of the calibration anion	19.00	g/mole	Fluoride
Air flow through tubes during sampling (flowmeter calibrated at 70F or 21.11C)	0.15	L/min	Air
Time for air collection	10.0	min	
Liquid extraction volume	300	ml_{sol}	Water
Concentration anion determined by ion chromatography	20.0	mg/L_{sol}	Fluoride

The total elution volume of 300ml is input into the equation:

The gas concentration (in ppmv) can be calculated as follows:

Fractional volume

$$= \frac{\left(\frac{20.0\ mg\ Fluoride}{liters\ sol}\right)\left(\frac{1\ liter\ sol}{1000ml\ soln}\right)(300\ ml\ soln)\left(\frac{mmole\ Fluoride}{19.00\ mg\ Fluoride}\right)\left(\frac{mole\ Fluoride}{1000\ mmoles\ Fluoride}\right)\left(\frac{mole\ HF}{mole\ Fluoride}\right)\left(\frac{24.1315\ Liters\ HFgas}{mole\ HF}\right)}{(1.5\ liters\ gas\ sampled)} \quad \text{C-4}$$

$$\text{ppmv acid} = \boldsymbol{Fractional\ volume\ acid} * \mathbf{10^6} = \mathbf{5{,}080}\ \boldsymbol{ppmv\ HF} \quad \text{C-5}$$

$$\text{\% acid} = \mathbf{5080}\ \boldsymbol{ppmv\ HF} * (1\%/10^6\ \text{ppmv}) = 0.508\%\ \text{HF} \quad \text{C-6}$$

C.2 Convert from µM/L anion (solution) to ppmv (gas)

The gas concentration can be calculated as follows:

The fractional volume of acid gas HX in the sampled gas at 21.11C and 1 atmosphere is defined as:

$$\text{Fractional volume} = \frac{\boldsymbol{Volume\ HX\ (liters)}}{\boldsymbol{Volume\ gas\ sampled\ (liters)}} \quad \text{C-7}$$

Assuming the flowmeter is calibrated for 70.0 degrees F or 21.1 degrees C:

The volume of 1 liter gas at 21.11 C and 1 atmosphere

=22.4 liters x (273.15+21.11)°K/273.15 °K =24.13 liters C-8

All units are shown in the equation below. The units that cancel out are crossed out.

$$\text{Fractional volume} = \frac{\left(\frac{\_\_\_\ \cancel{\mu moles\ X}}{\cancel{liters\ sol.}}\right)\left(\frac{1\ \cancel{liter\ sol.}}{1000\ \cancel{ml\ sol.}}\right)(\_\_\cancel{ml\ sol.})\left(\frac{1\ \cancel{mole\ X}}{10^6\ \cancel{\mu moles\ X}}\right)\left(\frac{\cancel{mole\ HX}}{\cancel{mole\ X}}\right)\left(\frac{24.13\ liter\ HX}{\cancel{mole\ HX}}\right)}{\_\_liters\ gas\ sampled} \quad \text{C-9}$$

where sol. ≡ solution.

The fractional volume of HX gas can be converted to ppmv:

$$\text{ppmv HX} = \boldsymbol{Fractional\ volume\ HX} * \mathbf{10^6} \quad \text{C-10}$$

C.3 Converting between solution concentration units

The conversion of µmoles/liter solution to ppm (mg anion/liter solution) is shown below:

$$\text{ppm} = \frac{mg\ anion}{liters\ solution} = \left(\frac{\_\_\_\cancel{\mu moles\ anion}}{liter\ solution}\right)\left(\frac{\_\_\ \cancel{\mu g\ anion}}{\cancel{\mu moles\ anion}}\right)\left(\frac{1\ mg\ anion}{1000\ \cancel{\mu g\ anion}}\right) \quad \text{C-11}$$

Where the molar mass of each anion is used as a conversion factor.

For example, if the user normally uses a maximum fluoride calibration concentration of 1000 µM, and chose to use a mg anion/L based calibration standard, the user can perform the following calculation, inserting the molar mass of fluoride 19.00 g/mole into the equation to find the equivalency in ppm units:

$$\frac{\boldsymbol{mg\ F}}{\boldsymbol{liters\ solution}} = \left(\frac{\mathbf{1000}\ \cancel{\boldsymbol{\mu moles\ F}}}{\boldsymbol{liter\ solution}}\right)\left(\frac{\mathbf{19.00}\ \cancel{\mu\boldsymbol{g\ F}}}{\cancel{\boldsymbol{\mu moles\ F}}}\right)\left(\frac{\mathbf{1}\ \boldsymbol{mg\ F}}{\mathbf{1000}\ \cancel{\boldsymbol{\mu g\ F}}}\right) \tag{C-12}$$

So, 1000µM fluoride = 19.00 mg fluoride/liter solution = 19.00ppm fluoride.

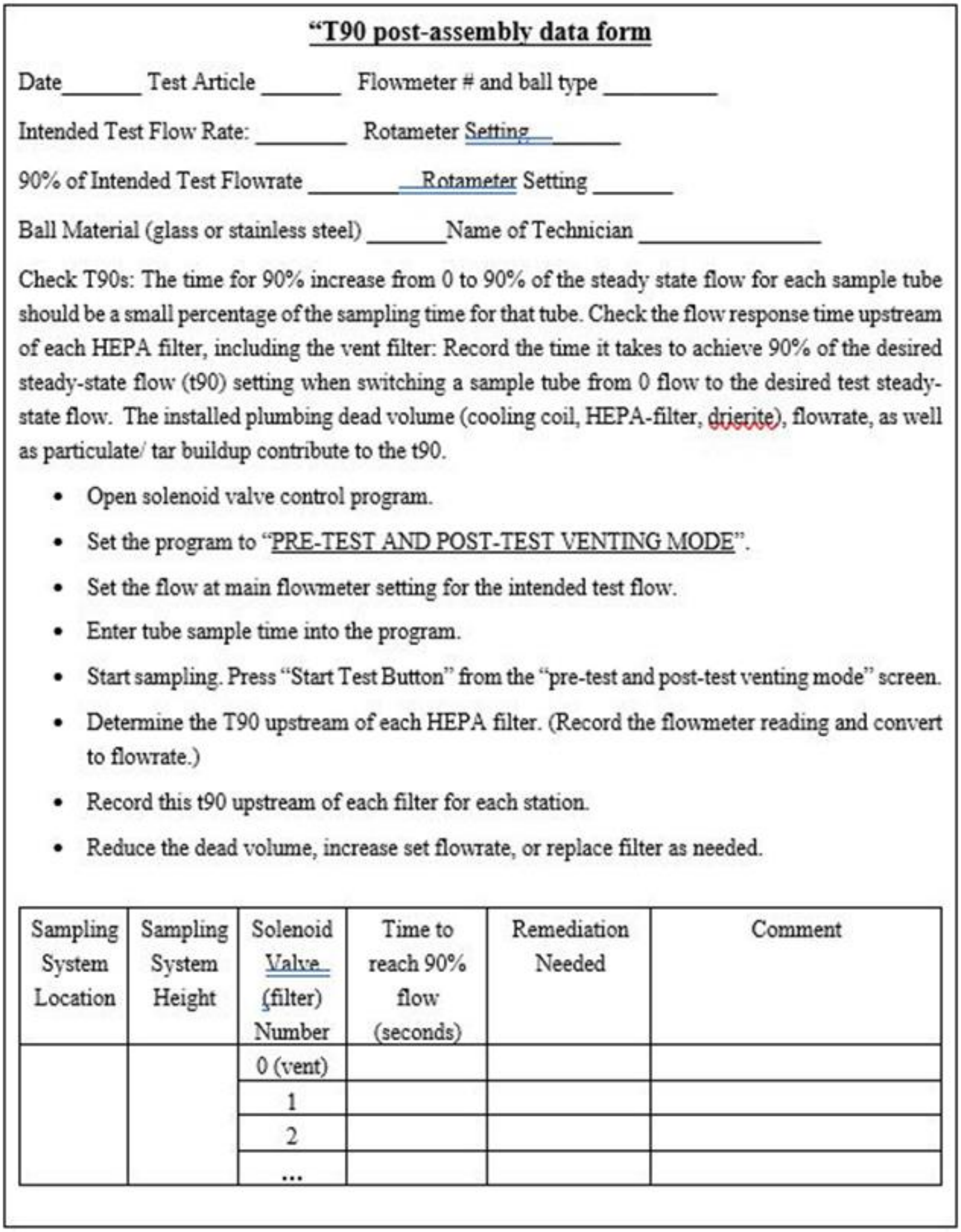
D Forms

The forms in this appendix are for one flowmeter sampling systems. Appropriate modifications should be made for multi-flowmeter sampling systems.

Shown below are the data forms for the t90 post-assembly, pre-test, test, and post-test checks. These completed forms are provided to the chemist, who will convert the analyzed solution concentrations to acid gas airborne concentrations.

Note that in this appendix, the procedures and data forms are provided for pre-test, test, and post-test checks, but only the data form is available for the t90 post-assembly check. Refer to section 2.2.10.3 of this report for the procedure related to post-assembly check for leaks and section 2.2.10.4 for the procedure related to post-assembly flow checks.

Form 1. T90 Post-assembly data form



“T90 post-assembly data form

Date______ Test Article ______ Flowmeter # and ball type _________

Intended Test Flow Rate: ________ Rotameter Setting ________

90% of Intended Test Flowrate ____________ Rotameter Setting _______

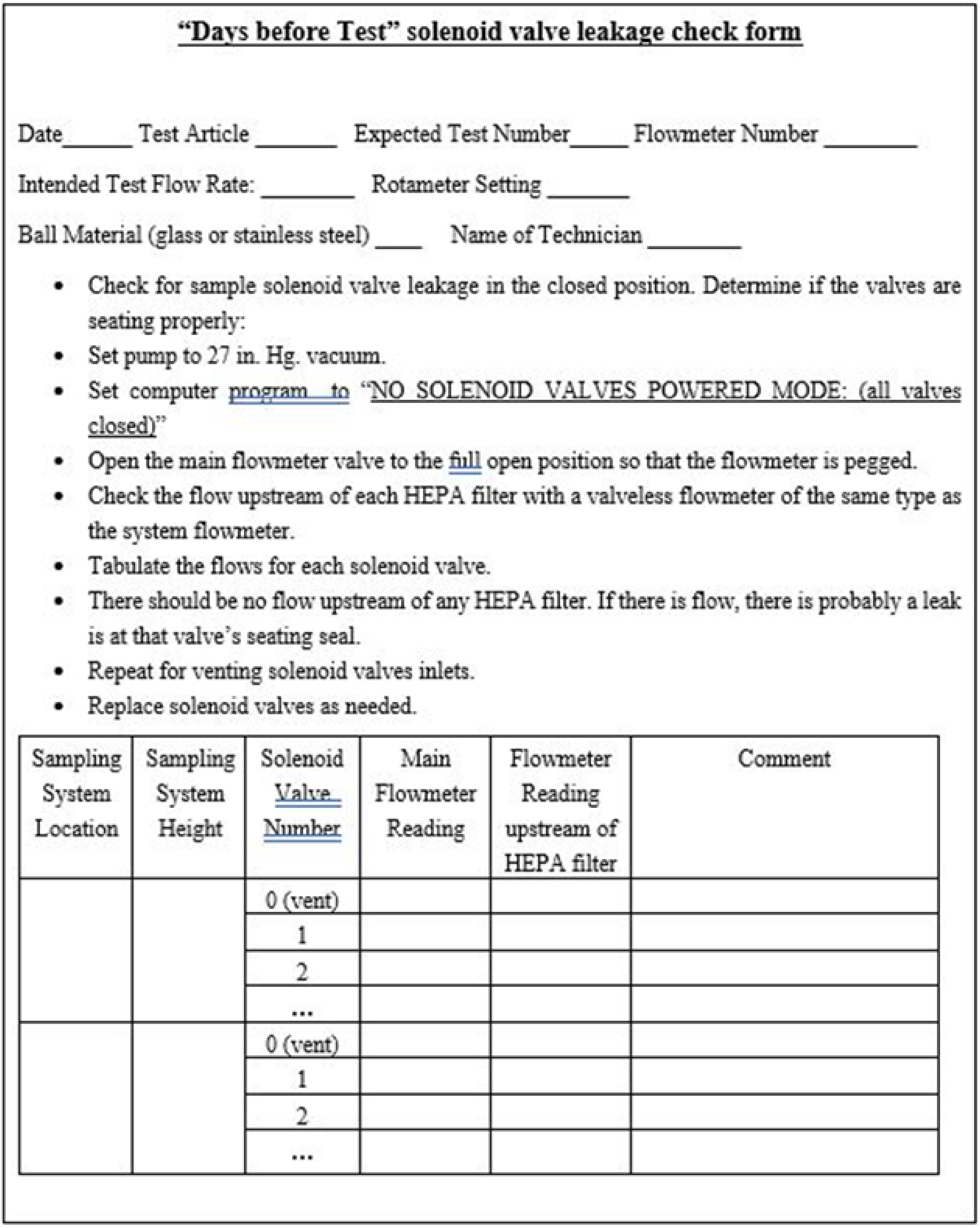
Ball Material (glass or stainless steel) ______Name of Technician _______________

Check T90s: The time for 90% increase from 0 to 90% of the steady state flow for each sample tube should be a small percentage of the sampling time for that tube. Check the flow response time upstream of each HEPA filter, including the vent filter: Record the time it takes to achieve 90% of the desired steady-state flow (t90) setting when switching a sample tube from 0 flow to the desired test steady-state flow. The installed plumbing dead volume (cooling coil, HEPA-filter, drierite), flowrate, as well as particulate/ tar buildup contribute to the t90.

- Open solenoid valve control program.
- Set the program to “PRE-TEST AND POST-TEST VENTING MODE”.
- Set the flow at main flowmeter setting for the intended test flow.
- Enter tube sample time into the program.
- Start sampling. Press “Start Test Button” from the “pre-test and post-test venting mode” screen.
- Determine the T90 upstream of each HEPA filter. (Record the flowmeter reading and convert to flowrate.)
- Record this t90 upstream of each filter for each station.
- Reduce the dead volume, increase set flowrate, or replace filter as needed.

Sampling System Location	Sampling System Height	Solenoid Valve (filter) Number	Time to reach 90% flow (seconds)	Remediation Needed	Comment
		0 (vent)			
		1			
		2			
		...			

Form 2. Solenoid valve leakage check



"Days before Test" solenoid valve leakage check form

Date_____ Test Article _______ Expected Test Number____ Flowmeter Number ________

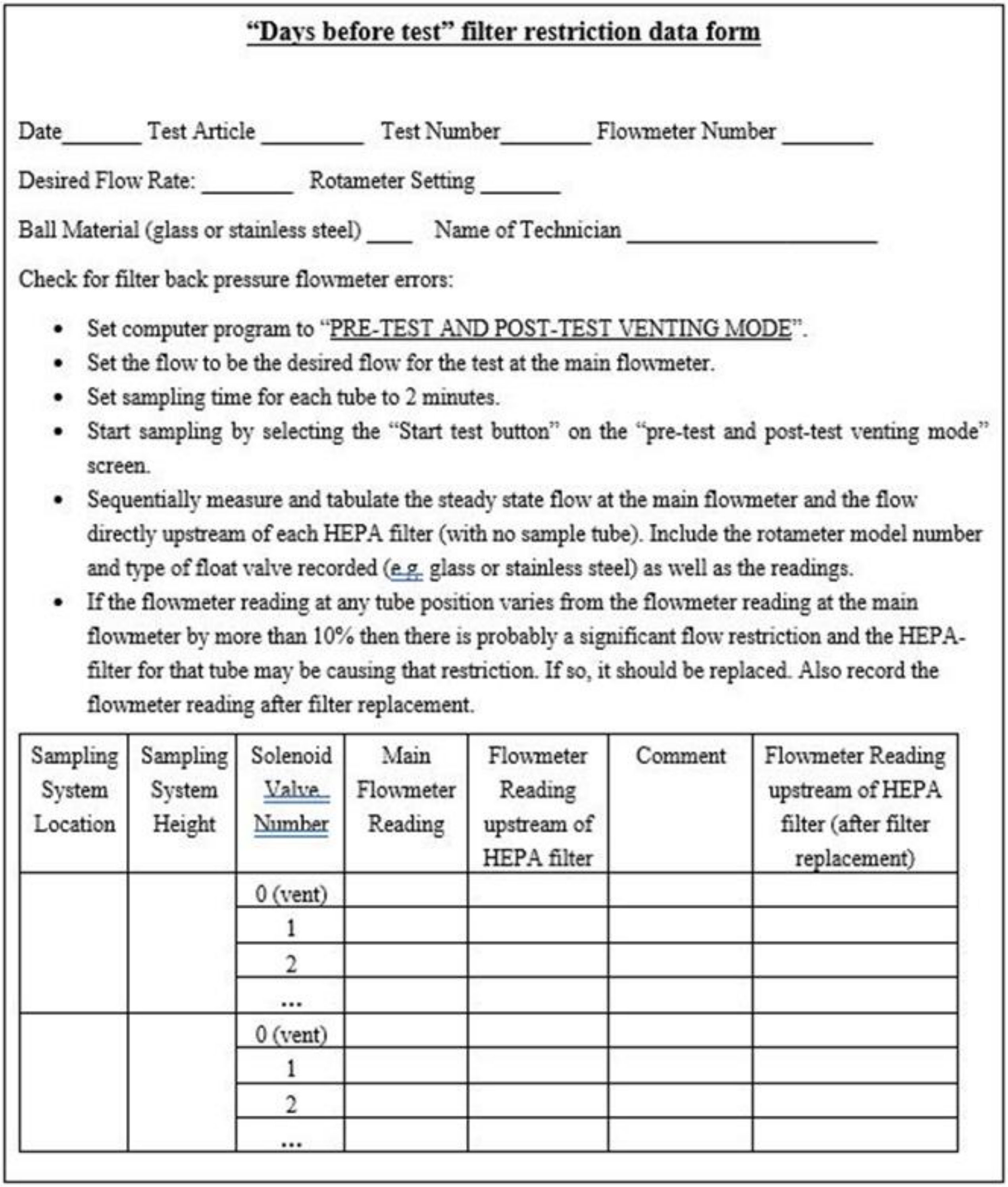
Intended Test Flow Rate: ________ Rotameter Setting _______

Ball Material (glass or stainless steel) ____ Name of Technician ________

- Check for sample solenoid valve leakage in the closed position. Determine if the valves are seating properly:
- Set pump to 27 in. Hg. vacuum.
- Set computer program to "NO SOLENOID VALVES POWERED MODE: (all valves closed)"
- Open the main flowmeter valve to the full open position so that the flowmeter is pegged.
- Check the flow upstream of each HEPA filter with a valveless flowmeter of the same type as the system flowmeter.
- Tabulate the flows for each solenoid valve.
- There should be no flow upstream of any HEPA filter. If there is flow, there is probably a leak is at that valve's seating seal.
- Repeat for venting solenoid valves inlets.
- Replace solenoid valves as needed.

Sampling System Location	Sampling System Height	Solenoid Valve Number	Main Flowmeter Reading	Flowmeter Reading upstream of HEPA filter	Comment
		0 (vent)			
		1			
		2			
		...			
		0 (vent)			
		1			
		2			
		...			

Form 3. Filter restriction



"Days before test" filter restriction data form

Date______ Test Article ________ Test Number_______ Flowmeter Number _______

Desired Flow Rate: _______ Rotameter Setting ______

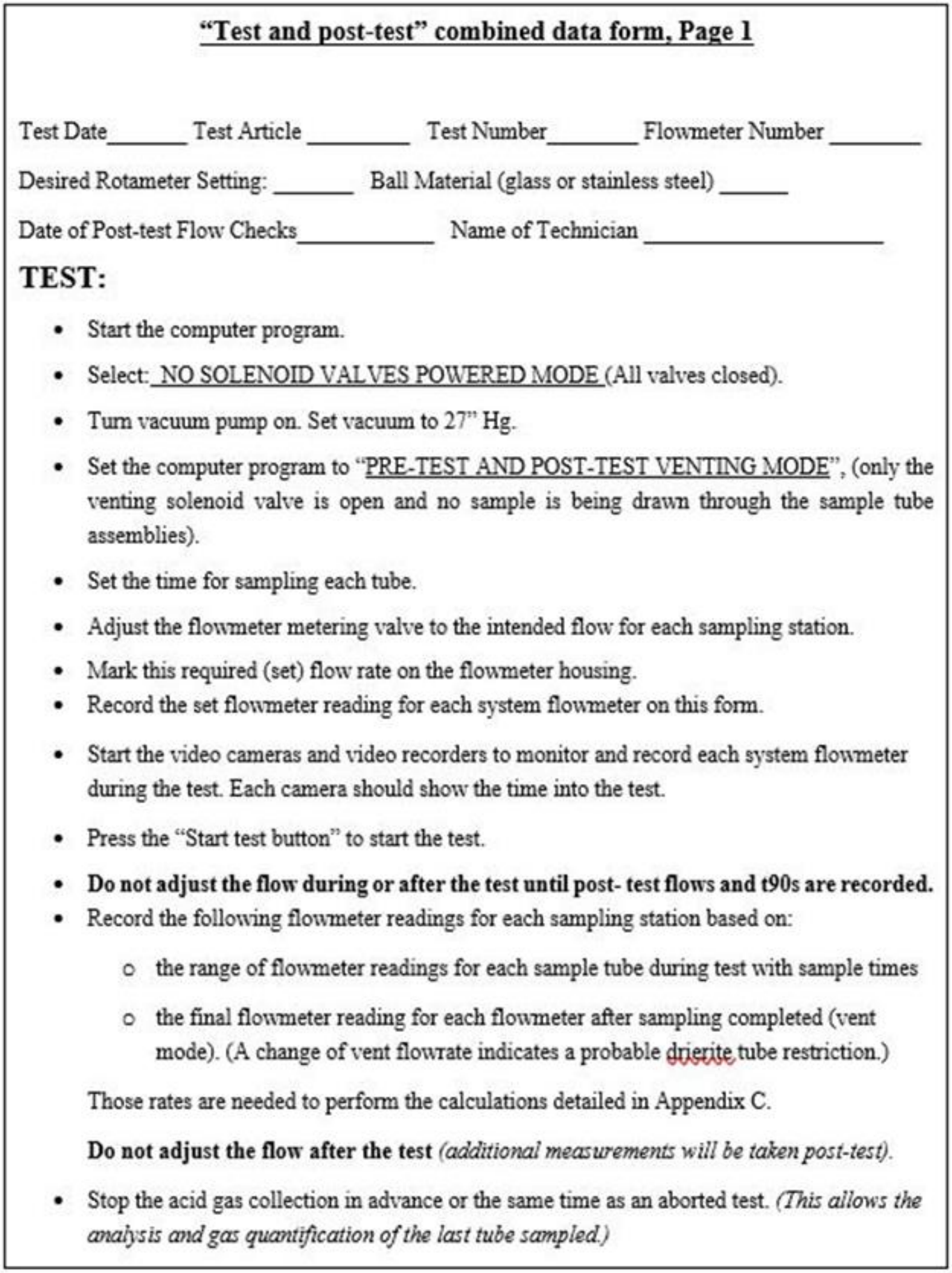
Ball Material (glass or stainless steel) ___ Name of Technician ____________________

Check for filter back pressure flowmeter errors:

- Set computer program to "PRE-TEST AND POST-TEST VENTING MODE".
- Set the flow to be the desired flow for the test at the main flowmeter.
- Set sampling time for each tube to 2 minutes.
- Start sampling by selecting the "Start test button" on the "pre-test and post-test venting mode" screen.
- Sequentially measure and tabulate the steady state flow at the main flowmeter and the flow directly upstream of each HEPA filter (with no sample tube). Include the rotameter model number and type of float valve recorded (e.g. glass or stainless steel) as well as the readings.
- If the flowmeter reading at any tube position varies from the flowmeter reading at the main flowmeter by more than 10% then there is probably a significant flow restriction and the HEPA-filter for that tube may be causing that restriction. If so, it should be replaced. Also record the flowmeter reading after filter replacement.

Sampling System Location	Sampling System Height	Solenoid Valve Number	Main Flowmeter Reading	Flowmeter Reading upstream of HEPA filter	Comment	Flowmeter Reading upstream of HEPA filter (after filter replacement)
		0 (vent)				
		1				
		2				
		...				
		0 (vent)				
		1				
		2				
		...				

Form 4. Test and post-test combined data



"Test and post-test" combined data form, Page 1

Test Date______ Test Article ________ Test Number_______ Flowmeter Number ________

Desired Rotameter Setting: _______ Ball Material (glass or stainless steel) _____

Date of Post-test Flow Checks___________ Name of Technician ____________________

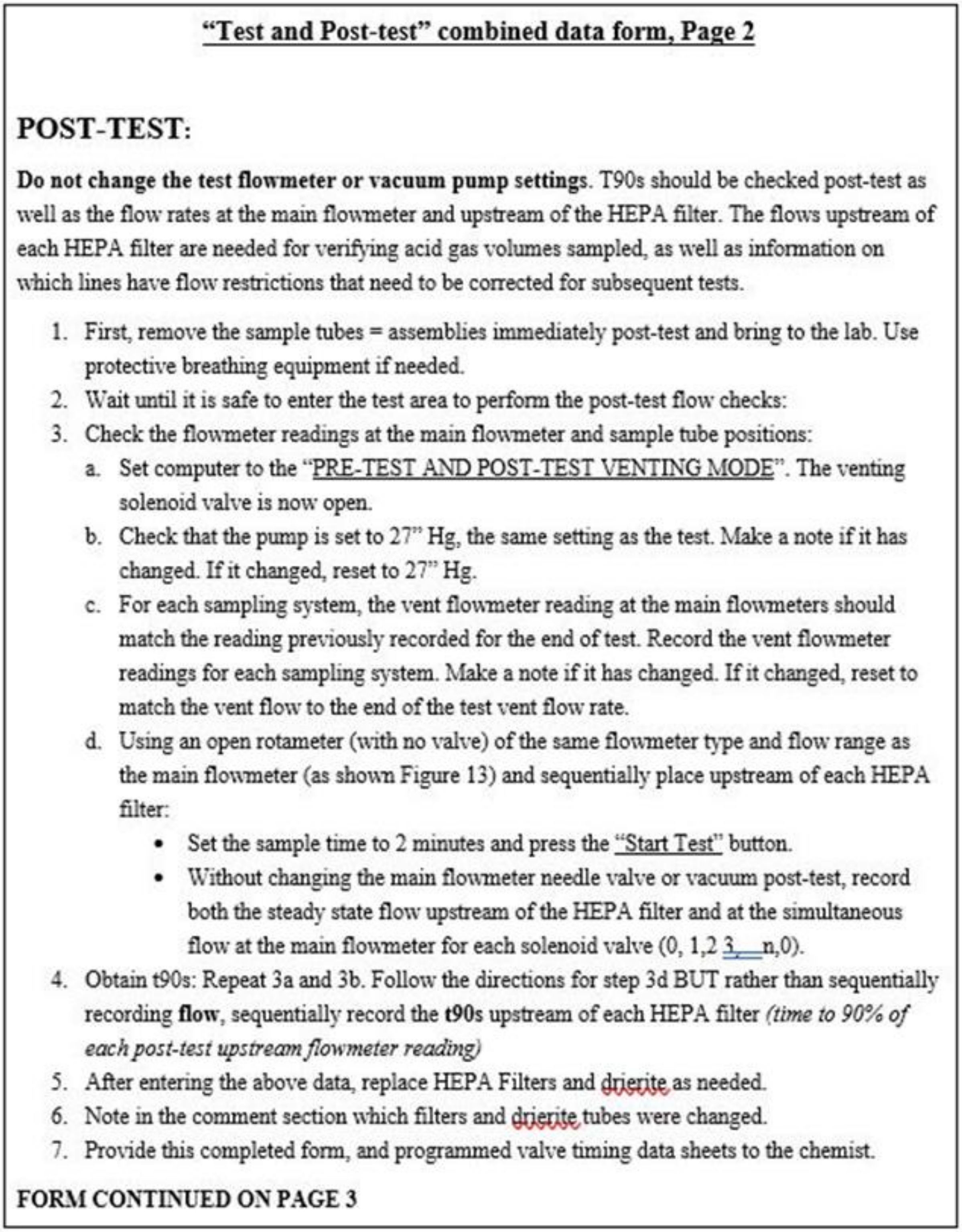
TEST:

- Start the computer program.
- Select: NO SOLENOID VALVES POWERED MODE (All valves closed).
- Turn vacuum pump on. Set vacuum to 27" Hg.
- Set the computer program to "PRE-TEST AND POST-TEST VENTING MODE", (only the venting solenoid valve is open and no sample is being drawn through the sample tube assemblies).
- Set the time for sampling each tube.
- Adjust the flowmeter metering valve to the intended flow for each sampling station.
- Mark this required (set) flow rate on the flowmeter housing.
- Record the set flowmeter reading for each system flowmeter on this form.
- Start the video cameras and video recorders to monitor and record each system flowmeter during the test. Each camera should show the time into the test.
- Press the "Start test button" to start the test.
- **Do not adjust the flow during or after the test until post- test flows and t90s are recorded.**
- Record the following flowmeter readings for each sampling station based on:
    - the range of flowmeter readings for each sample tube during test with sample times
    - the final flowmeter reading for each flowmeter after sampling completed (vent mode). (A change of vent flowrate indicates a probable drierite tube restriction.)

  Those rates are needed to perform the calculations detailed in Appendix C.

  Do not adjust the flow after the test *(additional measurements will be taken post-test).*

- Stop the acid gas collection in advance or the same time as an aborted test. *(This allows the analysis and gas quantification of the last tube sampled.)*



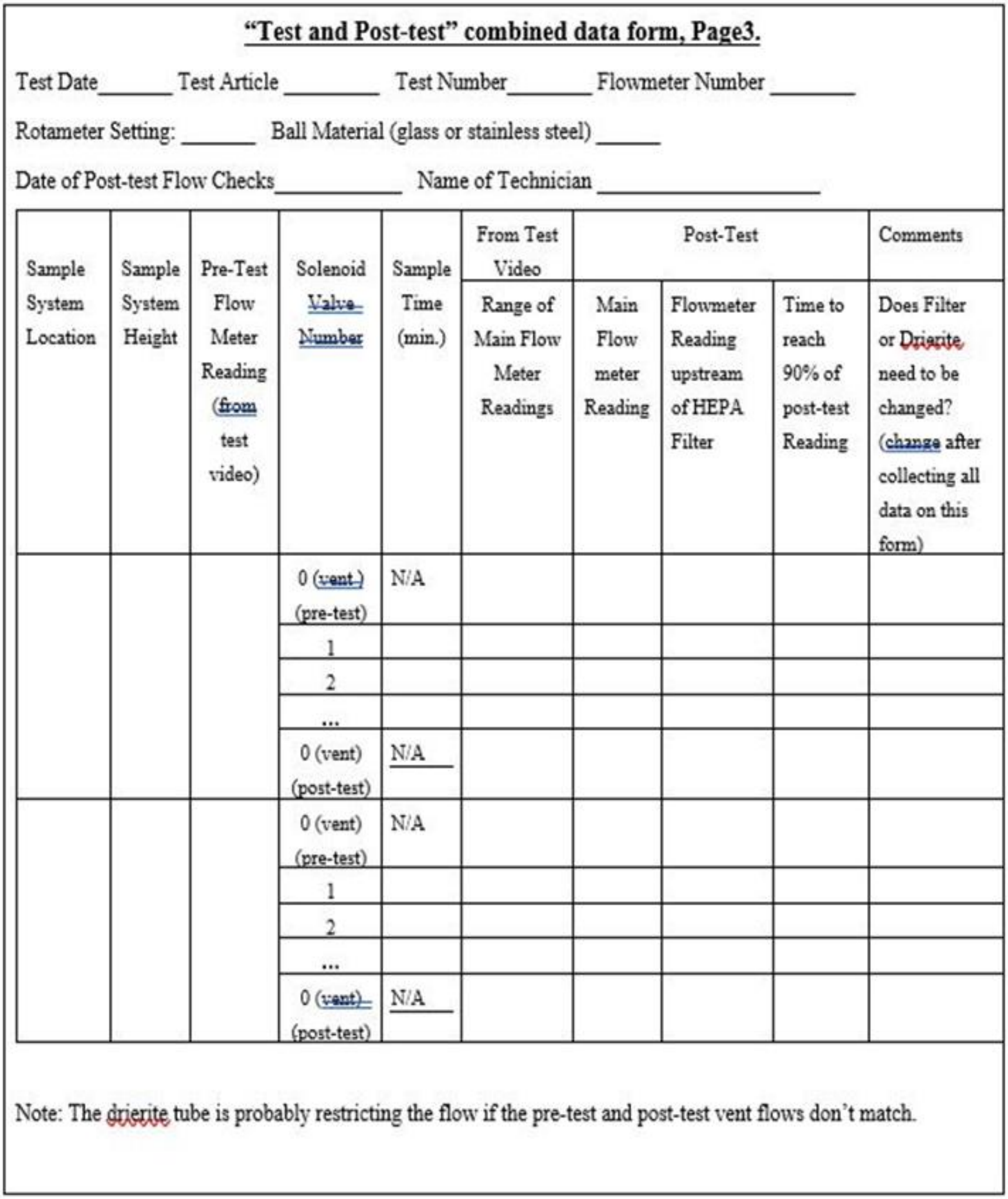
"Test and Post-test" combined data form, Page 2

POST-TEST:

Do not change the test flowmeter or vacuum pump settings. T90s should be checked post-test as well as the flow rates at the main flowmeter and upstream of the HEPA filter. The flows upstream of each HEPA filter are needed for verifying acid gas volumes sampled, as well as information on which lines have flow restrictions that need to be corrected for subsequent tests.

1. First, remove the sample tubes = assemblies immediately post-test and bring to the lab. Use protective breathing equipment if needed.
2. Wait until it is safe to enter the test area to perform the post-test flow checks:
3. Check the flowmeter readings at the main flowmeter and sample tube positions:
   a. Set computer to the "PRE-TEST AND POST-TEST VENTING MODE". The venting solenoid valve is now open.
   b. Check that the pump is set to 27" Hg, the same setting as the test. Make a note if it has changed. If it changed, reset to 27" Hg.
   c. For each sampling system, the vent flowmeter reading at the main flowmeters should match the reading previously recorded for the end of test. Record the vent flowmeter readings for each sampling system. Make a note if it has changed. If it changed, reset to match the vent flow to the end of the test vent flow rate.
   d. Using an open rotameter (with no valve) of the same flowmeter type and flow range as the main flowmeter (as shown Figure 13) and sequentially place upstream of each HEPA filter:
      - Set the sample time to 2 minutes and press the "Start Test" button.
      - Without changing the main flowmeter needle valve or vacuum post-test, record both the steady state flow upstream of the HEPA filter and at the simultaneous flow at the main flowmeter for each solenoid valve (0, 1,2 3,__n,0).
4. Obtain t90s: Repeat 3a and 3b. Follow the directions for step 3d BUT rather than sequentially recording **flow**, sequentially record the **t90s** upstream of each HEPA filter *(time to 90% of each post-test upstream flowmeter reading)*
5. After entering the above data, replace HEPA Filters and drierite as needed.
6. Note in the comment section which filters and drierite tubes were changed.
7. Provide this completed form, and programmed valve timing data sheets to the chemist.

FORM CONTINUED ON PAGE 3



“Test and Post-test” combined data form, Page3.

Test Date______ Test Article ________ Test Number_______ Flowmeter Number _______

Rotameter Setting: ______ Ball Material (glass or stainless steel) _____

Date of Post-test Flow Checks___________ Name of Technician __________________

Sample System Location	Sample System Height	Pre-Test Flow Meter Reading (from test video)	Solenoid Valve Number	Sample Time (min.)	From Test Video	Post-Test			Comments
					Range of Main Flow Meter Readings	Main Flow meter Reading	Flowmeter Reading upstream of HEPA Filter	Time to reach 90% of post-test Reading	Does Filter or Drierite need to be changed? (change after collecting all data on this form)
			0 (vent) (pre-test)	N/A					
			1						
			2						
			…						
			0 (vent) (post-test)	N/A					
			0 (vent) (pre-test)	N/A					
			1						
			2						
			…						
			0 (vent) (post-test)	N/A					

Note: The drierite tube is probably restricting the flow if the pre-test and post-test vent flows don’t match.