

## **DRAFT METHOD XXXX**

### **METHOD XXXX - SAMPLING AND ANALYSIS FOR HIGH LEVELS OF PHENOL AND CRESOL EMISSIONS FROM STATIONARY SOURCES**

#### **1.0 SCOPE AND APPLICATION.**

**1.1** Method XXXX is applicable to the collection and analysis of high levels (>20 ppmV in the gas phase and/or associated with particulate) of phenol and the cresols listed in Table XXXX-1. This method has been validated for these pollutant compounds at a fiberglass manufacturing process and is believed to be applicable to other processes where phenols and cresols may be emitted. This method is not inclusive with respect to specifications (e.g., equipment and supplies) and sampling procedures essential to its performance. Some material is incorporated by reference from other methods in the sampling procedure. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following test methods: EPA Method 1, EPA Method 2, EPA Method 3, EPA Method 4, and EPA Method 5.

**1.2** When this method is used to analyze unfamiliar sample matrices, compound identification should be supported by a least one additional qualitative technique. A gas chromatograph/mass spectrometer (GC/MS) may be used for the qualitative confirmation of results for the target analytes.

**1.3** The method detection limits (MDL) are listed in Table XXXX-1. The MDL for a specific sample may differ from the MDL listed in Table XXXX-1 depending on the nature of interferences in the sample matrix, the volume of sample collected, the amount of sample used in the procedure, and the use of sample concentration procedures.

## DRAFT METHOD XXXX

**TABLE XXXX-1. LIST OF ANALYTES, CAS NUMBERS, RETENTION TIMES, AND DETECTION LIMITS**

Compound Name	CAS No. <sup>a</sup>	Retention Time (minutes) <sup>b</sup>	Method Detection Limits (MDL) (ppbv) <sup>c</sup>
Phenol	108-95-2	9.5	700
<i>o</i> -Cresol	95-48-7	17.7	50
<i>m</i> -Cresol <sup>d</sup>	108-39-4	15.8	2390
<i>p</i> -Cresol <sup>d</sup>	106-44-5	15.8	2390

<sup>a</sup> Chemical Abstract Services Registry Number

<sup>b</sup> Analytical conditions (high performance liquid chromatography, HPLC): Reverse phase C18 column, 4.6 x 250 mm; isocratic elution using acetonitrile/0.1M sodium acetate buffer (30:70); flow rate 1.0 mL/min.; UV detector 274 nm, injection volume 30 µL.

<sup>c</sup> For an 849 Liter (30 cubic foot) sample, based on 10 times the levels detected in field train blanks without concentration.

<sup>d</sup> Chromatographic coelution under the analytical conditions used.

**1.4** Sample collection under this method must be performed by testers trained and experienced with isokinetic sampling techniques. The analytical procedures in this method are restricted to use by, or under the supervision of, analysts experienced in the use of chromatography and in the interpretation of chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method.

## **2.0 SUMMARY OF METHOD.**

**2.1** Gaseous and particulate pollutants are withdrawn from an emission source at an isokinetic sampling rate and are collected in a multicomponent sampling train. The primary components of the sampling train include a heated probe, a heated filter, three impingers containing 2N sodium hydroxide, an empty impinger, and an impinger containing silica gel.

## **DRAFT METHOD XXXX**

Phenol and cresols present in the stack gas stream react with the NaOH to form the corresponding sodium salts.

**2.2** An aliquot of the sample collected in the impinger is pH adjusted and is brought up to a known volume (25 mL). An aliquot of the sample may be concentrated using a rotary evaporator before pH adjustment to obtain lower detection limits.

**2.3** An aliquot of the pH-adjusted sample is then analyzed by high performance liquid chromatography (HPLC). Liquid chromatographic analytical conditions are described in Section 11.3. The analytical conditions permit the chromatographic separation and quantitative analysis of phenol and cresols in the extract by absorbance of UV light at 274 nanometers (nm).

**2.4** Filters are extracted with methylene chloride according to the procedures of Draft Method 3541; extracts are analyzed by gas chromatography/mass spectrometry (GC/MS) according to the analytical procedures of Method 8270. Retention of phenol and cresols on the filter depends upon the amount and nature of the particulate material present in the source; amounts of analytes may range from “not detected” to significant. If a representative number of filter extracts are analyzed and no analytes are observed, remaining extracts may be archived.

**3.0 DEFINITIONS.** Reserved

## DRAFT METHOD XXXX

### 4.0 INTERFERENCES.

4.1 High concentrations of oxygenated aromatic compounds, such as other phenolic compounds that have the same retention time or nearly the same retention time as the phenols and cresols and that also absorb at 274 nm, will interfere with the analysis. Prior knowledge of the qualitative composition of the gas stream will aid in minimizing this type of interference. The reagent must be stored in an uncontaminated environment both before and after sampling to minimize blank problems.

4.2 *m*-Cresol interferes with the determination of *p*-cresol and vice versa because the two compounds coelute under the HPLC analytical conditions used.

4.3 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware. These method interferences lead to discrete artifacts and/or elevated baselines in the chromatograms. All reagents and glassware must be routinely demonstrated to be free from interferences under the conditions of the analysis by analyzing laboratory reagent blanks.

4.3.1 Glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by rinsing with the last solvent used. This rinse should be followed by washing with hot water and detergent, and rinsing with tap water and distilled water. Glassware should then be drained and heated in a laboratory oven at 130°C (266°F) for several hours before use. Solvent rinses using methanol and methylene chloride may be substituted for the oven heating. After drying and cooling, glassware should be stored in a clean environment to prevent any accumulation of dust or other contaminants.

4.3.2 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.

## DRAFT METHOD XXXX

**4.4** Matrix interferences may be caused by contaminants that are absorbed from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the matrix being sampled. If interferences occur in subsequent samples, some cleanup of the solution may be necessary.

**4.5** The extent of interferences that may be encountered using liquid chromatographic techniques has not been fully assessed. Although the HPLC conditions described allow for a resolution of the phenol, *m*-/*p*-cresol, and *o*-cresol, other matrix components may interfere.

### **5.0 SAFETY.**

**5.1** The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined. However, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means are available. The laboratory is responsible for maintaining a current awareness file of Occupational Safety & Health Administration (OSHA) regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (MSDSs) should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available.

**5.2** Phenol is poisonous and caustic. Ingestion of even small amounts may cause nausea, vomiting, circulatory collapse, tachypnea, paralysis, convulsions, coma, greenish or smoky-colored urine, necrosis of mouth and gastrointestinal tract, icterus, or death from respiratory failure or sometimes from cardiac arrest. The average fatal dose is 15 g but death from as little as 1 g has been reported. Fatal poisoning may occur by skin absorption following application to large areas. Chronic poisoning with renal and hepatic damage may occur from industrial contact.

The cresols (*o*-, *m*-, and *p*-isomers) have both oral and percutaneous toxicity. Orally, 8 g or more produces rapid circulatory collapse and death. Chronic poisoning from oral or percutaneous absorption may produce digestive disturbances, nervous disorders with faintness,

## **DRAFT METHOD XXXX**

vertigo, mental changes, skin eruptions, jaundice, oliguria, and uremia. The cresols are a general protoplasmic poison.

### **6.0 EQUIPMENT AND SUPPLIES.**

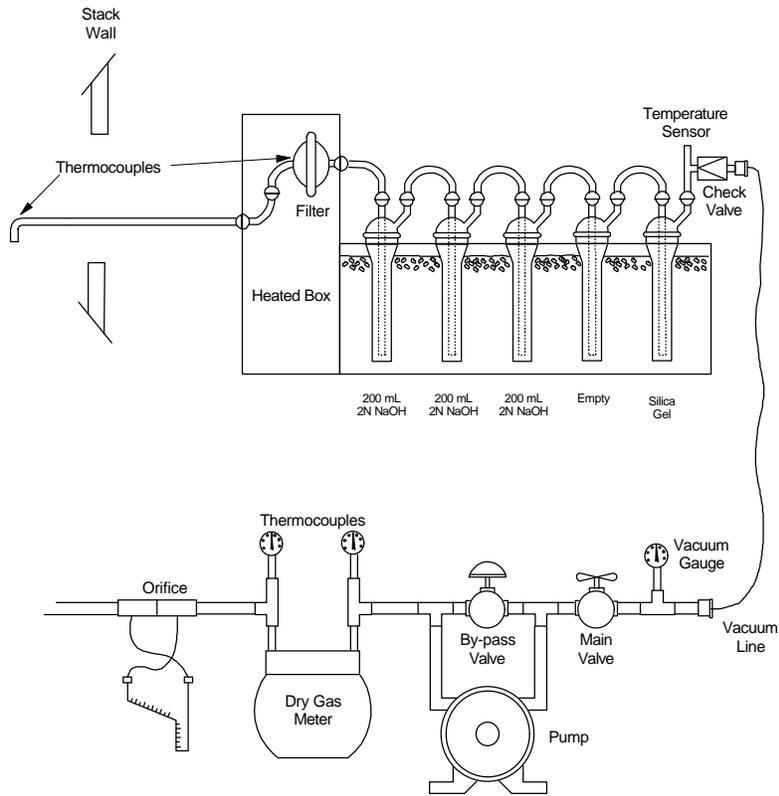
**6.1** The following items are required for sample collection.

**6.1.1** A schematic diagram of the sampling train used in this method is shown in Figure XXXX-1. This sampling train configuration is adapted from the EPA Method 5 procedures. The majority of the required equipment is identical to that used in EPA Method 5 train, with the only change being the use of caustic solution in the impingers.

**6.1.2** Construction details for the basic train components are given in APTD-0581 (see Martin, 1971, in Section 16.0, References). Commercial models of this equipment are also available. The following subsections list changes to APTD-0581 and identify allowable train configuration modifications.

**6.1.3** Basic operating and maintenance procedures for the sampling train are described in APTD-0576 (see Rom, 1972, in Section 16.0, References). Correct usage is important in obtaining valid results. All users of this methodology should therefore refer to APTD-0576 and adopt the operating and maintenance procedures outlined therein unless otherwise specified. The sampling train consists of the components detailed below.

**DRAFT METHOD XXXX**



**Figure XXXX-1. Sampling Train for High Levels of Phenol and the Cresols**

## DRAFT METHOD XXXX

**6.1.3.1** Probe Nozzle. Quartz or glass with sharp, leading edge, tapered 30° angle. The taper shall be on the outside to preserve a constant internal diameter. The nozzle shall be buttonhook or elbow design. A range of nozzle sizes suitable for isokinetic sampling should be available in increments of 0.16 cm (1/16 in.), e.g., 0.32-1.27 cm (1/8-1/2 in.), or larger if higher volume sampling trains are used. Each nozzle shall be calibrated according to the procedures outlined in Section 10.1.

**6.1.3.2** Probe liner. Borosilicate or quartz-glass tubing with a heating system capable of maintaining a probe gas temperature of  $120 \pm 14$  °C ( $248 \pm 25$  °F) at the exit end during sampling. (The tester may opt to operate the equipment at a temperature lower than that specified.) Because the actual temperature at the outlet of the probe is not usually monitored during sampling, probes constructed according to APTD-0581 and utilizing the calibration curves of APTD-0576 (or calibrated according to the procedure outlined in APTD-0576) are considered acceptable. Either borosilicate or quartz glass probe liners may be used for stack temperatures up to about 480 °C (900 °F). Quartz glass liners shall be used for temperatures between 280 and 900 °C (900 and 1650 °F). The softening temperature for borosilicate is 820 °C (1508 °F), and for quartz glass 1500 °C (2732 °F). Water-cooling of the stainless steel sheath will be necessary at temperatures approaching and exceeding 500 °C.

**6.1.3.3** Heated Filter. A pre-extracted glass or quartz filter, similar to that used with Method 5, is used to collect particulate material for subsequent extraction and analysis. The filter is Soxhlet extracted with methylene chloride over night. The filter is supported by a Teflon® filter support which is housed in an all-glass filter holder. The filter is maintained at  $120 \pm 14$  °C ( $248 \pm 25$  °F) during sampling.

## **DRAFT METHOD XXXX**

**6.1.3.4** Pitot tube. Type S, as described in Section 2.1 of promulgated EPA Method 2 (Section 6.1 of Reformatted Draft EPA Method 2), or other appropriate devices (see Vollaro, 1976 in Section 16.0, References). The pitot tube shall be attached to the probe to allow constant monitoring of the stack gas velocity. The impact (high-pressure) opening plane of the pitot tube shall be even with or above the nozzle entry plane (see EPA Method 2, Figure 6-2b) during sampling. The Type S pitot tube assembly shall have a known coefficient, determined as outlined in Section 4.0 of promulgated EPA Method 2 (Section 10.0 of Reformatted Draft EPA Method 2).

**6.1.3.5** Differential Pressure Gauge. Two inclined manometers or equivalent device as described in Section 2.2 of promulgated EPA Method 2 (Section 10.0 of Reformatted Draft EPA Method 2). One manometer shall be used for velocity-head readings and the other for orifice differential pressure ( $\Delta H$ ) readings.

**6.1.3.6** Temperature Sensor. A temperature sensor capable of measuring temperature to within  $\pm 3$  °C ( $\pm 5.4$  °F) shall be installed so that the temperature at the impinger outlet can be regulated and monitored during sampling.

**6.1.3.7** Impinger Train. The sampling train requires a minimum of five 500-mL impingers, connected in series immediately following the heated filter (as shown in Figure XXXX-1), with ground glass (or equivalent) vacuum-tight fittings. The first impinger shall be of the Greenburg-Smith design with the standard tip. The remaining four impingers shall be of the modified Greenburg-Smith design, modified by replacing the tip with a 1.3 cm (1/2 in.) inside diameter glass tube extending to 1.3 cm (1/2 in.) from the bottom of the outer cylinder. The first, second and third impingers shall contain 200 mL of 2N sodium hydroxide.

## DRAFT METHOD XXXX

The fourth impinger remains empty and the fifth impinger is filled with a known amount (2/3 full) of desiccant.

**6.1.3.8** Metering System. The necessary components of the metering system are a vacuum gauge, leak-free pump, temperature sensors capable of measuring temperature within 3 °C (5.4 °F), dry-gas meter capable of measuring volume to within 1%, and related equipment as shown in Figure XXXX-1. At a minimum, the pump should be capable of 4 cubic feet per minute (cfm) free flow, and the dry-gas meter should have a recording capacity of 0-999.9 cubic feet with a resolution of 0.005 cubic feet. Other metering systems capable of maintaining sample rates within 10% of isokineticity and of determining sample volumes to within 2% of the actual value may be used. The metering system must be used in conjunction with a pitot tube to enable checks of isokinetic sampling rates. Sampling trains using metering systems designed for flow rates higher than those described in APTD-0581 and APTD-0576 may be used, provided that the specifications of this method are met.

**6.1.3.9** Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg). The barometric pressure reading may be obtained from a nearby National Weather Service Station. In this case, the station value (which is the absolute barometric pressure) shall be requested and an adjustment for elevation differences between the weather station and sampling point be made at a rate of minus 2.5 mm (0.1 in.) Hg per 30 meters (100 ft.) elevation increase or plus 2.5 mm (0.1 in.) Hg per 30 meters (100 ft.) elevation decrease.

**6.1.3.10** Gas Density Determination Equipment. Temperature sensor and pressure gauge (as described in Sections 2.3 and 2.4 of Promulgated EPA Method 2 as well as Sections 6.3 and 6.4 of Reformatted Method 2), and gas analyzer, if necessary, as described in EPA Method 3. The temperature sensor

## **DRAFT METHOD XXXX**

shall, preferably, be permanently attached to the pitot tube or sampling probe in a fixed configuration so that the tip of the sensor extends beyond the leading edge of the probe sheath and does not touch any metal. Alternatively, the sensor may be attached just prior to use in the field. Note, however, that if the temperature sensor is attached in the field, the sensor must be placed in an interference-free arrangement with respect to the Type S pitot tube openings (see Promulgated EPA Method 2, Figure 2-7, as well as Reformatted Method 2, Figure 2-4). As a second alternative, if a difference of no more than 1% in the average velocity measurements is to be introduced, the temperature sensor need not be attached to the probe or pitot tube (subject to the approval of the Administrator).

**6.1.3.11** Calibration/Field Preparation Record. A permanently bound laboratory notebook, in which duplicate copies of data may be made as they are being recorded, is required for documenting and recording calibrations and preparation procedures (i.e., silica gel tare weights, quality assurance/quality control check results, dry-gas meter readings, and thermocouple calibrations, etc.). The duplicate copies should be detachable and should be stored separately in the test program archives.

**6.1.3.12** Viton® A O-ring.

**6.1.3.13** Heat Resistant Tape.

**6.1.3.14** Teflon® Tape.

**6.2** Sample Recovery. The following items are required for sample recovery.

**6.2.1** Probe Liner and Probe Nozzle Brushes. Teflon® bristle brushes with stainless steel wire or Teflon® handles are required. The probe brush shall have

## DRAFT METHOD XXXX

extensions constructed of stainless steel, Teflon®, or inert material at least as long as the probe. The brushes must be properly sized and shaped to brush out the probe liner and the probe nozzle.

**6.2.2** Wash Bottles. Three wash bottles are required. Teflon® or glass wash bottles are recommended; polyethylene wash bottles should not be used because organic contaminants may be extracted by exposure to organic solvents used for sample recovery.

**6.2.3** Glass Sample Storage Containers. Chemically resistant borosilicate amber glass bottles, 500 mL or 1000 mL. Bottles should be tinted to prevent photochemical reactions. Screw-cap liners shall be either Teflon® or constructed to be leak-free and resistant to chemical attack by caustic solution. Narrow-mouth glass bottles have been found to exhibit less tendency toward leakage.

**6.2.4** Graduated Cylinder and/or Balance. To measure impinger contents to the nearest 1 mL or 1 g. Graduated cylinders shall have subdivisions not >2 mL. Laboratory balances capable of weighing to  $\pm 0.5$  g or better are required.

**6.2.5** Plastic Storage Containers. Screw-cap polypropylene or polyethylene containers to store silica gel.

**6.2.6** Glass Funnel and Rubber Policeman. To aid in the transfer of material into and out of containers in the field.

**6.2.7** Coolers. To store and ship sample containers.

**6.2.8** Crushed Ice. Quantities ranging from 10-50 lb may be necessary during a sampling run, depending upon the temperature of ambient air and the moisture content of

## DRAFT METHOD XXXX

the gas stream. Samples must be stored and shipped cold; sufficient ice for this purpose must be allowed.

**6.2.9** Stopcock Grease. The use of silicone grease is not permitted. Silicone grease usage is not necessary if screw-on connectors and Teflon® sleeves or ground-glass joints are used.

**6.2.10** Silica Gel. Indicating type, 6-16 mesh. If previously used, dry at 180 °C (350 °F) for 2 hours before using. New silica gel may be used as received. Alternatively, other types of desiccants (equivalent to silica gel or better) may be used, subject to the approval of the Administrator.

**6.2.11** Impinger Solution. The impinger solution is prepared (Section 7.2.2) in the laboratory by dissolving 80 grams of sodium hydroxide in organic-free water and diluting to 1 liter with water (2N NaOH). This solution can be prepared in the laboratory or in the field and should be stored in glass containers and used within ten days of preparation. Alternatively, commercially-prepared NaOH solution may be used.

### **6.3** Reagent Preparation.

**6.3.1** Bottles/Caps. Amber 1- or 4-L bottles with Teflon®-lined caps are required for storing 2N NaOH solution.

**6.3.2** Large Glass Container. At least one large glass container (8 to 16 L) is required for preparing the aqueous 2N NaOH solution.

**6.3.3** Stir Plate/Large Stir Bars/Stir Bar Retriever. A magnetic stir plate and large stir bar are required to mix the aqueous 2N NaOH solution. A stir bar retriever is needed for removing the stir bar from the large container holding the NaOH solution.

## **DRAFT METHOD XXXX**

**6.3.4** Beakers. Beakers (150 mL, 250 mL, and 400 mL) are useful for holding/measuring liquids when preparing the aqueous 2N NaOH solution and for weighing NaOH pellets.

**6.3.5** Funnels. At least one large funnel is needed for pouring the aqueous 2N NaOH into bottles.

**6.3.6** Graduated Cylinders. At least one large graduated cylinder (1 to 2 L) is required for measuring organic-free reagent water when preparing the NaOH solution.

**6.3.7** Top-Loading Balance. A top loading balance readable to the nearest 0.1 g is needed for weighing the NaOH pellets used to prepare the aqueous 2N NaOH solution.

**6.3.8** Spatulas. Spatulas are needed for handling NaOH pellets when preparing the aqueous NaOH solution.

### **6.4** Analysis

**6.4.1** Vials. 10 and 25 mL, glass with Teflon®-lined screw caps or crimp tops.

**6.4.2** Analytical Balance. Capable of accurately weighing to the nearest 0.1 mg.

**6.4.3** Glass Ampules. 1 mL in size. Used for storing stock phenol and cresol standards.

**6.4.4** High Performance Liquid Chromatograph (Modular).

**6.4.4.1** Pumping system. Gradient with constant flow control capable of 1.0 mL/min.

## **DRAFT METHOD XXXX**

**6.4.4.2** High Pressure Injection Valve with 30  $\mu$ L loop.

**6.4.4.3** Column. 250 mm x 4.6 mm ID, 5  $\mu$ m particle size, C18 (or equivalent).

**6.4.4.4** Ultra-Violet (UV) Absorbance detector. 274 nm.

**6.4.4.5** Strip Chart Recorder Compatible With Detector. Use of a data system for measuring peak areas and retention times is recommended.

**6.4.5** Volumetric Flasks. 25 mL.

**6.4.6** Rotary Evaporator.

## **7.0 REAGENTS AND STANDARDS.**

**7.1** Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided that the reagent is of sufficiently high purity to use without jeopardizing accuracy.

**7.2** Organic-free reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One of SW-846 (see Reference 9 in Section 16.0).

**7.2.1** All laboratory glassware must be washed with laboratory detergent and water and rinsed with water, methanol, and methylene chloride prior to use.

## DRAFT METHOD XXXX

**NOTE:** NaOH pellets or solution should be handled with plastic gloves at all times with prompt and extensive use of running water in case of skin exposure.

**7.2.2** Preparation of Aqueous 2N NaOH Reagent: Each batch of NaOH reagent should be prepared according to the procedure described below.

**NOTE:** Reagent bottles for storage of cleaned NaOH solution must be rinsed with methanol and dried before use. Baked glassware is not essential to prepared NaOH reagent.

**7.2.2.1** Place an 8-L container under a fume hood on a magnetic stirrer. Add a large stir bar and fill the container half-full with organic-free reagent water. Save the empty bottle from the organic-free reagent water. Start the stirring bar and adjust it to stir as fast as possible. Weigh the NaOH pellets on a one-place balance (640 g/8 L) and add to the stirring water. Fumes may be generated and the water may become warm. Fill the 8-L container to the 8-L mark with organic-free water and stir overnight.

**7.2.2.2** Transfer the 2N NaOH reagent solution into a bottle that has been rinsed with methanol and allowed to dry.

**7.2.3** Shipment to the Field: Tightly cap the bottle containing 2N NaOH reagent using a Teflon®-lined cap. Seal the bottle with Teflon® tape. If numerous bottles are shipped, cushion the bottles to ensure that breakage does not occur.

**7.2.3.1** If the NaOH reagent has passed the Quality Control criteria in Section 9.2.4, the reagent may be packaged to meet necessary shipping requirements and sent to the sampling area. If the Quality Control criteria are not met, the reagent solution must be re-prepared.

## DRAFT METHOD XXXX

**7.3** Field Spike Standard Preparation. To prepare a phenol field spiking standard at 4.0 mg/mL, weigh 200 mg of phenol in a 50 mL volumetric flask. Fill the flask half full with water and shake vigorously. After all of the phenol dissolves, dilute to 50 mL with water.

**7.4** Hydrogen Chloride, HCl. Hydrochloric acid, anhydrous, is required for acidifying concentrated samples prior to analysis.

**7.5** Sulfuric Acid, H<sub>2</sub>SO<sub>4</sub> Concentrated. Reagent grade sulfuric acid (approximately 36N) is required for acidifying the samples.

**7.6** Methylene chloride, CH<sub>2</sub>Cl<sub>2</sub>. Methylene chloride (HPLC grade or equivalent) is required for rinsing glassware.

**7.7** Methanol, CH<sub>3</sub>OH. Methanol (HPLC grade or equivalent) is required for rinsing glassware.

**7.8** Acetonitrile, CH<sub>3</sub>CN. Acetonitrile (HPLC grade or equivalent) is required for rinsing glassware and in the mobile phase for HPLC analysis.

**7.9** Purified phenols and cresols are required for preparation of analytical standards.

**7.10** Sodium Acetate for Mobile Phase Buffer.

**7.11** Stock standard solutions.

**7.11.1** Preparation of Calibration Standards for Chromatographic Analyses.

**7.11.1.1** Stock Standard. Prepare a multi-component stock standard at a concentration of 200 ng/ $\mu$ L by weighing 40 mg ( $\pm$  0.01 mg) of purified phenol

## **DRAFT METHOD XXXX**

and cresols into small vials, dissolving the crystals in mobile phase (30% acetonitrile and 70% 0.1M sodium acetate buffer), quantitatively transferring the solution to a 200-mL volumetric flask and diluting to the line with mobile phase. From this stock solution, prepare 1-mL aliquots using 1-mL glass ampules. Seal and store the aliquots at 4°C (39°F). This procedure should be done as quickly as possible in a dehumidified room as the compounds are hygroscopic.

**7.11.1.2** Calibration Standards. Prepare calibration standards by diluting 125, 250, 625, 1,250, and 2,500  $\mu\text{L}$  of the multi-component stock solution to 5 mL with mobile phase to provide a standard curve with calibration points at 5, 10, 25, 50, and 100 ng/ $\mu\text{L}$  of phenol and cresols.

**7.11.1.3** Check Standard. Prepare a check standard at a concentration of 40 ng/ $\mu\text{L}$  of phenol or cresol by taking 1000  $\mu\text{L}$  of a 200 ng/ $\mu\text{L}$  multi-component stock standard prepared using a second source of phenol and cresol and diluting to 5 mL with mobile phase.

**7.11.2** Standard solutions must be replaced after six months, or sooner, if comparison with check standards indicates a problem.

## **8.0 SAMPLE COLLECTION, PRESERVATION, STORAGE AND TRANSPORT.**

**8.1** Because of the complexity of this method, field personnel should be trained in and experienced with the test procedures in order to obtain reliable results.

**8.2** Laboratory Preparation.

## **DRAFT METHOD XXXX**

**8.2.1** All the components must be maintained and calibrated according to the procedure described in APTD-0576 (Reference 1 in Section 16.0), unless otherwise specified.

**8.2.2** Weigh several 200 to 300 g portions of silica gel to the nearest 0.5 g and place the silica gel in airtight containers. Record on each container the total weight of the silica gel plus containers. As an alternative to preweighing the silica gel, the silica gel may be weighed directly in the impinger or sampling holder just prior to assembly of the sampling train.

### **8.3** Preliminary Field Determinations.

**8.3.1** Select the sampling site and the minimum number of sampling points according to EPA Method 1 or other relevant criteria. Determine the stack pressure, temperature, and range of velocity heads using EPA Method 2. Check the pitot lines for leaks according to Promulgated EPA Method 2, Section 3.1 (Reformatted EPA Method 2, Section 8.1). Determine the stack gas moisture content using EPA Approximation Method 4 or its alternatives to establish estimates of isokinetic sampling-rate settings. Determine the stack gas dry molecular weight, as described in Promulgated EPA Method 2, Section 3.6 (Reformatted EPA Method 2, Section 8.6). If integrated EPA Method 3 sampling is used for molecular weight determination, the integrated bag sample shall be taken simultaneously with, and for the same total length of time as, the sample run.

**8.3.2** Select a nozzle size based on the range of velocity heads so that it is not necessary to change the nozzle size in order to maintain isokinetic sampling rates. During the sampling run, do not change the nozzle. Ensure that the proper differential pressure gauge is chosen for the range of velocity heads encountered (see Section 2.2 of Promulgated EPA Method 2, as well as Section 8.2 of Reformatted EPA Method 2).

## DRAFT METHOD XXXX

**8.3.3** Select a suitable probe liner and probe length so that all traverse points can be sampled. For large stacks, to reduce the length of the probe, consider sampling from opposite sides of the stack.

**8.3.4** A typical sample volume to be collected is 1 dry standard cubic meter (dscm) (35.31 dry standard cubic feet [dscf]). The sample volume can be adjusted as necessitated by analytical detection limit constraints and/or estimated stack concentrations. A maximum limit should be determined to avoid exceeding the capacity of the reagent.

**8.3.5** Determine the total length of sampling time needed to obtain the identified minimum volume by comparing the anticipated average sampling rate with the volume requirement. Allocate the same time to all traverse points defined by EPA Method 1. To avoid timekeeping errors, the length of time sampled at each traverse point should be an integer plus one-half minute.

**8.3.6** In some circumstances (e.g., batch cycles) it may be necessary to sample for shorter times at the traverse points and to obtain smaller gas-volume samples. In these cases, careful documentation must be maintained in order to allow accurate concentration calculation.

### **8.4** Preparation of Collection Train.

**8.4.1** During preparation and assembly of the sampling train, keep all openings where contamination can occur covered with Teflon® film or aluminum foil until just prior to assembly or until sampling is about to begin.

**8.4.2** Place 200 mL of 2N NaOH absorbing solution in each of the first three impingers. The fourth impinger shall remain empty. The fifth impinger shall have 200 to 300 g of pre-weighed silica gel. Be careful to ensure that the silica gel is not entrained and

## DRAFT METHOD XXXX

carried out from the impinger during sampling. Place the silica gel container in a clean place for later use in the sample recovery. Alternatively, the weight of the silica gel plus impinger may be determined to the nearest 0.5 g and recorded. For moisture determination, weigh all of the impingers after filling them with reagent.

**8.4.3** When glass probe liners are used, install the selected nozzle using a Viton®-A O-ring when stack temperatures are <260 °C (500 °F) and a woven glass-fiber gasket when temperatures are higher. See APTD-0576 (Rom, 1972) for details. Other connecting systems using either 316 stainless steel or Teflon® ferrules may be used. Mark the probe with heat-resistant tape or by some other method to denote the proper distance into the stack or duct for each sampling point.

**8.4.4** Assemble the train as shown in Figure XXXX-1. During assembly, do not use any silicone grease on the ground-glass joints of the impingers. Use Teflon® tape, if required. Check all temperature sensors at ambient temperatures.

**8.4.5** Place crushed ice around the impingers.

**8.4.6** Turn on and set the probe heating and filter heating systems at the desired temperature. Allow time for the temperature to stabilize.

**8.5** Leak-Check Procedures.

**8.5.1** Pre-test Leak Check.

**8.5.1.1** A pre-test leak check is not required but is highly recommended.

## DRAFT METHOD XXXX

**8.5.1.2** After the sampling train has been assembled, turn on and set the probe heating system to the desired operating temperature. Allow time for the temperature to stabilize. If a Viton®-A O-ring or other leak-free connection is used in assembling the probe nozzle to the probe liner, leak-check the train at the sampling site by plugging the nozzle and pulling a 381-mm Hg (15-in. Hg) vacuum. Leakage rates in excess of 4% of the average sampling rate or  $> 0.00057 \text{ m}^3/\text{min}$  (0.020 cfm), whichever is less, are unacceptable.

**NOTE:** A lower vacuum may be used, provided that it is not exceeded during the test.

**8.5.1.3** The following leak check instructions for the sampling train described in APTD-0576 and APTD-0581 (References 1 and 2 of Section 16.0, respectively) may be helpful. Start the pump with the fine-adjust valve fully open and coarse-adjust valve completely closed. Partially open the coarse-adjust valve and slowly close the fine-adjust valve until the desired vacuum is reached. Do not reverse direction of the fine adjust valve, as liquid will back up into the train. If the desired vacuum is exceeded, either perform the leak check at this higher vacuum or end the leak check, as shown below, and start over.

**8.5.1.4** When the leak check is completed, first slowly remove the plug from the inlet to the probe. When the vacuum drops to 127 mm (5 in. Hg) or less, immediately close the coarse-adjust valve. Switch off the pumping system and reopen the fine-adjust valve. Do not reopen the fine-adjust valve until the coarse-adjust valve has been closed to prevent the liquid in the impingers from being forced backward in the sampling line and silica gel from being entrained backward into the fourth impinger.

**8.5.2** Leak Checks During the Sampling Run.

## **DRAFT METHOD XXXX**

**8.5.2.1** If, during the sampling run, a component change becomes necessary, a leak-check shall be conducted immediately after the interruption of sampling and before the change is made. The leak check shall be performed according to the procedure described in Section 8.5.1, except that it shall be performed at a vacuum greater than or equal to the maximum value recorded up to that point in the test. If the leakage rate is found to be no greater than 0.00057 m<sup>3</sup>/min (0.020 cfm) or 4% of the average sampling rate (whichever is less), the results are acceptable and no correction will need to be applied to the total volume of dry gas metered. If a higher leakage rate is obtained, the tester must void the sampling run.

**NOTE:** Any correction of the sample volume by calculation reduces the integrity of the pollutant concentration data generated and must be avoided.

**8.5.2.2** Immediately after a component change and before sampling is reinitiated, a leak check similar to a pre-test leak check must also be conducted.

### **8.5.3 Post-Test Leak Check.**

**8.5.3.1** A leak check of the sampling train is mandatory at the conclusion of each sampling run. The leak check shall be performed in accordance with the same procedures as the pre-test leak check, except that the post-test leak check shall be conducted at a vacuum greater than or equal to the maximum value reached during the sampling run. If the leakage rate is found to be no greater than 0.00057 m<sup>3</sup>/min (0.020 cfm) or 4% of the average sampling rate (whichever is less), the results are acceptable. If, however, a higher leakage rate is obtained, the tester shall record the leakage rate, correct the sample volume (as shown in

## DRAFT METHOD XXXX

Section 12.0 of this method) and consider the data obtained of questionable reliability, or void the sampling run.

### 8.6 Sampling Train Operation.

**8.6.1** During the sampling run, maintain a isokinetic sampling rate to within 10% of true isokinetic, below 28 L/min (1.0 cfm). Maintain a probe temperature of  $120^{\circ} \pm 14^{\circ}\text{C}$  ( $248^{\circ} \pm 25^{\circ}\text{F}$ ).

**8.6.2** For each run, record the data on a data sheet such as the one shown in Figure XXXX-2. Be sure to record the initial dry-gas meter reading. Record the dry-gas meter readings at the beginning and end of each sampling time increment, when changes in flow rates are made, before and after each leak check, and when sampling is halted. Take other readings indicated by Figure XXXX-2 at least once at each sampling point during each time increment and additional readings when



## DRAFT METHOD XXXX

significant adjustments (20% variation in velocity head readings) necessitate additional adjustments in flow rate. Level and zero the manometer. Because the manometer level and zero may drift due to vibrations and temperature changes, make periodic checks during the traverse.

**8.6.3** Clean the stack access ports prior to the test run to eliminate the chance of collecting deposited material. To begin sampling, verify that the probe heating systems are at the specified temperature, remove the nozzle cap, and verify that the pitot tube and probe are properly positioned. Position the nozzle at the first traverse point with the tip pointing directly into the gas stream. Immediately start the pump and adjust the flow to isokinetic conditions. Nomographs, which aid in the rapid adjustment of the isokinetic sampling rate without excessive computations, are available. These nomographs are designed for use with the Type S pitot tube with a coefficient of  $0.84 \pm 0.02$  and the stack gas equivalent density (dry molecular weight) is equal to  $29 \pm 4$ . APTD-0576 (Reference 1 in Section 16.0) details the procedure for using the nomographs. If the stack gas molecular weight and the pitot tube coefficient are outside the above ranges, do not use the nomographs unless appropriate steps (Shigehara, 1974, in Section 16.0, References) are taken to compensate for the deviations.

**8.6.4** When the stack is under significant negative pressure, take care to close the coarse-adjust valve before inserting the probe into the stack in order to prevent the impinger solutions from backing up into the probe. If necessary, the pump may be turned on with the coarse-adjust valve closed.

**8.6.5** When the probe is in position, block off the openings around the probe and stack access port to prevent unrepresentative dilution of the gas stream.

**8.6.6** Traverse the stack cross-section, as required by EPA Method 1. To minimize the chance of extracting deposited material, be careful not to bump the probe

## DRAFT METHOD XXXX

nozzle into the stack walls when sampling near the walls or when removing or inserting the probe through the access port.

**8.6.7** During the test run, make periodic adjustments to keep the temperature of the probe and the heated filter at the proper levels. Add more ice and, if necessary, salt, to maintain a temperature of  $<20^{\circ}\text{C}$  ( $68^{\circ}\text{F}$ ) at the silica gel outlet. Also, periodically check the level and zero of the manometer.

**8.6.8** A single train shall be used for the entire sampling run, except in cases where simultaneous sampling is required in two or more separate ducts; at two or more different locations within the same duct; or, in cases where equipment failure necessitates a change of trains. Additional train(s) may also be used for sampling when the capacity of a single train is exceeded.

**8.6.9** When two or more trains are used, components from each train shall be analyzed. If multiple trains have been used because the capacity of a single train would be exceeded, first impingers from each train may be combined, second impingers from each train may be combined, and third impingers from each train may be combined.

**8.6.10** At the end of the sampling run, turn off the coarse adjust valve, remove the probe and nozzle from the stack, turn off the pump, record the final dry gas meter reading, and conduct a post-test leak check as outlined in Section 8.5.3. Also, leak check the pitot lines as described in EPA Method 2 (Section 8.1 of Reformatted Method 2). The lines must pass this leak check in order to validate the velocity-head data.

**8.6.11** Calculate percent isokineticity (as described in Section 6.11 of Method 5, as well as see Section 12.11 of Reformatted Method 5) to determine whether the run was valid or another test should be performed.

## DRAFT METHOD XXXX

### 8.7 Sample Recovery.

#### 8.7.1 Preparation.

**8.7.1.1** Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period. Allow the probe to cool. When the probe can be handled safely, wipe off all external particulate matter near the tip of the probe nozzle and place a cap over the tip to prevent losing or gaining particulate matter. Do not cap the probe tip tightly while the sampling train is cooling because a vacuum will be created drawing liquid from the impingers back through the sampling train.

**8.7.1.2** Before moving the sampling train to the cleanup site, remove the probe from the sampling train and cap the open outlet, being careful not to lose any condensate that might be present. Remove the umbilical cord from the last impinger and cap the impinger. If a flexible line is used, let any condensed water or liquid drain into the impingers. Cap off any open impinger inlets and outlets. Ground glass stoppers, Teflon® caps, or caps of other inert materials may be used to seal all openings.

**8.7.1.3** Transfer the probe and impinger/condenser assembly to an area that is cleaned and protected from wind so that the chances of contaminating or losing the sample are minimized.

**8.7.1.4** Inspect the train before and during disassembly, and note any abnormal conditions.

**8.7.1.5** Save a portion of all washing solutions (2N NaOH) used for cleanup as a blank. Transfer 200 mL of each solution directly from the wash bottle

## DRAFT METHOD XXXX

and place each in a separate prelabeled sample “blank” container (see Section 9.2.2).

### 8.7.2 Sample Containers.

**8.7.2.1** Container No. 1. Using two people, rinse the probe/nozzle with 2N NaOH by tilting and rotating the probe while squirting solvent into the upper end so that all of the surfaces are wetted with the rinse solution. Let the solvent drain into the container. If particulate is visible, use a Teflon® brush to loosen/remove the particulate material and follow with a second rinse. After the rinses have been collected, seal the container and add the proper label.

**8.7.2.2** Container No. 2. Disassemble the filter holder and carefully remove the filter with Teflon® tweezers and place in a precleaned glass petri dish. Cover the petri dish, add the proper label, and seal with Teflon® tape. Rinse the front half of the filter holder, the filter support, and any other connecting glass pieces with 2N NaOH and add the rinses to Container No. 1. Mark the liquid level in Container No. 1 and seal for shipment.

**8.7.2.3** Container No. 3. Rinse the back half of the filter holder with 2N NaOH and add to Container No. 3. Pour the contents of Impinger No. 1 into Container No. 3 along with the 2N NaOH rinses of the impinger. Mark the liquid level, seal the container, and add the proper sample label.

**8.7.2.4** Container No. 4. Add the contents of Impingers No. 2, 3, and 4 along with the respective rinses to Container No. 4. Mark the liquid level, seal the container, and add the proper label.

## **DRAFT METHOD XXXX**

**8.7.2.5** Moisture determination. If a moisture determination is to be made, measure the volume (or weight) gain of each impinger as well as the impinger containing the silica gel before transferring the contents to the sample containers.

**8.7.2.6** Sample preparation for shipment. Prior to shipment, recheck all sample containers to ensure that the caps are well secured. Seal the lids with Teflon® tape. Ship all samples upright, packed in ice, using the proper shipping materials as prescribed for hazardous materials.

### **9.0 QUALITY CONTROL.**

**9.1** Sampling. Sampling quality control procedures are listed in Table XXXX-2. See Reference 3 in Section 16.0 for additional Method 5 quality control.

**9.2** Analysis. The quality assurance program required for this method includes the analysis of the field, reagent and method blanks, procedure validations, and analysis of field spikes.

The assessment of combustion data and positive identification and quantitation of phenol/cresols are dependent on the integrity of the samples received and the precision and accuracy of the analytical methodology. Quality assurance procedures for this method are designed to monitor the performance of the analytical methodology and to provide the required information to take corrective action if problems are observed in laboratory operations or in field sampling activities. Table XXXX-3 lists laboratory quality control procedures.

**DRAFT METHOD XXXX**

**TABLE XXXX-2. SAMPLING QUALITY CONTROL PROCEDURES**

<b>Criteria</b>	<b>Control Limits<sup>a</sup></b>	<b>Corrective Action</b>
Final Leak Rate	0.00057 m <sup>3</sup> /min or 4% of sampling rate, whichever is less.	None: Results are questionable and should be compared with other train results.
Dry Gas Meter Calibration	Post average factor agrees ±5% of pre-factor.	Adjust sample volumes using the factor that gives the smallest volume.
Individual Correction Factor (γ)	Agree with 2% of average factor.	Redo correction factor.
Average Correction Factor	1.00 ± 1%.	Adjust the dry gas meter and recalibrate.
Intermediate Dry Gas Meter	Calibrated every six months against EPA standard.	--
Analytical Balance (top loader)	±0.1 g of NBS Class S Weights.	Repair balance and recalibrate.
Barometer	Within 2.55 mm Hg of mercury-in-glass barometer.	Recalibrate.

<sup>a</sup> Control limits are established based on previous test programs conducted by the EPA.

**DRAFT METHOD XXXX**

**TABLE XXXX-3. LABORATORY QUALITY CONTROL PROCEDURES  
FOR HPLC ANALYSIS**

<b>Parameter</b>	<b>Quality Control Check</b>	<b>Frequency</b>	<b>Acceptance Criteria</b>	<b>Corrective Action</b>
Linearity Check	Run 5-point curve.	At setup or when check standard is out-of-range	Correlation coefficient 0.995	Check integration, reintegrate. If necessary recalibrate.
Retention Time	Analyze check standard	1/20 injections	Within three standard deviations of average calibration relative retention time	Check instrument function for plug, etc. Heat column: Adjust gradient
Calibration Check	Analyze check standard	1/20 injections minimum. 2/set	±15% of calibration curve	Check integration, remake standard. Or recalibrate.
System Blank	Analyze mobile phase	1/day	0.1 level of expected analyte	Locate source of contamination; reanalyze
Matrix Spike/Matrix Spike Duplicate	Analyze spiked sample	1/set or 1/20 samples	±20% of spiked amount	Check integration, check instrument function, reanalyze , reprepare if possible
Replicate Samples	Analyze duplicate sample aliquot	1/set or 1/20 samples	±20% of first aliquot	Check integration, check instrument function, reanalyze, reprepare if possible
Replicate Analyses	Re-inject sample	1/20 samples or 1/set	±15% of first injection	Check integration, check instrument function, reanalyze
Method Blank	Analyze 2N NaOH	1/set or 1/20 samples	0.1 level of expected analyte	Locate source of contamination, reanalyze, reprepare if possible

## **DRAFT METHOD XXXX**

**9.2.1** Field Train Blanks. Field blanks must be submitted with the samples collected at each sampling site. The field blanks include the sample bottles containing aliquots of sample recovery solvents, water, and unused NaOH reagent. At a minimum, one complete sampling train will be assembled in the field staging area, taken to the sampling area, and leak-checked at the beginning and end of the testing (or for the same total number of times as the actual sampling train). The probe of the blank train shall be heated during the sample test. The train will be recovered as if it were an actual test sample. No gaseous sample will be passed through the blank sampling train.

**9.2.2** Reagent Blanks. A 200 mL aliquot of 2N NaOH will be collected in the field as a separate sample and returned to the laboratory for analysis to evaluate artifacts that may be observed in the actual samples.

**9.2.3** Laboratory Method Blanks. A method blank must be prepared for each set of analytical operations, to evaluate contamination and artifacts that can be derived from glassware, reagents, and sample handling in the laboratory.

**9.2.4** Field Spike. A field spike is performed by introduction of 2 mL of the Field Spike Standard into an impinger containing 200 mL of NaOH solution. Standard impinger recovery procedures are followed and the spike is used as a check on field handling and recovery procedures. An aliquot of the Field Spike Standard is retained in the laboratory for comparative analysis.

**9.2.5** Preparation of NaOH Reagent. Take two aliquots of the NaOH reagent. The size of the aliquots depends on the exact sampling procedure used, but 100 mL is reasonably representative. To ensure that the background in the reagent is acceptable for field use, analyze one aliquot of the reagent according to the procedure in Section 11. Save the other aliquot of aqueous 2N NaOH for use as a laboratory method blank when the analysis is performed.

## **DRAFT METHOD XXXX**

### **10.0 CALIBRATION AND STANDARDIZATION.**

**NOTE:** Maintain a laboratory log of all calibrations.

**10.1 Probe Nozzle.** Probe nozzles shall be calibrated before their initial use in the field. Using a micrometer, measure the inside diameter of the nozzle to the nearest 0.025 mm (0.001 in.). Make measurements at three separate places across the diameter and obtain the average of the measurements. The difference between the high and low numbers shall not exceed 0.1 mm (0.004 in.). When the nozzles become nicked, dented, or corroded, they must be replaced. Each nozzle must be permanently and uniquely identified.

**10.2 Pitot Tube Assembly.** The Type S pitot tube assembly must be calibrated according to the procedure outlined in Section 4 of Promulgated EPA Method 2 (Section 10.1 of Reformatted Draft EPA Method 2), or assigned a nominal coefficient of 0.84 if it is not visibly nicked or corroded, and, if it meets design and intercomponent spacing specifications.

#### **10.3 Metering System.**

**10.3.1 Calibration Prior to Use.** Before its initial use in the field, the metering system shall be calibrated according to the procedure outlined in APTD-0576 (see Reference 1 of Section 16.0). Instead of physically adjusting the dry-gas meter dial readings to correspond to the wet-test meter readings, calibration factors may be used to correct the gas meter dial readings mathematically to the proper values. Before calibrating the metering system, it is suggested that a leak-check be conducted. For metering systems having diaphragm pumps, a leak check procedure may not detect leakages within the pump. For these cases, the following leak check procedure will apply. Make a ten-minute calibration run at 0.00057 m<sup>3</sup>/min (0.020 cfm). At the end of the run, take the difference of the measured wet-test and dry-gas meter volumes and divide the difference by 10 to get the leak rate. The leak rate should not exceed 0.00057 m<sup>3</sup>/min (0.020 cfm).

## **DRAFT METHOD XXXX**

**10.3.2 Calibration After Use.** After each field use, check the calibration of the metering system by performing three calibration runs at a single intermediate orifice setting (based on the previous field test). Set the vacuum at the maximum value reached during the test series. To adjust the vacuum, insert a valve between the wet-test meter and the inlet of the metering system. Calculate the average value of the calibration factor. If the value has changed by more the 5%, recalibrate the meter over the full range of orifice settings, as outlined in APTD-0576 (Reference 1 of Section 16.0).

**10.3.3 Leak check of metering system.** The portion of the sampling train from the pump to the orifice meter (see Figure XXXX-1) should be leak checked prior to initial use and after each shipment. Leakage after the pump will result in less volume being recorded than is actually sampled. Use the following procedure. Close the main valve on the meter box. Insert a one-hole rubber stopper with rubber tubing attached into the orifice exhaust pipe. Disconnect and vent the low side of the orifice manometer. Close off the low side orifice tap. Pressurize the system to 13 - 18 cm (5 - 7 in.) water column by blowing into the rubber tubing. Pinch off the tubing and observe the manometer for 1 minute. A loss of pressure on the manometer indicates a leak in the meter box. Leaks, if present, must be corrected.

**NOTE:** If the dry-gas meter coefficient values obtained before and after a test series differ by >5%, either the test series must be voided or calculations for the test series shall be performed using whichever meter coefficient value (i.e., before or after) gives the lower value of total sample volume.

**10.4 Probe Heater.** The probe heating system must be calibrated before its initial use in the field according to the procedure outlined in APTD-0576 (Reference 1 of Section 16.0). Probes constructed according to APTD-0581 (Reference 2 of Section 16.0) need not be calibrated if the calibration curves in APTD-0576 (Reference 1 of Section 16.0) are used.

## **DRAFT METHOD XXXX**

**10.5** Temperature Sensors. Each temperature sensor must be permanently and uniquely marked on the casing. All mercury-in-glass reference thermometers must conform to ASTM E-1 63C or 63F specifications. Temperature sensors should be calibrated in the laboratory with and without the use of extension leads. If extension leads are used in the field, the temperature sensor readings at the ambient air temperatures, with and without the extension lead, must be noted and recorded. Correction is necessary if using an extension lead produces a change  $>1.5\%$ .

**10.5.1** Impinger and Dry-Gas Meter Temperature Sensors. For the temperature sensors used to measure the temperature of the gas leaving the impinger train, a three-point calibration at ice water, room air, and boiling water temperatures is necessary. Accept the temperature sensors only if the readings at all three temperatures agree to  $\pm 2^{\circ}\text{C}$  ( $\pm 3.6^{\circ}\text{F}$ ) with those of the absolute value of the reference thermometer.

**10.5.2** Probe and Stack Temperature Sensor. For the temperature sensors used to indicate the probe and stack temperatures, a three-point calibration at ice water, boiling water, and hot oil bath temperatures must be performed. Use of a point at room air temperature is recommended. The thermometer and thermocouple must agree to within  $1.5\%$  at each of the calibration points. A calibration curve (equation) may be constructed (calculated) and the data extrapolated to cover the entire temperature range suggested by the manufacturer.

**10.6** Barometer. Adjust the barometer initially and before each test series to agree to within  $\pm 2.5$  mm Hg (0.1 in. Hg) of the mercury barometer or the correct barometric pressure value reported by a nearby National Weather Service Station (same altitude above sea level).

**10.7** Top-Loading Electronic Balance. Calibrate the balance before each test series, using Class S standard weights. The weights must be within  $\pm 0.5\%$  of the standards, or the balance must be adjusted to meet these limits.

## DRAFT METHOD XXXX

### 10.8 Analytical Calibration.

**10.8.1** Establish liquid chromatographic operating parameters to produce a retention time equivalent to that indicated in Table XXXX-1. Suggested chromatographic conditions are provided in Section 11.2. Prepare calibration standards according to the procedure in Section 7.11.1. Calibrate the chromatographic system using the external standard technique (Section 10.8.2).

#### 10.8.2 External Standard Calibration Procedure.

**10.8.2.1** Analyze each calibration standard using the chromatographic conditions listed in Section 11.2, and tabulate peak area against concentration injected. The results may be used to prepare calibration curves for each analyte listed in Table XXXX-1.

**10.8.2.2** The working calibration curve must be verified on each working day by the measurement of one or more calibration standards. If the response for any analyte varies from the previously established responses by more than 15% (see Table XXXX-3), the test must be repeated using a fresh calibration standard, but only after it is verified that the analytical system is in control. Alternatively, a new calibration curve may be prepared for that compound. If an autosampler is available, it is convenient to prepare a calibration curve daily by analyzing standards along with test samples.

**10.8.2.3** Periodically use the check standard prepared in Section 7.11.1.3 to check the instrument response and calibration curve.

## DRAFT METHOD XXXX

### 11.0 PROCEDURES.

#### 11.1 Analysis of Stack Gas Samples: Impinger Contents

**11.1.1** Measure the sample volume. Decide whether the samples need to be concentrated or diluted. Perform analysis. If analytes saturate, dilute the solution. If analytes are not observed, concentrate.

**11.1.2** If the sample does not need to be concentrated remove a 15 mL aliquot and place it in a 25 mL volumetric flask. Add about 40 drops of concentrated sulfuric acid to lower the pH to <2. Check the pH. Add more acid if needed to lower pH to <2. Dilute the sample to the line with water and mix well.

**11.1.3** If the sample needs to be concentrated, remove a 50 mL aliquot and place it in a 100 mL round bottom flask. Use a rotary evaporator to reduce the volume to about 10 to 15 mL. Transfer the sample to a 25 mL graduated cylinder. Use anhydrous HCl to lower the pH to <2. Dilute the sample to a known volume with water. Record the volume.

**11.1.4** Transfer the pH adjusted sample to a bottle and store at 4°C (39°F).

#### 11.2 Chromatographic Conditions.

Column: C18, 250 mm x 4.6 mm ID, 5 $\mu$ m particulate size

Mobile Phase: Acetonitrile 0.1M Sodium Acetate Buffer (30:70)

Flow Rate: 1.0 mL/min.

UV Detector: 274 nm

Injector Volume: 30  $\mu$ L

## DRAFT METHOD XXXX

### 11.3 HPLC Analysis.

**11.3.1** Analyze samples by HPLC, using conditions established in Section 11.2. Table XXXX-1 lists the retention times and MDLs that were obtained under these conditions. Other HPLC columns, chromatographic conditions, or detectors may be used if the requirements for Section 9.2. are met, or if the data are within the limits described in Table XXXX-1.

**11.3.2** The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time for a compound can be used to calculate a suggested window size; however, the experience of the analyst should weigh heavily in the interpretation of the chromatograms.

**11.3.3** If the peak area exceeds the linear range of the calibration curve, a smaller sample volume should be used. Alternatively, the final solution may be diluted with mobile phase and reanalyzed.

**11.3.4** If the peak area measurement is prevented by the presence of observed interferences, cleanup is required. However, no method has been evaluated for this procedure.

**11.4** Analysis of Filters. The amount of phenol and the cresols retained on the sampling train filter will be a function of the amount and type of particulate material present in the stationary source that is tested. Extensive retention of phenol and cresols on the filter of the sampling train is not expected. With high levels (>20 ppm) of phenol and/or the cresols present in the source, the amount of phenol/cresol retained on the filter will usually be in the range of 0.1 to 1.0 ppb, much less than 1% of the total amount of analyte observed in the analysis of the contents of the first impinger. However, the filters should be extracted according to the procedures of

## DRAFT METHOD XXXX

Draft Method 3542. A representative number (approximately 10%) should be analyzed by GC/MS according to the analytical procedures of Method 8270 to verify that retention of phenol and cresols is 1% of the analyte concentration observed in the first impinger. If the concentration of analyte observed on the filter is 1% of the concentration of analyte in the first impinger, the remaining filter extracts may be archived. If the concentration of analyte observed on the filter is >1% of the concentration of analyte in the first impinger, the remaining filter extracts should be analyzed by gas chromatography/ mass spectrometry and the analyte recovered from the filter should be added to the concentration of analyte from the first impinger.

### 12.0 DATA ANALYSIS AND CALCULATIONS.

Carry out calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures to the correct number of significant figures after final calculations.

#### 12.1 Nomenclature:

AIC	=	Acceptable Impurity Concentration ( $\mu\text{g}/\text{mL}$ )
$A_n$	=	Cross-sectional area of nozzle, $\text{m}^2$ ( $\text{ft}^2$ ).
$B_{ws}$	=	Water vapor in the gas stream, proportion by volume.
$C_d$	=	Type S pitot tube coefficient (nominally $0.84 \pm 0.02$ ), dimensionless.
$C_r$	=	Concentration of phenols in stack gas ( $\text{mg}/\text{dscm}$ )
EAC	=	Expected Analyte Concentration (ppbv)
FW	=	Formula weight of analyte ( $\text{g}/\text{mole}$ )
I	=	Percent of isokinetic sampling.
$L_1$	=	Individual leakage rate observed during the leak-check conducted prior to the first component change $\text{m}^3/\text{min}$ (cfm).
$L_a$	=	Maximum acceptable leakage rate for a leak-check, either pre-test or following a component change; equal to $0.00057 \text{ m}^3/\text{min}$ (0.020 cfm) or 4% of the average sampling rate, whichever is less.
$L_i$	=	Individual leakage rate observed during the leak-check conducted prior to the "i <sup>th</sup> " component change ( $i = 1, 2, 3 \dots n$ ) $\text{m}^3/\text{min}$ (cfm).
$L_p$	=	Leakage rate observed during the post-test leak-check, $\text{m}^3/\text{min}$ (cfm).
$M_d$	=	Stack-gas dry molecular weight, $\text{g}/\text{g-mole}$ ( $\text{lb}/\text{lb-mole}$ ).
MVOL	=	Total volume of recovered sample (mL)

## DRAFT METHOD XXXX

$M_w$	=	Molecular weight of water, 18.0 g/g-mole (18.0 lb/lb-mole).
$P_{bar}$	=	Barometric pressure at the sampling site, mm Hg (in. Hg).
$P_C$	=	Concentration of phenol in sample ( $\mu\text{g/mL}$ )
$P_s$	=	Absolute stack-gas pressure, mm Hg (in. Hg).
$P_{std}$	=	Standard absolute pressure, 760 mm Hg (29.92 in. Hg).
$P_T$	=	Total phenol in sample ( $\mu\text{g}$ )
$R$	=	Ideal gas constant, 0.06236 mm Hg-m <sup>3</sup> /K-g-mole (21.85 in. Hg-ft <sup>3</sup> /R-lb-mole).
RVOL	=	Volume of NaOH reagent that will be used in the impingers (mL)
SVOL	=	Volume of air sampled at standard conditions (L)
$T_m$	=	Absolute average dry-gas meter temperature, K ( $^{\circ}\text{R}$ ).
$T_s$	=	Absolute average stack-gas temperature, K ( $^{\circ}\text{R}$ ).
$T_{std}$	=	Standard absolute temperature, 293 K (528 $^{\circ}\text{R}$ ).
$V_{adj}$	=	Volume of sample aliquot after pH adjustment
$V_{aliqu}$	=	Volume of aliquot used
$V_{lc}$	=	Total volume of liquid collected in the impingers and silica gel, mL.
$V_m$	=	Volume of gas sample as measured by dry-gas meter, dscm (dscf).
$V_{m(std)}$	=	Volume of gas sample measured by the dry-gas meter, corrected to standard conditions, dscm (dscf).
$V_{w(std)}$	=	Volume of water vapor in the gas sample, corrected to standard conditions, scm (scf).
$V_s$	=	Stack-gas velocity, calculated by EPA Method 2, Equation 2-9, using data obtained from EPA Method 5, m/sec (ft/sec).
$\gamma$	=	Dry-gas-meter calibration factor, dimensionless.
$\Delta H$	=	Average pressure differential across the orifice meter, mm H <sub>2</sub> O (in. H <sub>2</sub> O).
$\rho_w$	=	Density of water, 0.9982 g/mL (0.002201 lb/mL).
$\Theta$	=	Total sampling time, min.
$\Theta_1$	=	Sampling time interval from the beginning of a run until the first component change, min.
$\Theta_i$	=	Sampling time interval between two successive component changes, beginning with the interval between the first and second changes, min.
$\Theta_p$	=	Sampling time interval from the final ( $n^{\text{th}}$ ) component change until the end of the sampling run, min.
13.6	=	Specific gravity of mercury.
60	=	sec/min.
100	=	Conversion to percent.

**12.2** Average Dry Gas Meter Temperature and Average Orifice Pressure Drop. See field data sheet.

## DRAFT METHOD XXXX

**12.3 Dry-Gas Volume.** Correct the sample measured by the dry-gas meter to standard conditions (20°C, 760 mm Hg [68°F, 29.92 in. Hg]) by using Equation XXXX-1:

$$V_{m(\text{std})} = V_m \gamma \frac{T_{\text{std}}}{T_m} \frac{P_{\text{bar}} + \Delta H/13.6}{P_{\text{std}}} = K_1 V_m \gamma \frac{P_{\text{bar}} + \Delta H/13.6}{T_m} \quad \text{Eq. XXXX-1}$$

where:

$$\begin{aligned} K_1 &= 0.3853 \text{ K/mm Hg for metric units, or} \\ K_1 &= 17.64 \text{ }^\circ\text{R/in. Hg for English units.} \end{aligned}$$

It should be noted that Equation XXXX-1 can be used as written, unless the leakage rate observed during any of the mandatory leak-checks (i.e., the post-test leak-check or leak-checks conducted prior to component changes) exceeds  $L_a$ . If  $L_p$  or  $L_i$  exceeds  $L_a$ , Equation XXXX-1 must be modified as follows:

- a. Case I (no component changes made during sampling run): Replace  $V_m$  in Equation XXXX-1 with the expression:

$$V_m - (L_p - L_a) \Theta$$

- b. Case II (one or more component changes made during the sampling run): Replace  $V_m$  in Equation XXXX-1 by the expression:

$$V_m - (L_1 - L_a) \theta_1 - \sum_{i=2}^N (L_i - L_a) \theta_i - (L_p - L_a) \theta_p$$

and substitute only for those leakage rates ( $L_i$  or  $L_p$ ) that exceed  $L_a$ .

**12.4 Volume of Water Vapor Condensed.**

## DRAFT METHOD XXXX

$$V_{w(\text{std})} = V_{1c} \frac{P_w}{M_w} \frac{RT_{\text{std}}}{P_{\text{std}}} = K_2 V_{1c} \quad \text{Eq. XXXX-2}$$

where:

$$\begin{aligned} K_2 &= 0.001333 \text{ m}^3/\text{mL} \text{ for metric units, or} \\ K_2 &= 0.04707 \text{ ft}^3/\text{mL} \text{ for English units.} \end{aligned}$$

### 12.5 Moisture Content.

$$B_{\text{WS}} = \frac{V_{w(\text{std})}}{V_{m(\text{std})} + V_{w(\text{std})}} \quad \text{Eq. XXXX-3}$$

**NOTE:** In saturated or water-droplet-laden gas streams, two calculations of the moisture content of the stack gas shall be made, one from the impinger analysis (Equation XXXX-3) and a second from the assumption of saturated conditions. The lower of the two values of  $B_{\text{WS}}$  shall be considered correct. The procedure for determining the moisture content based upon assumption of saturated conditions is given in the **NOTE** to Section 1.2 of Promulgated EPA Method 4 (Section 4.0 of Reformatted Draft EPA Method 4). For the purposes of this method, the average stack-gas temperature may be used to make this determination, provided that the accuracy of the in-stack temperature sensor is  $\pm 1^\circ\text{C}$  ( $2^\circ\text{F}$ ).

### 12.6 Conversion Factors.

<u>From</u>	<u>To</u>	<u>Multiply by</u>
scf	$\text{m}^3$	0.02832
$\text{g}/\text{ft}^3$	$\text{gr}/\text{ft}^3$	15.43
$\text{g}/\text{ft}^3$	$\text{lb}/\text{ft}^3$	$2.205 \times 10^{-3}$

## DRAFT METHOD XXXX

g/ft<sup>3</sup>                      g/m<sup>3</sup>                      35.31

### 12.7 Isokinetic Variation.

#### 12.7.1 Calculation From Raw Data.

$$I = \frac{100 T_s [K_3 V_{1c} + (V_m \gamma / T_m) (P_{\text{bar}} + \Delta H / 13.6)]}{60 \theta V_s P_s A_n} \quad \text{Eq. XXXX-4}$$

where:

$$\begin{aligned} K_3 &= 0.003454 \text{ mm Hg} \cdot \text{m}^3 / \text{mL} \cdot \text{K} \text{ for metric units, or} \\ K_3 &= 0.002669 \text{ in. Hg} \cdot \text{ft}^3 / \text{mL} \cdot ^\circ \text{R} \text{ for English units.} \end{aligned}$$

#### 12.7.2 Calculation For Intermediate Values.

$$\begin{aligned} I &= \frac{T_s V_{m(\text{std})} P_{\text{std}} 100}{T_{\text{std}} V_s \theta A_n P_s 60 (1 - B_{\text{ws}})} \\ &= K_4 \frac{T_s V_{m(\text{std})}}{P_s V_s A_n \theta (1 - B_{\text{ws}})} \end{aligned} \quad \text{Eq. XXXX-5}$$

where:

$$\begin{aligned} K_4 &= 4.320 \text{ for metric units, or} \\ K_4 &= 0.09450 \text{ for English units.} \end{aligned}$$

**12.8** Concentration of Phenol/Cresol in Sample. A least squares linear regression analysis of the calibration standards shall be used to calculate a correlation coefficient, slope, and intercept. Concentrations are the X-variable, and response is the Y-variable.

**12.9** Calculation of Total Weight of Phenol/Cresol in the Sample. To determine the total phenol/cresol use the following equation:

**DRAFT METHOD XXXX**

$$P_T = P_C \times \text{MVOL} \times \frac{V_{\text{adj}}}{V_{\text{aliq}}} \quad \text{Eq. XXXX-6}$$

**12.10** Phenol/Cresol Concentration in Stack Gas. Determine the phenol/cresol concentration in the stack gas using the following equation:

$$C_f = \frac{K (\text{Total Phenol/Cresol, mg})}{V_{m(\text{std})}} \quad \text{Eq. XXXX-7}$$

where:

$$\begin{aligned} K &= 35.31 \text{ ft}^3/\text{m}^3 \text{ if } V_{m(\text{std})} \text{ is expressed in English units} \\ &= 1.00 \text{ m}^3/\text{m}^3 \text{ if } V_{m(\text{std})} \text{ is expressed in metric units} \end{aligned}$$

**12.11** Calculate the Acceptable Concentrations of Impurities in NaOH Reagent as follows:

$$\text{AIC} = 0.1 \times \frac{\text{EAC} \times \text{SVOL} \times \frac{\text{FW}}{22.4}}{\text{RVOL} \times 1000} \quad \text{Eq. XXXX-8}$$

where:

0.1 is the acceptable contaminant concentration,  
22.4 is a factor relating ppbv to g/L,  
1,000 is a unit conversion factor.

## **DRAFT METHOD XXXX**

### **13.0 METHOD PERFORMANCE.**

**13.1** Method performance evaluation: The expected method performance parameters for precision, accuracy, and detection limits are provided in Table XXXX-4.

**13.2** The MDL concentrations listed in Table XXXX-1 were obtained using field train blank sample results instrument detection limits.

**14.0 POLLUTION PREVENTION.** Reserved.

### **15.0 WASTE MANAGEMENT.**

**15.1** Disposal of Excess NaOH Reagent. Excess NaOH reagent may be returned to the laboratory and recycled or treated as aqueous waste for disposal purposes.

## DRAFT METHOD XXXX

**TABLE XXXX-4. EXPECTED METHOD PERFORMANCE BASED ON EPA METHOD 301 VALIDATION TEST  
TEST MATRIX: FIBERGLASS MANUFACTURING**

<b>Compound</b>	<b>Precision (% RSD)<sup>a</sup></b>	<b>Bias (Correction Factor)<sup>b</sup></b>	<b>Detection Limit (ppbv)<sup>c</sup></b>	<b>Concentration Level (ppmv)</b>
Phenol	±11	0.83	700	40
<i>o</i> -Cresol	±14	0.88	50	40
<i>m</i> -Cresol <sup>d</sup>	±13	0.84	2390	40
<i>p</i> -Cresol <sup>d</sup>	±13	0.84	2390	40

<sup>a</sup> Relative Standard Deviation (%) for dual spiked trains as calculated by EPA Method 301.

<sup>b</sup> Bias Correction Factor for dual spiked trains as calculated by EPA Method 301.

<sup>c</sup> Based on ten times the levels measured in the field train blank samples for a 849 L (30 cubic foot) sample.

<sup>d</sup> *m*-Cresol and *p*-cresol coelute in the chromatographic analysis.

### 16.0 REFERENCES.

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## **DRAFT METHOD XXXX**

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### **17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA.**

DRAFT METHOD XXXX

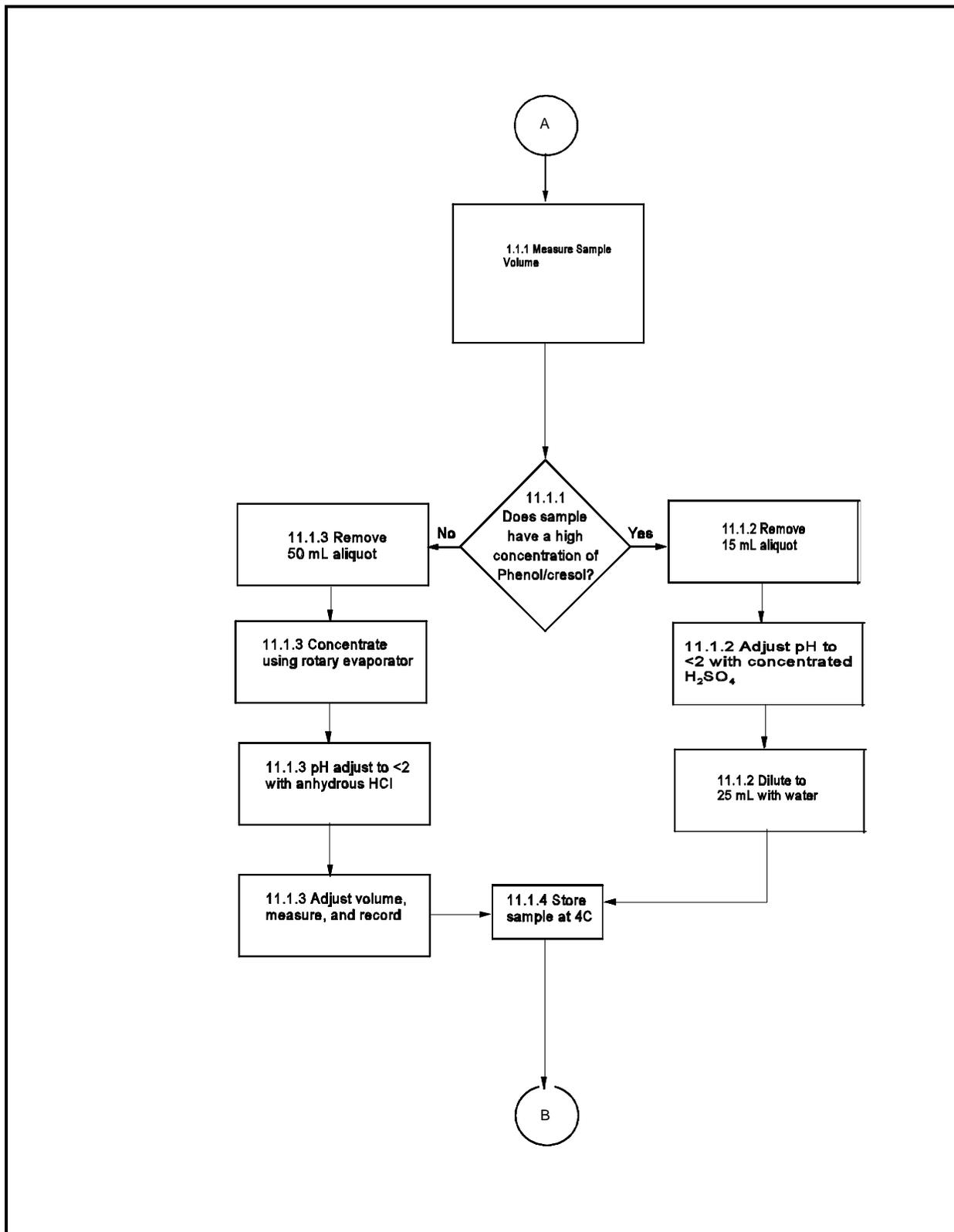
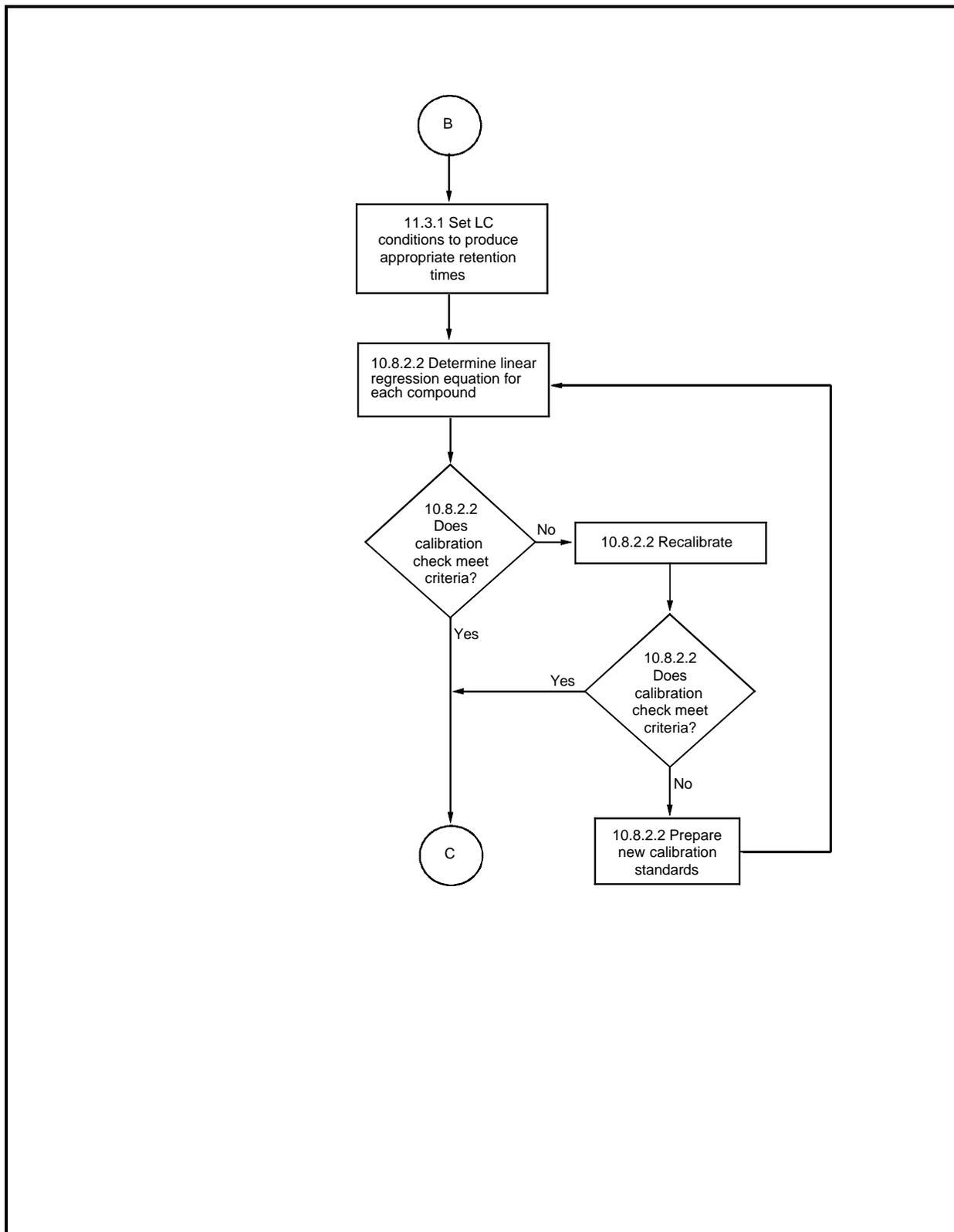


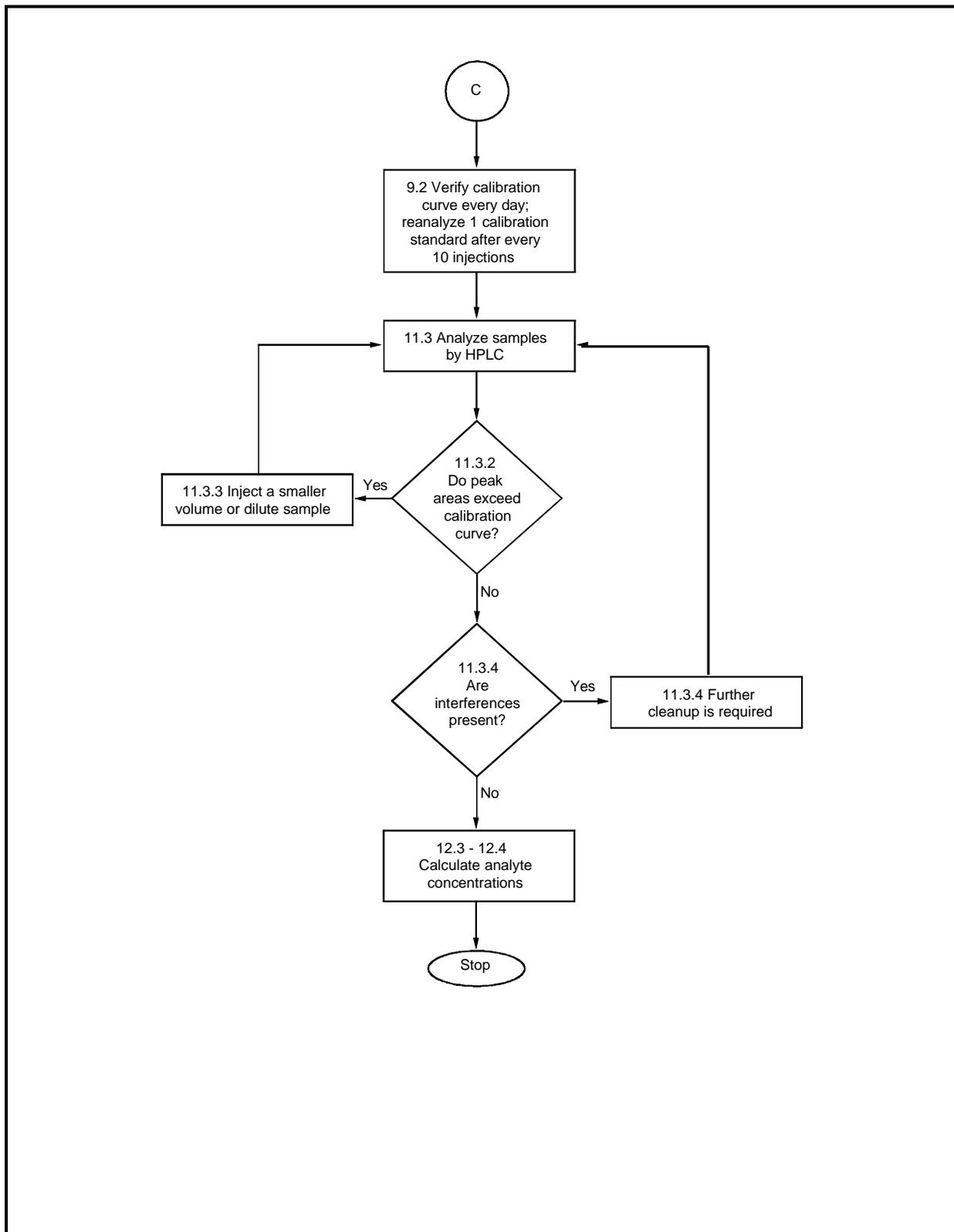
Figure XXXX-3. Phenols and Cresols by High Performance Liquid Chromatography (HPLC)

**DRAFT METHOD XXXX**



**Figure XXXX-3. Phenols and Cresols by High Performance Liquid Chromatography (HPLC) (continued).**

**DRAFT METHOD XXXX**



**Figure XXXX-3. Phenols and Cresols by High Performance Liquid Chromatography (HPLC) (continued)**

**DRAFT METHOD XXXX**