

5100-615A
August 24, 2010
Supersedes
5100-615
November 29, 2007

U.S. DEPARTMENT OF AGRICULTURE
FOREST SERVICE

PROTOCOL FOR EVALUATING
OFF-GAS TOXICITY OF
FIRE SHELTER MATERIAL

1. **Application**
- 1.1 This test shall apply to materials intended for use in the New Generation M2002 fire shelters.
- 1.2 The fire shelter composite material consists of the shell outer laminate and shell inner laminate.
- 1.3 A single piece of fire shelter composite material shall be used as the test specimen.
- 1.4 The test specimen shall not include edges, seams, or other non-uniform parts.
- 1.5 This test method includes the means to evaluate the potential toxicity of smoke evolved from the burning of emergency forest fire shelters.
- 1.6 The toxicity is evaluated by assessment of the predicted effects of individual toxicants in the smoke and is based solely on the concentrations of those toxicants.
- 1.7 The predicted human response to the measured toxicants shall be based on the National Academy of Science's "Acute Exposure Guideline Levels" (AEGLE). See Appendix A for AEGLE values.
- 1.8 Generation of the smoke and analysis of the gases shall be performed in a single chamber laboratory apparatus as shown in Appendix C, Figure 1.

Beneficial comments (recommendations, additions, deletions) and any pertinent data that may be used in improving this document should be addressed to: USDA Forest Service, Missoula Technology and Development Center, 5785 Highway 10 West, Missoula, MT 59808, ddavis02@fs.fed.us.

- 1.9 Gas analyses shall be performed for the toxic gases typically present in the smoke from organic glues and resins that might be part of the shelter design. In addition, analyses of certain, possible “unusual” products shall be performed.

2. **Significance**

- 2.1 The potential toxicity of the smoke produced from the thermal exposure of forest fire shelters is an important issue. Evolution of toxic fumes from the glues, resins, or other combustible components used in the construction materials could compromise the field effectiveness of an otherwise robust design.
- 2.2 A laboratory test method is described for quality control purposes.

3. **Test Limitations**

- 3.1 This test procedure is limited to measurement of the concentrations of certain toxic gases produced under fixed laboratory combustion conditions. Results from the laboratory cannot be extrapolated directly to real field conditions because of differences in exposure.
- 3.2 The gas analysis data are limited to the laboratory protocol and within the limitations and precision of the individual analytical methods.
- 3.3 The primary intent of this test method is to provide a means for comparing the potential toxicity of the smoke from the fire shelter composite material under fixed laboratory combustion conditions.

4. **Safety Considerations**

- 4.1 The two primary safety concerns with this test apparatus and procedure are hot surfaces and potentially toxic smoke. In addition, operators should be aware of the fact that the combustion chamber is glass or quartz and is breakable.
- 4.2 Smoke will be released from the specimen during a test run. The apparatus shall be located in a laboratory exhaust hood or in another suitable location with adequate ventilation.
- 4.3 Absorption through the skin of condensed smoke from the inside surfaces of the chambers is possible. Workers shall wear rubber gloves when handling or cleaning the inside of the apparatus.

5. **Summary of Test Method**

- 5.1 This test method was designed to screen forest fire emergency shelter materials for potentially

toxic combustion products.

- 5.2 The laboratory method includes exposure of the test specimen to open flames under controlled conditions and analysis of the chemical products in the smoke. The purpose of this test method is to characterize the potential for the shelter composite to produce a noxious or toxic atmosphere under specified laboratory conditions.

6. Definitions

- 6.1 For definitions of common fire-related terms, see ASTM E176 - 09A
- 6.2 For definitions of smoke toxicity terms, see ASTM E1678 - 10
- 6.3 For further descriptions of AEGL criteria and updated information on guideline levels, see the EPA website for "Acute Exposure Guideline Levels"
<http://www.epa.gov/oppt/aeql/pubs/chemlist.htm>.

7. Test Apparatus

- 7.1 Overview – The smoke toxicity apparatus consists of glass product collection chamber that sits atop an electric cup furnace. One end of the glass chamber consists of a stainless steel sample holder that allows a sample of material under test to be restrained during exposure to flames. The apparatus is used either to expose a sample of material to a high temperature environment under controlled conditions or to expose a sample of material to flames on one side and collect the products produced from the opposite side. A schematic drawing of the overall test setup is presented in Appendix C, Figure 1. A description of the components used in the test setup is given in Appendix C, Table 1.
- 7.2 Combustion Chamber
- 7.2.1 The open flame module comprises one end of the 42-liter glass product collection chamber. This module permits open flame exposure of a 150 mm (6 in.) square portion of a specimen that is approximately 200 mm (8 in.) square. The combustion products from the back (i.e., unexposed) side of the specimen are collected in the collection chamber. Combustion products produced from the front (exposed) side of the specimen are not collected.
- 7.2.2 Operators shall use caution while operating the open flame module. Vigorous flaming or spalling on the front side of the specimen could cause flames, hot particles or toxic gases to be ejected from the module in the direction of the operator. Gases could potentially evolve from the front of the specimen.
- 7.2.3 The number of gas sampling tubes that penetrate the walls of the 42-liter product collection chamber ("sampling ports") is dependent on the number of separate analyzers in use and whether or not "return" lines are employed.
- 7.2.4 The locations of the sampling ports have not been specified. Generally, the sampling ports should be located so that the sample is obtained approximately mid height in the product

collection chamber. This can be done by locating the sampling ports at mid height or by extending the sample lines to appropriate locations within the sample chamber.

7.2.5 Return lines from any of the analyzers shall not be near the inlet sampling ports for those analyzers.

7.3 Gas Analyzers

7.3.1 The combustion atmosphere shall be sampled for the concentrations of the following species: carbon monoxide (CO), carbon dioxide (CO₂), oxygen (O₂), hydrogen cyanide (HCN), hydrogen chloride (HCl), hydrogen fluoride (HF), and the nitrogen oxides (NO and NO₂, which may be analyzed together and reported as NO_x or may be analyzed separately).

7.3.2 In addition, sampling and analysis of fluorine- and phosphorus-containing organic compounds shall be performed, unless it has been demonstrated (e.g., by elemental analyses) that no fluorine or phosphorus exists in any components of the shelter.

7.3.3 Analyses of CO, CO₂ and O₂ are typically performed with continuous, non-destructive analyzers. For these gases, the atmosphere should be returned to the product collection chamber after passing through the analysis cells.

7.3.4 Analysis of each of the other gases entails changes in the atmosphere by passing through a reaction or sorption medium. These gas samples may be returned to the apparatus, but it should be noted that the particular species will be depleted of the species being measured, in accordance with the relative volume of atmosphere removed from the chamber.

7.3.5 The report should indicate the volume of gas removed from the system that is either not returned or has passed through a reactive medium. This volume should be held to as small a value as possible.

7.3.6 Analysis of nitrogen oxides (NO and NO₂) is generally performed with a continuous analyzer specific to those species (however, certain automobile exhaust analyzers include NO_x along with CO, CO₂, and other gases.).

7.3.7 Analysis of HCN, HCl and HF are performed by drawing the atmosphere through solution "bubblers" or "impingers" which contain a basic (0.1 molar sodium hydroxide) aqueous solution. After drawing the atmosphere through the solution for a known period of time at a measured flow rate, the solutions are subsequently analyzed for the appropriate anion (i.e., CN, Cl or F, respectively). Further description of the appropriate solution and the equations used for calculating the gaseous concentrations from the solution concentrations are presented in Appendix B.

7.3.8 Note: Gas concentrations are generally reported in units of ppm (parts-per-million) on a volume-volume basis. The solution concentrations are sometimes also reported in ppm, but on a weight-volume basis (e.g., mg/L). These two sets of "ppm" measurements are very different from one another.

7.3.9 Sampling of gases which contain organic fluorine (F) and organic phosphorus (P) must be compatible with the analysis protocol selected. The analysis technique usually selected is gas chromatography/mass spectrometry (gc/ms). Sampling is generally conducted using evacuated Tedlar® bags or evacuated metal bottles (coated to protect against corrosion by HF).

7.3.10 Analysis of gases by gas detector tubes is not permitted.

8. Laboratory Exhaust Hood

- 8.1 The entire combustion and exposure apparatus must be contained within a laboratory exhaust hood, or in a suitably ventilated environment, in order to protect the operators from potential toxic gases.
- 8.2 The most critical parts of the test, from the point of view of worker safety, are at the beginning when specimens may be flaming, and at the end when the product sampling chamber must be opened to vent the gases prior to the next test.
- 8.3 The wearing of gas masks with filter/sorption cartridges, suitable for the gases listed, is recommended when cleaning the chamber.

9. Calibration of Equipment

9.1 Gas analyzers

- 9.1.1 Each gas analyzer used shall be calibrated with standard, certified calibration gases prior to each day's test runs.
- 9.1.2 Aqueous solutions for trapping HCN, HCl and HF are generally stable for long periods. Furthermore, the exact sodium hydroxide concentration in any given absorbing solution is not critical to the analytical procedures. In any event, a fresh solution should be prepared every few months, or more frequently if the solutions take on any color or cloudiness. In addition, it is standard practice to submit a "blank" absorbing solution (i.e., one that has not been subjected to sample gas flow) for analysis at the same time as the samples from a series of test runs. If any measurable level of the anions of interest appears in the blank, fresh absorbing solution must be prepared before conducting further tests. It is also advisable to submit a blank sample that has had an appropriate volume of chamber atmosphere passed through it for analysis to ensure that contamination from inadequate cleaning of the apparatus does not bias a subsequent result.

10. Test Specimens

10.1 Specimen Preparation

- 10.1.1 Three different specimens shall be tested.
- 10.1.2 All specimens to be tested shall be conditioned at a temperature of 21°C, ±3°C (70°F, ±5°F) and a relative humidity of 65%, ±5% until equilibrium is reached, as determined in accordance with ASTM D 1776-08A Standard Practice for Conditioning and Testing Textiles, or for at least 24 hours, whichever is shorter.

10.1.3 Specimens shall be cut to approximately 200 mm x 200 mm (8 in. x 8 in.). The exposed area of the specimen mounted in the module is approximately 150 mm x 150 mm (6 in. x 6 in.).

11. Specimen Handling Cautions

11.1 Specimens may contain glass fibers or metal foil. Caution should be exercised in handling cut specimens. Gloves are recommended.

12. Test Procedure

12.1 Start Up – Continuous Gas Analyzers

12.1.1 All sampling lines should be purged prior to each test.

12.1.2 Use the recommended gas flow rate for the particular analyzers used. Record the flow rate used and whether or not the sample atmosphere is returned to the test chambers.

12.1.3 Determine the analysis delay time prior to conducting any tests in accordance with 12.1.4. In no case should the analyzer delay time exceed 30 seconds. The analyzer delay time is the time required for the analyzer to reach 90 percent of the value of a test gas, when it is introduced at the point of “sampling” (i.e., in the test chamber).

12.1.4 The simplest way to determine the delay time is to equilibrate the combustion and analytical chambers with a constant concentration of a calibration gas (e.g., CO₂). Both chambers must be filled to minimize any decrease in concentration as a result of sampling. Gas sampling is started and the time required for the analyzer to reach 90 percent of the concentration in the chamber is determined. Disconnecting the sample line and determining the time for the analyzer to indicate 10% of the initial concentration should yield the same delay time. In the event the delay time is found to exceed 30 seconds the analyzer delay time can be minimized by using shorter sampling lines or higher sample flow rates, as appropriate.

12.1.5 A method for signifying the start time of the test on the continuous readout of the gas analyzers must be determined prior to starting a test. Typically, since the analyzers are started before introducing the specimen, the “time” on the analyzer readout corresponding to the start of the test is noted. Other methods that achieve the same end are acceptable.

12.2 Start Up – Solution Bubblers

12.2.1 Typically, “midget impingers” or small gas “bubblers” are used to contain the trapping solution for the acid gases (HCN, HCl and HF). The midget impingers can contain up to about 30 cc of liquid. The optimum amount of liquid is typically 20 cc and the optimum gas flow is from 1.0 L/m. for most samples. Avoid conditions that cause the liquid to splash over into the exit tube of the bubbler.

12.2.2 Higher flow rates and smaller liquid volumes produce higher ion concentrations for any given gas concentration (calculations are shown in Appendix B), thus the flow rate chosen should be the highest possible with no liquid carry over to the exit tube.

12.2.3 Bubbler tips with “fritted discs” should not be used. While the very fine openings dramatically decrease bubble size and therefore increase gas/solution contact, they easily become clogged with oily smoke products. Locating a filter before the bubbler is not an option due to the likely sorption of the gaseous species of interest on the filter.

12.2.4 A moisture trap and drying tube should be placed between the bubbler(s) and the flow meter in order to protect the flow meter from moisture which would interfere with accurate readings.

12.3 Start Up – Grab Samples for Subsequent Analysis

12.3.1 Grab samples are samples of the combustion atmosphere obtained over a usually brief duration (ranging from only a few seconds to a minute or longer, depending on the sampling method), with the intent of analyzing the gas after the test is over.

12.3.2 Examples of three types of grab samples are as follows: 1) an inert (e.g., Tedlar), flattened bag, into which the gas will be introduced; 2) an inert, evacuated, metal bottle which will fill with gas when opened; and 3) a sorbent such as activated charcoal, which is designed to capture certain chemical species.

12.3.3 The Tedlar bag is the simplest procedure. It is connected to the test chamber by rigid teflon tubing and the bag is placed inside a small air-tight box. The box is evacuated at the time gas sampling is desired, causing the bag to draw gas inside in an effort to compensate for the vacuum. The vacuum draw on the box must be stopped when the bag appears to be full, so that the bag does not burst. Sample bags of 1L volume shall be used to minimize the amount of gas removed from the chambers during testing.

12.3.4 Subsequent analyses of the gases in a grab sample are typically gas chromatography/mass spectrometry to look for evidence of unusually toxic gases containing phosphorus or fluorine.

12.4 Flame Exposure Test Startup

12.4.1 No preheating is required for the open flame module. Ensure, by physical inspection during test runs and/or by preliminary testing that the seal between the glass chamber lid and the product collection chamber is intact. The seal consists of a split length of soft silicone tubing that may become brittle with age. It should be replaced if there are any gaps that would allow decomposition products to leak from the collection chamber.

12.4.2 The specimen must be positioned in the open flame module prior to the start of the test.

12.5 Procedure

12.5.1 Prior to starting a test verify that the on line analyzers register atmospheric concentrations of carbon dioxide and oxygen. If readings other than ambient are obtained it will be necessary to further purge the apparatus and sampling lines, or recalibrate the analyzers.

12.5.2 At a pre-determined time prior to applying the burners to the specimen, start the analytical gas sampling pumps and the continuous analyzers’ recording system.

12.5.3 Light the burner and set it aside in a safe place.

12.5.4 Start the run clock at the same time that the lit burners are applied to the specimen. The start of

the run must be noted with respect to the readouts from the continuous gas analyzers.

- 12.5.5 Bring the burner flame into contact with the surface and expose the entire 150mm x 150mm (6 in. x 6 in.) area uniformly by moving the flame over the surface. Do not hold the burner/flame in one location for more than a few seconds as this will likely result in the flame burning through the material. Continue exposing the outer surface of the material for a period of 1 minute.
- 12.5.6 Observe the evolution of smoke from the backside of the specimen. Record the nature of the smoke (e.g., white vs. black, and relative quantity) and the run time during which smoke is produced.
- 12.5.7 Check to ensure that gas sampling and analysis are taking place. Continue to sample from the product collection chamber for a period of 10 minutes from the time the flames were first applied to the surface. Obtain samples for intermittent gas analyses (grab sample) half way through the test (approximately 5 minutes after first flame application).
- 12.5.8 Open the top of the product collection chamber (note that it may be hot). Provide for safe removal of the gases inside the chamber (e.g., by an exhaust hood).
- 12.5.9 It has been found helpful to insert a small fan inside the analytical chamber to aid in purging the interior of the sample collection chamber.
- 12.5.10 Remove and examine the specimen in accordance with the following:
 - 12.5.10.1 Inspect and record the appearance of the residue, including melting, delamination, darkening, etc.
 - 12.5.11 Disassemble the solution bubblers and save the solution in accordance with the instructions included in Section 12.8.
- 12.6 Cleaning and Safety Considerations – Post Test
 - 12.6.1 Smoke, and its condensation products, may contain lethal and/or noxious components. Minimize the exposure of workers to inhalation of gases or skin contact with the condensation products.
 - 12.6.2 The entire system (chambers and circulation tubes) must be ventilated in order to return the chamber atmosphere to ambient conditions.
 - 12.6.3 The insides of the chambers should be cleaned with a damp towel (alcohol may be more effective than water), followed by a dry towel, between runs. If it can be shown by experience that ventilation of the system is adequate to remove volatile products after a given test, then wet and/or dry wiping may be reserved for use between runs for a substantially different specimen.
- 12.7 Instructions for continuous analyzers – Post Test
 - 12.7.1 Correct the analyzer read-out for the following:
 - Time of start of test
 - Conduct the calculations to determine concentration-time products (Section 13)

12.8 Instructions for aqueous solutions – Post Test

12.8.1 Aqueous solutions are used to capture HCN, HCl and HF.

12.8.2 The calculations depend on the following: analysis of the species of interest in solution, measurement of the average gas flow rate for the duration of the sampling, the time of sampling and the final volume of aqueous solution.

12.8.3 Disconnect the bubbler (impinger) from the sampling line.

12.8.4 Rinse the impinger interior with a minimum volume of distilled water and add this rinse to the volume of the bubbler.

12.8.5 Add distilled water or the basic test solution to make the total volume 25 ml. Divide the solution in two and place each sample into a dark glass sample bottle and label with run number and date.

12.8.6 The vials must have a suitable cap that will not leak or contaminate the aqueous solution.

12.8.7 Send half of the sample to the analytical laboratory and retain the other half in case there are any questions about the resultant analytical information.

12.8.8 The bubblers must be thoroughly rinsed between tests. Use of detergent is discouraged for fear of any residual anions.

12.8.9 The final rinse before refilling for another test must be with distilled water.

12.9 Handling of Gas Samples for gc/ms – Post Test

12.9.1 The gas samples obtained for gc/ms analysis of fluorine- and phosphorus- containing organic products must be labeled appropriately and shipped to the analytical laboratory. Transfer of gases from one “bag” to another is not permitted. Reuse of either sample bags or vials is not permitted.

12.9.2 Presentation of Results and Calculations

12.9.3 Results for each test run should include the following:

Identification of specimen

Time and extent of flaming

Time and nature of smoke evolution

Surface area of specimen (for laminated products)

Results of chemical analyses of gases

13. **Calculations**

13.1 Methods of calculation of the various gas species, in terms of concentration-time products (e.g., ppm-min.), are given in the Appendix B.

14. **Report**

14.1 Required Information:

Name and address of laboratory

Name(s) of operator(s), and supervisors if appropriate

Complete description of specimen tested (including physical form, shape color, thickness, size, etc.)

Reference to this test procedure and any deviations from the standard procedure

Results of chemical analyses of gases over the duration of the run

Calculation of concentration-time (ct) products for each gas

Appendix A. The Acute Exposure Guideline Levels (AEGLs), from the U.S. EPA, are shown below (Concentrations in ppm_{vol})

AEGL 2: irreversible or other serious, long-lasting effects, or impaired ability to escape

Gas	AEGL 2, 10 min.
HCN	17
HCl	100
HF	95
NO ₂	20
CO	420

Appendix B Calculation Methods for Toxic Gas Concentrations

1. CO (carbon monoxide) and CO₂ (carbon dioxide)
 - 1.1 Report the average concentration over the duration of the test.

2. HCl (hydrogen chloride gas)
 - 2.1 Report the average concentration over the duration of the test.
 - 2.2 HCl will be absorbed from the gas phase into 0.1 molar sodium hydroxide aqueous solution in an impinger/bubbler and then chloride ion will be analyzed in the solution. The equation below illustrates the conversion of chloride ion (Cl) as ppm by weight (or mg/L) in solution to HCl as ppm by volume in the gas phase. The operator must be careful not to confuse the two different parts-per-million (ppm) concentration measurements. Abbreviations are described in Section 2.3, following the equation.

Eqn. 1:

$$HCl_g(ppm) = \frac{24.5 \times Cl_s \times 1000 \times V_s}{35.5 \times V_{air} \times t}$$

- 2.3 The following terms and constants are used in Equation 1:

$HCl_g(ppm)$ = average gas-phase concentration of HCl, ppm, over the duration of the sampling

Cl_s = solution concentration of chloride, mg/L (or ppm by weight)

V_s = solution volume of the impinger/bubbler, cc

V_{air} = volume flow rate of sample gas through impinger, cc/min. (corrected to 25 °C if necessary)

t = sampling time (i.e., of gas through impinger), minutes

24.5 is molar volume of a standard gas at 25 °C (L/mole)

35.5 is atomic weight of chlorine (g Cl per mole of HCl)

1000 is a conversion factor (to end up with L HCl in 10⁶ L air)

3. HF (hydrogen fluoride gas)

3.1 Report the average concentration over the duration of the test.

3.2 HF will be absorbed from the gas phase into 0.1 molar sodium hydroxide aqueous solution in an impinger/bubbler, along with HCl and HCN. Fluoride ion will be analyzed in solution. The equation below illustrates the conversion of fluoride ion (F) as ppm by weight (or mg/L) in solution to HF as ppm by volume in the gas phase. As with HCl and HCN, the operator must be careful not to confuse the two different parts-per-million (ppm) concentration measurements.

Eqn. 2:

$$HF_g (ppm) = \frac{24.5 \times F_s \times 1000 \times V_s}{19.0 \times V_{air} \times t}$$

3.3 The same terms and constants as given above for HCl are applicable to Equation 2, substituting "CN" for "Cl" and using the atomic weight of C plus N (26.0) in place of that for Cl (35.5).

4. HCN (hydrogen cyanide gas)

4.1 Report the average concentration over the duration of the test.

4.2 HCN will be absorbed from the gas phase into 0.1 molar sodium hydroxide aqueous solution in an impinger/bubbler, along with HCl and HF. Cyanide ion will be analyzed in solution. The equation below illustrates the conversion of cyanide ion (CN) as ppm by weight (or mg/L) in solution to HCN as ppm by volume in the gas phase. As for HCl, the operator must be careful not to confuse the two different parts-per-million (ppm) concentration measurements.

Eqn. 3:

$$HCN_g (ppm) = \frac{24.5 \times CN_s \times 1000 \times V_s}{26.0 \times V_{air} \times t}$$

4.3 The same terms and constants as given above for HCl are applicable to Equation 3, substituting "CN" for "Cl," and using the atomic weights of C plus N (26.0) in place of that for Cl (35.5).

5. NO_x (nitrogen oxides)

5.1 Report the average concentration over the duration of the test.

5.2 The nitrogen oxides (NO and NO₂) will be evaluated directly by a continuous measurement device specifically calibrated for nitrogen oxides (e.g., an automotive exhaust analyzer).

Appendix C Laboratory Smoke Toxicity Test Apparatus

(dimensions in mm [inches])

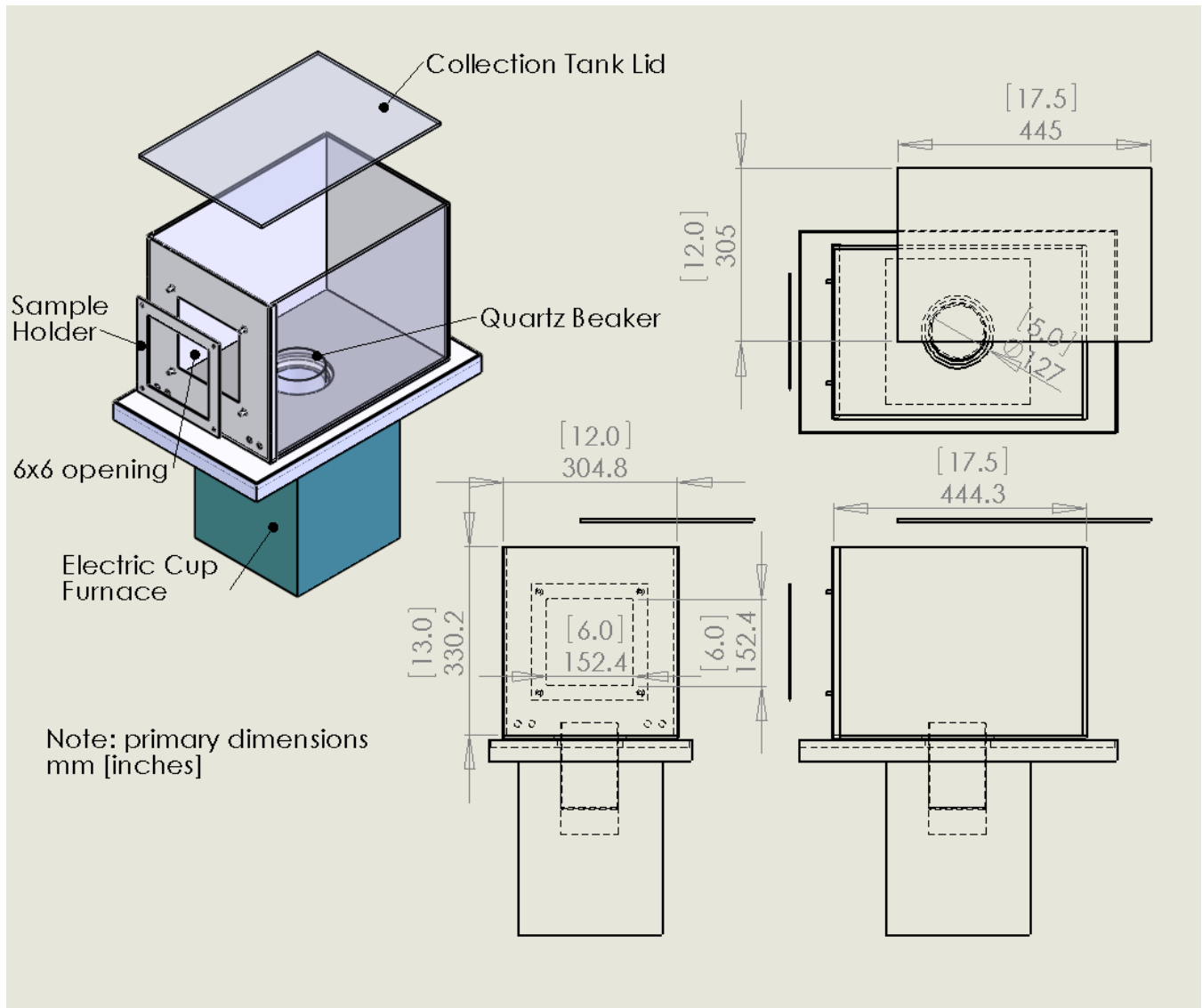


Figure 1. Schematic drawing of the overall test setup

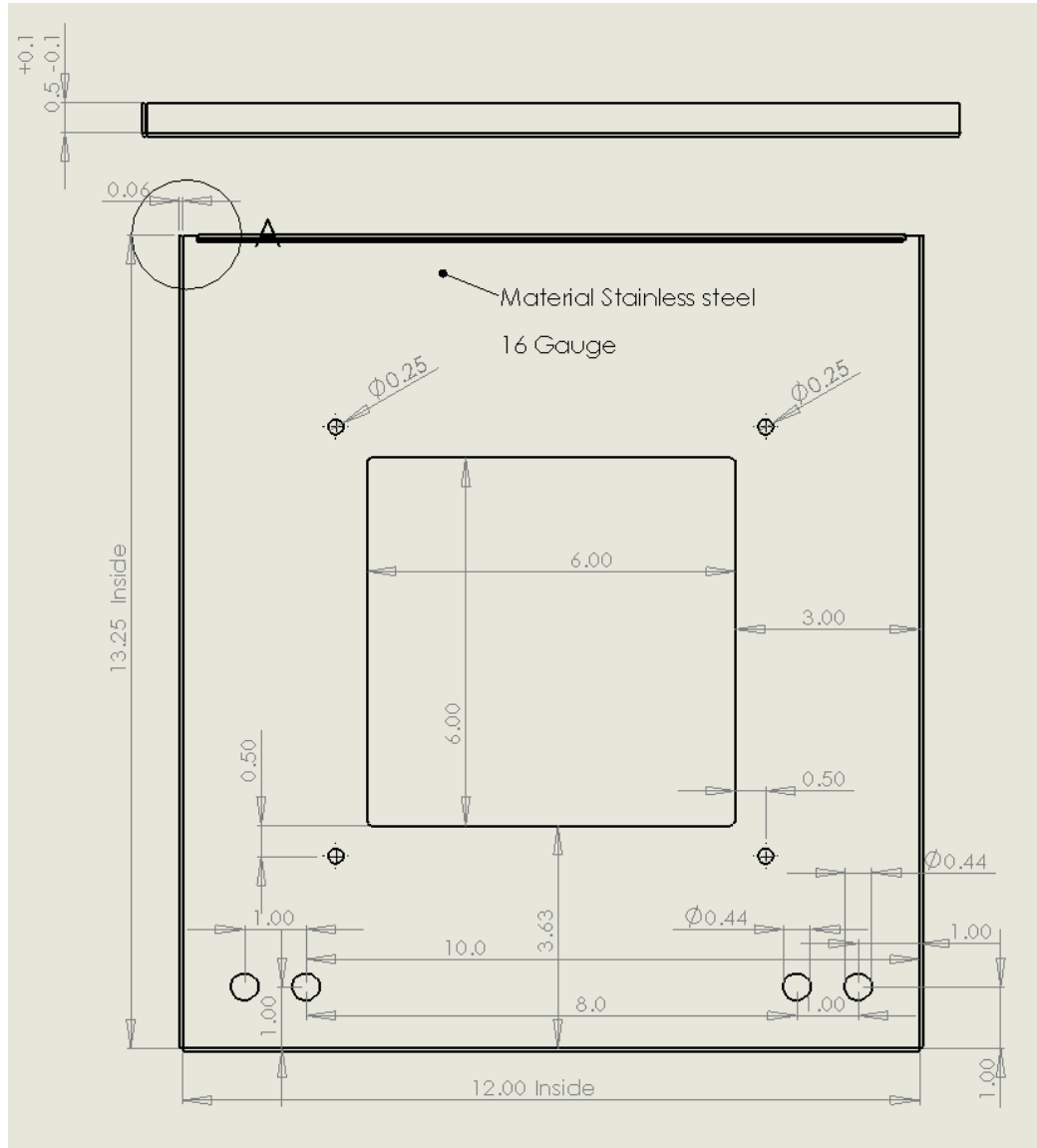
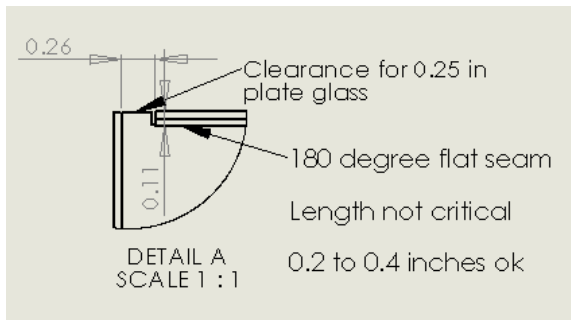


Figure 2. Chamber End Panel and Sample Holder Detail

Table 1. Description of components for laboratory smoke toxicity test apparatus

DESCRIPTION	SUPPLIER	NOTES
Product Collection Chamber (42 L) 2 Plate 17.25 x 13.25 x 0.25 in. 2 Plates 17.50 x 12 x 0.25 in. 1 Plate 12.0 x 13.0 x 0.25 in. 1 Plate (stainless steel) as per drawing		Seal seams with silicone. Water jet cut 5 in. diameter hole in center of one 17.5 x 12 piece (bottom of chamber)
Fittings (4) bulkhead fittings 1/4" x 1/4"	Swagelok or Hylok	Swagelok # SS-400-61BT Hylok # CBU-1
Silicone Tubing (top gasket) 1/2"OD with 1/16" wall, soft	McMaster Carr	Part # 3038K221
Tedlar Sample bag	SKC Instruments 863 Valley View Road, Pa	Part # 232-01
Propane Torch (40 mm flat burner)	Silverline Tools, UK	Part # 456996

Note: Components are available by other suppliers.



40 mm flat burner tip