Designation: D7295 – 11

Standard Practice for
Sampling and Determination of Hydrogen Cyanide (HCN) in Combustion Effluents and Other Stationary Sources[1]

This standard is issued under the fixed designation D7295; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This practice is used to determine the concentration of gaseous hydrogen cyanide (HCN) from any combustion device or atmosphere where cyanide may be present. While primarily designed for the measurement of gas phase HCN, the sample collection described in this practice also includes cyanide ion (CN^-) absorbed particles that may be present in the sampling atmosphere.

1.1.1 Samples can be collected from a closed chamber such as the NBS smoke box described in Test Method E662 provided it is equipped with sampling ports.

1.1.2 Open chambers such as industrial work areas or large scale fires can be monitored for HCN with this practice.

1.1.3 The HCN emissions of a flow through system can be determined by sampling from its discharge stack. Examples of such systems include large scale manufacturing applications and the cone calorimeter described in Test Method E1354.

1.2 This practice can be used to monitor HCN levels in lab scale fire smoke effluents in order to estimate toxicity of gases produced from burning materials. See Guide E800.

1.3 The concentration range of hydrogen cyanide will be dependent on the volume of gas sampled, the volume of sodium hydroxide solution placed in the impinger during sampling, and the analytical method used to measure cyanide. For example, the lower limit of detection would be 0.002-mg/m^3 when 0.1-m^3 of combustion effluent is collected into 100-mL sodium hydroxide solution based on a detection limit of 0.002 mg/L cyanide in the impinger solution when using the flow injection analysis (FIA) system described in Test Method D6888.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1193 Specification for Reagent Water
D1356 Terminology Relating to Sampling and Analysis of Atmospheres
D2036 Test Methods for Cyanides in Water
D2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water
D3154 Test Method for Average Velocity in a Duct (Pitot Tube Method)
D3614 Guide for Laboratories Engaged in Sampling and Analysis of Atmospheres and Emissions
D3685/D3685M Test Methods for Sampling and Determination of Particulate Matter in Stack Gases
D4841 Practice for Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents
D5337 Practice for Flow Rate Adjustment of Personal Sampling Pumps
D6696 Guide for Understanding Cyanide Species
D6888 Test Method for Available Cyanide with Ligand Displacement and Flow Injection Analysis (FIA) Utilizing Gas Diffusion Separation and Amperometric Detection
D7365 Practice for Sampling, Preservation and Mitigating Interferences in Water Samples for Analysis of Cyanide
E337 Test Method for Measuring Humidity with a Psychrometer (the Measurement of Wet- and Dry-Bulb Temperatures)
E662 Test Method for Specific Optical Density of Smoke Generated by Solid Materials
E800 Guide for Measurement of Gases Present or Generated During Fires
E1354 Test Method for Heat and Visible Smoke Release Rates for Materials and Products Using an Oxygen Consumption Calorimeter

3. Terminology

3.1 Refer to Terminology D1356 for terminology related to sampling and analysis of atmospheres.

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[1] This practice is under the jurisdiction of ASTM Committee D22 on Air Quality and is the direct responsibility of Subcommittee D22.03 on Ambient Atmospheres and Source Emissions.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

3.2 For definitions of terms related to cyanide testing, refer to Guide D6696 and Test Method D6888.

3.3 For definitions of terms related to the measurement of gases present or generated during fires, refer to Guide E800.

3.4 For additional information related to sampling and analysis of atmospheres, see Guide D3614.

4. Summary of Practice

4.1 A known volume of gaseous sample is bubbled through an impinger containing 0.1–M sodium hydroxide solution utilizing a calibrated pumping system. Particulates that may pass through the impinger are captured on a glass fiber filter then recombined back into the impinger solution prior to analysis. Because HCN is soluble in aqueous solutions, it may be present in water droplets formed from either a wet scrubber system or condensation in the stack. Because of this, samples that contain moist air should be sampled near isokinetic conditions.

4.2 During the sampling process, hydrogen cyanide (HCN) is converted to cyanide ion (CN^-) in the sodium hydroxide solution. The CN^- is analyzed with a flow injection analysis (FIA) system described in Test Method D6888 or with a suitable analytical method such as ion chromatography described in Test Methods D2036.

4.2.1 Colorimetric and ion selective electrode methods, also described in Test Methods D2036 can be used for screening purposes.

4.3 The concentration of HCN in the atmosphere or stack is calculated as described in 9.6.

5. Significance and Use

5.1 Hydrogen cyanide is highly toxic. In relatively low quantities, hydrogen cyanide can cause asphyxia and death.

5.2 The National Fire Protection Association has assigned a flammability rating of 4 (severe fire hazard) to hydrogen cyanide.

6. Apparatus

6.1 *Sample Collection Train*

6.1.1 *Constant Flow Pumping System*—Pumps used to collect samples should be able to accurately pump from 0.1-L/min to 15-L/min or at the desired flow rate. Personal industrial hygiene sampling pumps or high volume sampling pumps may be utilized. More than one sample can be collected with a single pump using a manifold with flow control valves. The system should be calibrated as described in Practice D5337 or using a suitable commercially available calibrator.

6.1.2 *Impinger Sample Collection Vessels*—Standard mini or midget impingers with standard tip. Greenberg-Smith impingers equipped with a standard tip with 500-mL capacity may be used when larger flow rates are desired. Impinger connections should consist of leak free ground glass joints to avoid the loss of HCN during sampling and should be free of any silicone grease. The use of a single impinger has shown to yield an average of 97 % efficiency in combustion effluents; however, higher efficiencies are possible using additional impingers in series. Without prior knowledge of the atmosphere, it is recommended to use a backup impinger to determine if breakthrough occurs. Test each impinger for cyanide as a separate sample in order to demonstrate capture efficiency; mathematically combine the results by adding the observed concentrations.

6.1.3 *Sample Collection Tubing and Probes*—Collection tubing and probes should be constructed of inert material such PTFE or PTFE-lined stainless steel. Vinyl tubing can be used in the sample train where flexible tubing is necessary, but the aforementioned are preferred. The sample lines should be heated at 120 ± 5°C when sampling stack emissions in moist air in order to prevent condensate from forming in the sample train.

6.1.4 *Glass Fiber Filters*—Type A/E, 1 µm binder free borosilicate glass fiber filter and cassette assembly cartridge for air sampling applications. The filters are used between the impingers and pumping system to capture fine particulates that may pass through the impingers and to protect the pumping system. It is recommended to use 13-mm filters for mini-impingers and 47-mm filters for Greenberg-Smith impingers.

6.1.5 *Duplicate and Matrix Spike Sample Trains*—It is recommended to setup duplicate impingers to evaluate precision. In addition, a second set of impingers can be fortified with a known amount of cyanide (see 8.11) to evaluate recovery. Fig. 1 shows an example of such a system.

6.1.6 *Thermometer*—Measure the temperature of the stack or atmosphere with a mercury thermometer or an equivalent digital thermometer capable of accurately reading within ±0.1°C.

7. Interferences

7.1 Sulfide, aldehydes, and oxidizing agents in the atmosphere are possible interferences.

7.2 Prior to conducting sampling and analysis, review 9.4 in order to avoid cyanide degradation or inaccurate results.

8. Reagents and Materials

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the American Chemical Society, where such specifications are available[3]. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

8.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Type I, II, or III of Specification D1193.

8.3 *Impinger Solution* (0.10 M NaOH)—In a 1-L volumetric flask, dissolve 4.0 g NaOH in approximately 800-mL laboratory water and dilute to 1L.

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[3] *Reagent Chemicals, American Chemical Society Specifications*, Am. Chemical Soc., Washington, DC. For suggestions on the testing of reagents not listed by the American chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia.*

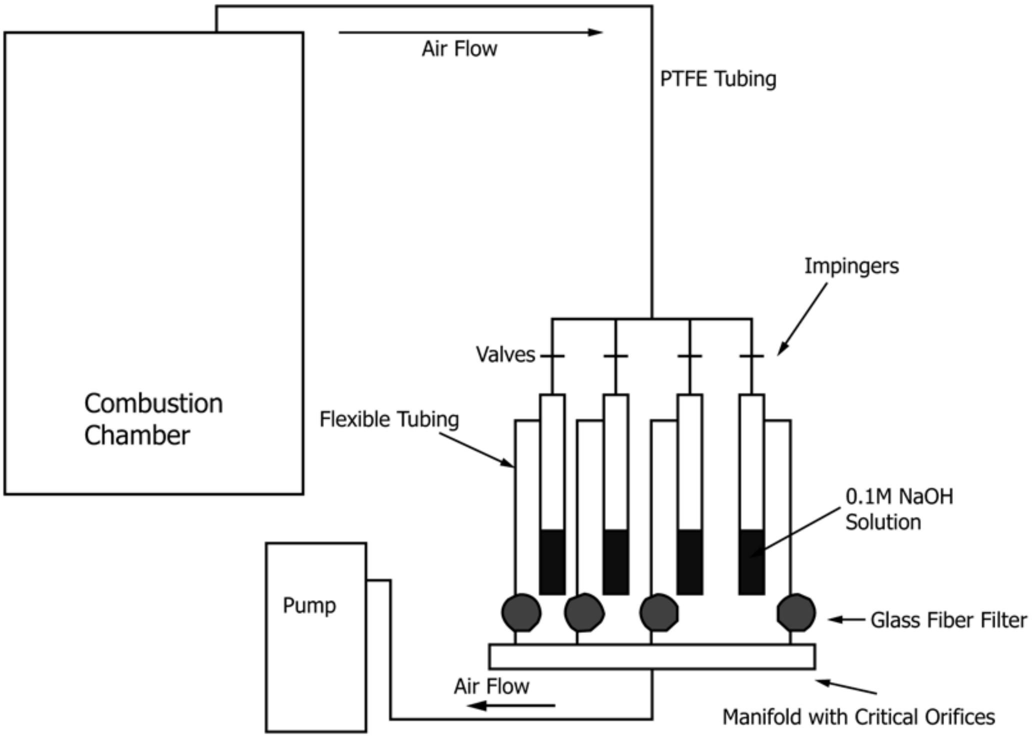

FIG. 1 Example of Sample Train (Closed Chamber Sampling, Non-Isokinetic)

8.4 *Ethylenediamine (EDA) Solution*—Weigh 3.5 g EDA into a 100-mL volumetric flask and dilute to volume with water.

8.5 *Cadmium Chloride,* granular, powdered.

8.6 *Lead Acetate Test Strips,* used to test for the presence of sulfide in the impinger solutions.

8.7 *Leur Lock Syringe Filter*—0.45 µm filter attached to syringe

8.8 *KI Starch Paper Test Strips,* used to indicate the presence of oxidizing agents

8.9 *Sodium Arsenite*—$NaAsO_2$ is used to neutralize oxidizing agents

8.10 *pH Indicator Strips,* wide range pH paper.

8.11 *Cyanide Matrix Spike Solution (1000 µg/mL* CN^-*)*—Dissolve 2.51 g of KCN and 2.0 g of NaOH in 1 L of water. Standardize with silver nitrate solution as described in Test Methods D2036, paragraph 16.2. Store the solution under refrigeration and check concentration approximately every six months and correct if necessary. Commercially prepared solutions are also available and can be used for spiking purposes. (**Warning—**Because of the toxicity of cyanide, great care must be exercised in its handling. Acidification of cyanide solutions produces toxic hydrocyanic acid (HCN). All manipulations must be done in the hood so that any HCN gas that might escape is safely vented.)

9. Procedure

9.1 *Stack Evaluation (Flow Through Systems):*

9.1.1 Determine the velocity of the stack as described in Test Method D3154 or U.S. EPA Method 2.[4]

9.1.2 Because HCN is soluble in aqueous solutions, it may be present in water droplets formed from either a wet scrubber system or condensation in the stack. Because of this, samples that contain moist air should be sampled near isokinetic conditions. To determine if the moisture in the stack is saturated, test with the wet bulb/dry bulb procedure described in Test Method E337 or estimate the moisture content by U.S. EPA Method 4.[5]

9.1.3 If isokinetic sampling is required, see Test Methods D3685/D3685M or U.S. EPA Method 5[6] to determine the probe diameter and sampling flow rate. This flow rate will be maintained during the entire sampling event.

9.2 *Open and Closed Chamber Systems (Non-Flow Through Systems):*

9.2.1 When samples are collected from workplace monitoring areas or closed chamber combustion devices, the sampling rate (which will determine the volume of sample collected) should be selected based on the expected concentration of HCN or the required detection limit.

9.2.2 Since open and closed chamber systems are not flow dependent (that is, there is no measurable flow) isokinetic sampling is not possible. Adequate sampling rates and sampling times should be used to collect a representative sample.

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[4] Method 2, Velocity—S-Type Pitot, U.S. Environmental Protection Agency.

[5] Method 4, Moisture Content, U.S. Environmental Protection Agency.

[6] Method 5, Particulate Matter, U.S. Environmental Protection Agency.

When comparing combustion emissions from various materials, it is recommended to keep the sampling rate constant for each test burn.

9.3 *Sampling:*

9.3.1 Assemble the sample train with an impinger that contains a known volume of the impinger solution (0.1 M NaOH). The volume of impinger solution will depend on the size of impinger. It is recommended to use 100 mL of the impinger solution when using Greenberg-Smith impingers or 20 mL of impinger solution when using mini-impingers. Connect a glass fiber filter (see 6.1.4) between each impinger and the pumping system. The filter will capture any fine particulate that passes through the impinger and will protect the pumping system and valves.

NOTE 1—This practice is primarily used to determine the concentration of HCN and any particulate cyanides that are easily dissociated into free cyanide. To specifically determine the particulate cyanides, a prefilter can be placed prior to the impinger(s). After sampling, this filter and the captured solids are extracted with 0.1M NaOH then analyzed per the test methods described in 9.5. If the particles contain strong-acid dissociable metal cyanide complexes such as potassium ferricyanide or potassium ferrocyanide, it will be necessary to digest the extract and particles with the total cyanide procedure described in Test Methods D2036, Test Method A prior to analysis.

9.3.2 If necessary, heat the sample probe and transfer line to 120°C during sampling in order to prevent condensation in the sample probe and transfer line.

9.3.3 Check the sample train system for leaks prior to sampling. Start the pumps and collect sample for a known amount of time. The sampling time will vary depending on the amount of cyanide emissions that are expected. Stack samples are typically sampled for 30 to 60 minutes; however, fire smoke effluents may require substantially shorter sampling times depending on the combusted material. Workplace environments may need sampled for longer periods of time in order to achieve the required detection limits.

9.3.4 If any of the impinger solution is lost from volatilization during sampling, adjust to the original volume with reagent water upon completion of sampling, or measure the remaining volume with a graduated cylinder. Transfer the impinger solutions into labeled polyethylene bottles.

9.3.5 When sampling acidic atmospheres, verify that the pH of each impinger solution is greater than pH 12 with indicating test strips, pH meter, or with an indicating solution such as Alizarin Yellow (Mordant Orange), which can be added to the solution before collection. If Alizarin Yellow is used as an indicator, the sampling should be stopped if the reagent changes from blood red to pale yellow. It may be necessary to recollect the samples with impingers that contain a higher concentration (up to 1M NaOH) of sodium hydroxide and/or use additional impingers in the sample train.

9.3.6 The filters from 6.1.4 should be combined with the corresponding impinger solutions then agitated. The samples can be transported to the laboratory at this stage. Upon receipt in the laboratory, allow the solids to settle for at least ten minutes, after which time the samples may be filtered if necessary; however, the samples can usually be decanted instead.

9.3.7 After collection, samples should be transported to the laboratory and analyzed as soon as possible. If the samples are not immediately analyzed, they should be stored at 4°C. The samples should remain stable for up to 14 days as long as interferences are not present. To extend the storage time, establish the estimated holding time in accordance with Practice D4841. If interferences are suspected, they should be mitigated as described in 9.4.

9.4 *Elimination of Interferences:*

9.4.1 Some materials may liberate aldehydes during combustion. Cyanides can react with aldehydes in aqueous solutions to form cyanohydrins. If the sampled atmospheres are known or suspected to contain formaldehyde, acetaldehyde, or other water soluble aldehydes, then add 20-mL of EDA solution (see 8.4) to 1-L of the impinger solution (see 8.3) prior to collecting samples. The addition of EDA will inhibit the reaction of cyanide with aldehydes, which will prevent the loss of cyanide due to the formation of cyanohydrins.

9.4.2 The sulfide abatement reagent used in the flow injection analysis of Test Method D6888 will effectively remove up to 50-mg/L S^{2-}. If larger concentrations of sulfide are suspected, then the samples will require additional sulfide abatement immediately after sampling is complete.

9.4.2.1 Test for sulfide by placing a drop of sample from the impinger on lead acetate paper. If the paper turns black, sulfide is present at concentrations high enough to cause interference. If the sample contains sulfide as indicated with a lead acetate test strip or is known to contain sulfides that will interfere with the test method, refer to Practice D7365 for additional sulfide abatement techniques.

NOTE 2—Lead acetate and lead carbonate have historically been used to remove sulfide interference for the analysis of cyanide; however, cyanide ion can rapidly convert to thiocyanate in the presence of lead. Therefore, it is not recommended to use these reagents for sulfide removal unless the samples are immediately filtered after treatment.

9.4.2.2 Samples that are known or suspected to contain sulfide should be analyzed as soon as possible.

9.4.3 Oxidizing agents may decompose the cyanide in the impinger solution.

9.4.3.1 Verify the presence of oxidizing agents by testing the impinger solution with a potassium iodide (KI) starch test strip. If positive, add 100 mg/L $NaAsO_2$, which will reduce more than 50 mg/L of chlorine.

9.4.3.2 If the impingers test positive for oxidizing agents, it is recommended to resample with the $NaAsO_2$ added to the impingers prior to sampling to avoid cyanide loss during sample collection. In this case, a second impinger fortified with cyanide (matrix spike) should also be analyzed to demonstrate recovery.

9.5 *Analytical Determination:*

9.5.1 The samples should be analyzed for cyanide with flow injection utilizing gas diffusion separation and amperometric detection as described in Test Method D6888 or with an analytical method capable of producing equivalent results.

NOTE 3—This practice was evaluated with Test Method D6888 as the quantitative step. If another analytical method is employed, it is the user's responsibility to demonstrate precision and bias that meet the requirements of the sampling program.

TABLE 1 U.S. EPA Method 301 Validation

	Statistical Summary for Cyanide Determinations	
SDs	Standard Deviation of spiked samples	0.284
SDu	Standard Deviation of unspiked samples	0.156
Sm	Mean of spiked samples	12.8
Mm	Mean of the Unspiked Samples	3.40
% RSDs	Relative Standard Deviation of Spiked Samples	2.23
% RSDu	Relative Standard Deviation of Unspiked Samples	4.59
B	Numerical value of the Bias	-0.646
% Bias	Percentage of Bias	-6.46
SDM	Standard Deviation of Mean	0.324
T	Bias Significance, t-statistical value	1.991
CV	Critical Value, 11 degrees of Freedom	2.201
CF	Correction Factor is not applied	t < CV

Statistical data pass all requirements of U.S. EPA Method 301 Field Validation

Impinger volume = 100 mL 0.1M NaOH
Samples collected for 10 minutes at 10 L/min.
Matrix Spike/Matrix Spike Duplicate = 10.0 mg/L CN^- in each impinger (equivalent to 10 mg/m^3)
Test sample = smoldering polyurethane panel in NBS smoke box

9.5.1.1 The sample is acidified in the flow injection system with 1M H_2SO_4 with sulfide abatement reagent where HCN gas diffuses through a hydrophobic gas diffusion membrane into an alkaline acceptor stream.

9.5.1.2 The cyanide is then determined with a flow through amperometric detection system.

9.5.1.3 Results are calculated as milligrams cyanide ion (CN^-) per litre of impinger solution.

9.5.2 Commonly used colorimetric and ion-selective electrode methods should only be used for screening purposes since these methods are subject to interferences that may be present in combustion gas effluents and industrial atmospheric samples. For further discussion on these interferences see Test Methods D2036.

9.6 *Calculations:*

9.6.1 If the cyanide ion (CN^-) concentration was initially measured in µg/L, convert to mg/L by dividing the result by 1000.

9.6.2 Calculate and report the concentration of HCN in the sampled atmosphere; the temperature of the atmosphere must be specified for each measurement.

$$HCN,\ mg/m^3 = (1.039\ C\ V)/(F\ T)$$
$$HCN,\ ppmv = [(HCN,\ mg/m^3)\ 24.45]/27.03$$

where:

C = Concentration of CN^- in impinger solution, mg/L
V = Volume of impinger solution, mL
F = Flow of sample pump, L/min
T = Time of sample collection, min.

10. Precision and Bias

10.1 This practice was evaluated and validated in a single laboratory. In the lab study, this procedure was found to be suitable for measuring HCN during combustion of several natural and synthetic matrices including wood, wool, flax, and polyurethane materials. Precision and bias were determined according to a U.S. EPA Field Validation Method 301.[7] The data are summarized in Table 1.

10.2 The determinative step of this practice is based on Test Method D6888. Test Method D6888 was evaluated for precision and bias with an interlaboratory study consisting of 10 laboratories as described in Practice D2777. The interlaboratory data are summarized in Test Method D6888.

11. Keywords

11.1 amperometry; combustion gases; cyanide; fire gases; flow injection analysis; hydrogen cyanide; stack emissions; workplace monitoring

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[7] Method 301, Validation Protocol, U.S. Environmental Protection Agency.